THE

ANALYTICAL CHEMISTRY

OF

THE NOBLE METALS

by

F. E. BEAMISH

PERGAMON PRESS
OXFORD · LONDON · EDINBURGH · NEW YORK
TORONTO · PARIS · FRANKFURT

Pergamon Press Ltd., Headington Hill Hall, Oxford
4 & 5 Fitzroy Square, London W.1
Pergamon Press (Scotland) Ltd., 2 & 3 Teviot Place, Edinburgh 1
Pergamon Press Inc., 44–01 21st Street, Long Island City, New York 11101
Pergamon of Canada, Ltd., 6 Adelaide Street East, Toronto, Ontario
Pergamon Press S.A.R.L., 24 rue des Écoles, Paris 5e
Pergamon Press GmbH, Kaiserstrasse 75, Frankfurt-am-Main

First edition 1966

Library of Congress Catalog Card No. 65-17949

PRINTED IN GREAT BRITAIN BY BELL AND BAIN LTD., GLASGOW
(2320/65)

CONTENTS

This book is dedicated to
the fragrant memory of
MY PARENTS,
and to
MY WIFE *and* MY TWO SONS

FOREWORD

PRIOR to the past two or three decades few accurate quantitative methods were recorded for the determination of the seven noble metals. Whereas the methods of separation were often ingenious, few gave a complete analytical separation. A notable exception is the specific removal of osmium by oxidation with nitric acid, which has been recognized from the time of the discovery of osmium. Some two decades later, immediately following the discovery of ruthenium, the volatility of the tetroxide of that metal was recognized. Thus separational techniques advanced to the stage where both osmium and ruthenium could be readily isolated from the remaining noble and associated base metals. Despite the absence of refined analytical methods it is clear that some of the most useful separations for the remaining four platinum metals originated in the early work of the chemical researchers. No one can examine exhaustively the publications of the early twentieth century and escape some recognition of the debt owed to the chemists of this period. The most generally useful method of isolating platinum, viz., by the hydrolytic separation of rhodium, palladium and iridium, has a very early beginning, and it was upon this foundation that the National Bureau of Standards at Washington developed the present method of separation by which quadrivalent platinum is so readily isolated. Similarly the perfected techniques proposed by the Bureau for the separation of base metals from platinum metals by the use of nitrite complexes has its origin in an early recognition of the resistance of the platinum metal–nitrite complex to hydrolysis.

In the history of the development of analytical methods for the platinum metals we encounter a strange paradox. Generally it is a fact that coincident with an improvement in the economic status of a metal there is a corresponding impetus in the development of methods for its separation and determination. Uranium is a recent example. Along with the great improvement in the economics of the platinum metals, however, one fails to find a really significant advance in the recorded analytical methods for these metals. This situation is sometimes ascribed to the analytical difficulties arising out of the complexity of the chemistry of the platinum metals. This fact provides only a partial reason for what seems to have been an avoidable situation.

Even a cursory examination of the growth of the economy of the platinum metals indicates beyond question that the industrial development of the metals rapidly became concentrated within a few competing centres. The present author, in his initial researches, was abruptly confronted with this frustrating situation. In the light of the recent and rapid accumulation of analytical methods it is clear that the decades of secretive restrictions were relatively stagnant periods in the development of methods for the separation and determination of the platinum metals. One cannot now find evidence that this concentration of interest resulted in any really worth-while analytical advancement. Perhaps the recognition of this fact is responsible for the present, relatively free and generous flow of analytical information from at least some of the centres of industrial production. Anyway, the past two decades have seen a rapid increase in the number of effective analytical methods of separation and determination.

Concerning separational methods, the classical assay with lead as a collector remains superior. Data have been accumulated to explain its optimum area of application and its peculiar deficiencies. Despite these deficiencies it is the author's opinion that the classical assay, in so far as its metallurgical aspect is concerned, will direct with reasonable safety the commercial discovery of significant platinum metal values. Gradually, new fire assay techniques and wet methods of separation are being developed. At the present time these must be accepted only as ancillary or confirmatory separations in their relationship to the classical lead collection. However, the recently developed methods of separation by ion-exchange will increasingly find applications of both scientific and industrial value. It is not at all improbable that these applications will involve some replacement of fire assay procedures and of some existing methods of refining.

While the present volume was conceived in enthusiasm and confidence it was written with great reservations and a growing humility. One cannot overestimate the amount of information pertinent to the analytical chemistry of the platinum metals which lies more or less concealed in the vast volume of chemical literature which has accumulated over a period of a century and a half.

In this volume the choice of analytical methods presented to the reader is, to some degree, made on the basis of personal experience, and, while it is recognized that this procedure is open to the objection that familiarity encourages acceptance, it is hoped that most of the recorded procedures will be applicable within the conditions specified.

Some effort has been made to suggest fertile and useful areas of research within specific procedures. It is scarcely an exaggeration to suggest that no field of analytical research offers a more potentially useful scope for investigations, both fundamental and practical, than the chemistry pertinent to the analysis of the platinum metals. The field of extractive metallurgy has been strangely neglected by the analytical researcher, whose method of approach would surely contribute to the efficiency of methods of industrial extraction and refining. To an even greater degree this is true for industrial procedures which involve wet extractions.

The present method of presentation was devised to avoid the excessive repetition of directions. Thus the section dealing with separations contains a minimum of determinative methods, and following each separational technique the reader is directed to appropriate methods of determination. These determinative methods are discussed separately under the headings: gravimetric, volumetric, spectrophotometric and spectrographic. Some overlapping seemed unavoidable, however, particularly in those instances where separational techniques were closely integrated with determinative methods.

The author is painfully aware of the probable existence of errors of judgment in the recommendation of specific methods as well as errors arising from the misinterpretation of data. When these become evident the author begs the indulgence and co-operation of the reader. Should this compilation prove sufficiently useful it is hoped that personal communications will assist in the elimination of these errors in any future editions.

ACKNOWLEDGEMENT

IN WRITING this book, no part presented difficulties comparable to writing an adequate acknowledgement. It became evident that at best only partial success could attend the efforts to recognize all the assistance involved in its preparation. Obviously, any compilation of wide-ranging analytical methods must owe its existence to the work of many investigators from many laboratories. In this context, I acknowledge gratefully not only the consent of the respective journals to use their published material, but particularly the generously expressed consent of the authors. The contributions emanating from our own analytical laboratory are the products of more than three decades of research. My part during this period has been confined largely to providing a congenial working atmosphere and perhaps offering a word of technical or personal advice during those inescapable periods of frustration and failure. From each of the many researchers I received in return a maximum effort, consistent loyalty and continued friendship. While the productivity varied, as it must, with ability, each gave generously according to his full capacity. In a very real sense, this book is part of their contribution.

During this long period there has been an accumulation of indebtedness to colleagues, associates and institutions. On innumerable occasions my colleagues in similar and other areas of research responded generously to requests for advice and discussion. Regrettably, the sources and details of this invaluable assistance are in most instances long forgotten, and they must therefore go unrecognized.

Concerning institutions, their co-operation was necessary to ensure the continuation of the research programme.

From the Falconbridge Nickel Company at Thornhill, Ontario, the author received not only necessary equipment and finances, but active participation in many aspects of the research projects. A tangible demonstration of this interest is made evident by the inclusion of Chapter 6, which was prepared by Mr. Clyde Lewis, Manager of the Falconbridge Laboratories.

The platinum metal researches were assisted through the provision of an appreciable proportion of the financial requirements by the National Research Council at Ottawa. These were obtained through the normal channels of scholarships for worthy students and through specific financial grants. Scholarships and financial grants were also provided by the Graduate School of the University of Toronto. Without these, many of the research projects would have been materially curtailed.

Perhaps no requirement was more essential than a comfortable working environment and efficient general services. These were amply provided by the Department of Chemistry at the University of Toronto. In so far as services are concerned it would be a gross injustice not to acknowledge specifically the able assistance of the librarian for the Department of Chemistry. Miss B. Mitchell spared no effort to secure the required literature, and not infrequently provided pertinent data from sources unknown to the author. The services of typists, readers and critics are also gratefully acknowledged.

Viewed within this background of assistance, co-operation and pertinent literature, my own contributions recede almost to inappreciable proportions.

F. E. **Beamish**

CHAPTER 1

THE ACTION OF ACIDS, BASES, OXYGEN AND CHLORINE ON THE NOBLE METALS

The Action of Mineral Acids

Although the six platinum metals and gold are classified as " noble metals ", certain of these metals are as readily corroded as some of the base metals. The degree of corrosive action depends upon such factors as the presence and character of impurities, fineness or compactness, the metallurgical history of the preparation and sometimes the technique of dissolution.

The fact that a platinum metal may normally resist corrosion by a single mineral acid is no guarantee that some dissolution will not occur in the presence of certain impurities. This fact becomes important when an attempt is made to purify a precipitate by selective corrosion. An example of this is the recommended procedure for the removal by nitric acid of such base metals as copper from a precipitate of platinum. This technique may result in losses of platinum into the acid extract of copper. It has been reported that a mixture of platinum and mercury is readily attacked by nitric acid,[1] the extent of the corrosion of the platinum depending upon the proportion of mercury. The present author has found that each of the six platinum metals, alloyed at about 2600°F with relatively large amounts of an iron–copper–nickel alloy, is quantitatively attacked by hydrochloric acid, following the addition of small amounts of nitric acid. It has also been shown that the response to mineral acids of the platinum metals collected by the lead assay button cannot be predicted on the basis of the corresponding action with pure metals. In these instances platinum and rhodium are attacked to an appreciable degree by nitric acid. A partial explanation of this susceptibility to acid attack may be the presence of base metal impurities, traces of which are invariably carried into the button.

When the platinum metals are alloyed with a base metal one may expect that corrosion of the base metal will produce a high degree of fineness of the platinum metal; one may also expect that the high temperature treatment may sometimes result in the formation of less resistant intermetallic compounds. Furthermore, one cannot exclude the possibility of an electrolytic action simply because some known potentials suggest inertness to an acid when so little is known concerning even the identity of such intermetallic compounds.

Although the action of mineral acids on platinum metals is little understood one may apply general principles with some assurance of practical value. It is not improbable that each of the platinum metals, given sufficient fineness, will respond in some degree to the corrosive action of even single mineral acids, particularly in the presence of air, and to a greater extent to mixed acids such as *aqua regia*.

It is well known that most of the platinum metals will respond to the corrosive action of hydrochloric acid containing dissolved oxygen.[2] In fact, small amounts of platinum may be thus dissolved completely when heated for a sufficient time in a sealed tube containing oxygen. It has been recorded that this corrosive action requires the presence of light[3] or, at least, it is considerably retarded in the absence of light. There is also the suggestion that the presence of a platinum metal or the presence of light of certain wavelengths may catalyse the oxidation of hydrochloric acid to produce some corrosive chlorine species. Whatever the explanation, one of the most effective corrosive reagents for all of the platinum metals, or their compounds, is a mixture of hydrochloric acid and a chlorate, heated in a sealed tube. Strong hydrochloric acid with hydrogen peroxide corrodes gold and platinum.[4]

The explanation of the corrosion by sulphuric acid is particularly obscure, despite the fact that commercially significant losses of platinum occurred in some of the early methods of manufacturing sulphuric acid.[5] Many of the early researchers believed that " pure sulphuric acid ", even at elevated temperatures, was without significant effect upon platinum sheet;[6] for impure sulphuric acid, there was little agreement concerning the identity of the corroding impurity. In some instances the corrosion was ascribed to an attack by oxides of nitrogen.[6, 7] Others believed that the oxides of nitrogen assisted in resisting the attack by sulphuric acid,[8] and evidence was offered to suggest that the corroding action was due to the oxygen content of the acid[9] or to excess of sulphur trioxide. The corrosive action of oxygen was discussed by Delépine[10, 11, 12] who, in his later work,[12] suggested that $Pt(OH)(HSO_4)_2$, sulphur dioxide and water were produced by the action of hot concentrated sulphuric acid on platinum; thus this reaction was encouraged by oxygen (by reaction with the sulphur dioxide).

Concerning the influence of the metallurgical history on the susceptibility of the platinum metals to various corrosive reagents, one must expect, by analogy to many other metals and compounds, that a prior, high temperature treatment may encourage resistance to corrosion by acids. Certain palladium salts, evaporated from solutions and subjected to excessive temperatures, become resistant even to *aqua regia*. Commercial platinum wire may also resist attack by this acid. On the other hand platinum, after subjection to very high temperatures in air or oxygen, may become more reactive (see—pp. 4 and 28).

RUTHENIUM AND OSMIUM

Ruthenium is available in both alloy and massive form. Pure ruthenium powder or sponge is not appreciably attacked by hot, single or mixed mineral acids. However, hydrochloric acid with sodium chlorate or with nitric acid will corrode ruthenium quantitatively when heated together in a closed system. Whereas hydrochloric acid containing oxygen will in some circumstances attack the finely powdered metal, the reaction is not quantitative.

It has been stated that finely divided osmium may be attacked by concentrated sulphuric acid, by *aqua regia*, and particularly by fuming nitric acid.[13] However, this finding, and references in the early literature which state that osmium is attacked by hydrochloric acid containing oxygen, by hot sulphuric acid, by *aqua regia* and by concentrated nitric acid, should not be accepted as evidence of quantitative corrosion, but merely as a precaution against treatment of the finely divided osmium with these oxidizing reagents when quantitative recovery is required. One cannot, with *any* of the platinum metals, disregard the effects of unknown impurities in precipitates etc.; in some instances at least the reputed dissolution of the metals will have resulted from the presence of impurities.

RHODIUM AND IRIDIUM

Rhodium metal or powder, under the usual analytical conditions, will resist attack by *aqua regia* and by all single mineral acids except concentrated sulphuric acid. The latter, particularly when hot, will readily dissolve rhodium powder to form a yellow solution which resists quantitative precipitation as sulphide. One must not conclude from this fact that under all conditions rhodium is thus attacked. Rhodium metal extracted by a fire assay treatment may effectively resist corrosion by all acids, and its dissolution may require fusion mixtures. It is generally accepted that pure compact rhodium is resistant to attack by any acid. Rhodium black is said to be soluble in *aqua regia* and in hydrochloric acid containing air. However, these acids are not recommended for the quantitative dissolution of any form of rhodium metal. While there are few data regarding the effect of impurities on the corrosion, sufficient have been recorded to emphasize that here, too, prediction concerning any specific inertness of rhodium toward acids should be made with caution.

Iridium sponge is exceedingly resistant to attack by mineral acids, single or mixed, hot or cold. As are the other platinum metals, iridium is said to be attacked by hydrochloric acid in the presence of air, when heated under pressure, but this method is not acceptable for quantitative analytical work.

The misapplication of qualitative data is well illustrated for iridium, small amounts of which in a very fine form are attacked by *aqua regia*. This fact resulted in the inclusion of *aqua regia* in an otherwise acceptable procedure for the quantitative and selective dissolution of iridium from a platinum metals assay bead.[14] The fact is that in this condition, the metal is not appreciably attacked by *aqua regia* of any strength.

PALLADIUM AND PLATINUM

Palladium metal is readily attacked by nitric and sulphuric acids and particularly by *aqua regia*. The massive form resists any extensive attack by hydrochloric acid free from oxidizing constituents. Precipitated palladium metal, however, can be corroded quantitatively by hydrochloric acid. The evaporation of palladium solutions, followed by the excessive heating of the residue, may result in a form of a palladium residue which is only attacked with difficulty even by *aqua regia*. Selenic acid will dissolve finely divided palladium, particularly at elevated temperatures.[15]

Platinum in the form of sponge is readily attacked by *aqua regia*, the optimum composition of which has been examined by various authors.[16] Opinions have differed as to the effect of hot nitric acid on platinum ware, but there is reasonable agreement that on pure platinum the effect is negligible.[17] Massive platinum in the form of wire etc. is sometimes resistant to corrosion by *aqua regia* and the quantitative dissolution of large amounts must be accompanied by processes other than direct acid treatments. Platinum powder is attacked by hydrochloric acid containing oxygen, although the method is not used for quantitative analytical work. For this purpose, mixtures of a chlorate and hydrochloric acid, heated in sealed tubes, are effective for all forms of platinum. Various authors have discussed the degree of corrosion of platinum by concentrated sulphuric acid.[5–12, 18] One may conclude that from an analytical point of view any finely divided form of platinum is appreciably corroded by hot concentrated sulphuric acid, but any prediction concerning the significance of the loss of platinum is hazardous.

Concerning the noble metals, suitable corroding acids for the precipitated forms are: for platinum and gold—*aqua regia*; for palladium—*aqua regia* or hot mineral acids; for rhodium—hot concentrated sulphuric acid; for iridium, ruthenium and osmium—none.

In general, the analytical chemist will avoid the use of sulphuric acid in the preparatory dissolution of the platinum metals as the subsequent analytical treatment is subject to interference owing to the stability of the sulphate complexes. Conversion to a chloride is often, therefore, a necessary prerequisite to determination. For example, the hydrogen sulphide precipitation of rhodium, and the hydrolytic separation of platinum(IV) salts are affected adversely when solutions of the metals are prepared by heating with sulphuric acid.

The Action of Bases

RUTHENIUM

Ruthenium metal, oxides and insoluble salts are readily attacked by fusion with oxidizing mixtures of alkali metal compounds such as alkali peroxides or hydroxides together with a nitrate. Early researchers believed that the fusion with sodium peroxides at low red heat produced the perruthenate.[19] Recently it has been stated that alkali fusions produce ruthenites.[20] The fact remains, however, that the fused mass is readily soluble in aqueous mineral acid solutions. Whereas quantitative precipitations can be made from the resulting alkaline solutions, it is preferable, because of the almost certain contamination, to distil or extract the tetroxide from the basic solution. Fusions with sodium hypochlorite will also corrode the metal to produce the volatile oxide, and an adaptation of this method has been used for the quantitative recovery of ruthenium[21] (Procedure 3). The method involves the production *in situ* of hypochlorite by passing chlorine into the mixture of sodium hydroxide solution and metal. Amounts of ruthenium metal of the order of 500 mg were thus dissolved and distilled. No data have been recorded to indicate the maximum amount of ruthenium which can be so treated. One must not assume that this hypochlorite conversion will remove ruthenium from natural or synthetic alloys such as the acid insoluble residue resulting from the parting of an assay bead.

OSMIUM

Osmium metal is also converted to the octavalent oxide when mixed with a caustic solution, and chlorine is added to form the hypochlorite. Fusions with oxidizing alkaline solutions produce osmates. Recently Watanabe[20] stated that, contrary to earlier literature, alkaline fusions of osmium form osmium(VIII) oxide, which dissolves to form $[OsO_4(OH)_2]^{2-}$.

RHODIUM

Recent work by Lux, Renauer and Betz[22] indicates that the fusion of rhodium metal with sodium hydroxide results in the formation of a brown coating of oxide, accompanied by some dissolution of metal in the fused caustic medium. Rhodium metal proved to be much less resistant to fusions with potassium hydroxide than to fusions with sodium hydroxide. Alloys of 70 per cent platinum and 30 per cent rhodium are more resistant than pure platinum to attack by fusion with potassium hydroxide. Rhodium metal can be fused with alkaline mixtures containing nitrate etc. or with sodium peroxide, but little is known about the identity of the fused products. It is generally assumed that the fused product is a mixture of water-insoluble oxides. The fused mass is readily soluble in acids. Rhodium metal may also be attacked by fusion with alkali metal hydrogen sulphates, this method being frequently used to separate rhodium from iridium. The procedure is not recommended for quantitative separations. One should note that such fusions may have little or no effect on rhodium admixed with other platinum metals in the condition they are found in a fire assay " insoluble ".

Iridium

Iridium sponge is readily attacked by an alkaline-oxidizing fusion such as sodium peroxide or a mixture of an alkali metal hydroxide and nitrate. The soluble product is probably a basic iridate. An important analytical peculiarity of the aqueous or acid solution of the fused mass is the marked difficulty experienced in removing adsorbed iridium salts from a filter paper through which the solution has been filtered. Compared to rhodium, iridium metal is much more susceptible to attack by fusions with sodium hydroxide at 410°C. With potassium hydroxide the attack is relatively rapid. The coating of oxide in both instances is readily attacked by *aqua regia*.[22]

Palladium

Palladium sponge, fused with sodium peroxide, yields a soluble salt said to be a palladite or perhaps a palladate. Fused mixtures of potassium hydroxide and nitrate react with palladium, but with less ease than with iridium, rhodium, osmium or ruthenium.

Palladium metal is readily attacked by fusions with either sodium or potassium hydroxide; with the latter the corrosion is quite rapid. In both instances black porous coatings are formed.[22] The metal, like rhodium, is somewhat attacked by fused potassium hydrogen sulphate.

Gold

The corrosive action of caustic fusions on gold metal was investigated by Lux *et al.*[22] Fusions with anhydrous sodium hydroxide resulted in the formation of a difficultly soluble corrosion product. Potassium hydroxide, however, produced a soluble aurate. The amount of corrosion reaches a constant value that depends upon the temperature and the oxygen and water vapour pressures.

Platinum

The reactions of platinum with alkali hydroxides and oxidizing mixtures are of particular importance because of the widespread use of platinum laboratory equipment. In so far as methods of dissolution for analytical purposes are concerned, caustic fusions of platinum are inapplicable, but a knowledge of the platinum products is of importance when alloys with the more insoluble platinum metals are to be thus corroded. Under these circumstances the fused mass probably contains water-insoluble oxides of platinum and types of oxygen-containing salts.

Lux *et al.*[22] found that fusions of potassium hydroxide in platinum crucibles resulted in the corrosion of the platinum, although the metal remained bright and the fused mass remained clear. The appreciable loss of platinum was determined directly by the metal weight losses.

It has been reported[23] that mixtures of alkali carbonates with platinum, palladium, rhodium or iridium heated at 600–1000°C in a stream of oxygen produce a series of oxide complexes corresponding to (alkali metal)$^+$–BO_2 and –BO_3. More recently, it has been found[24] that mixtures of alkaline earth carbonates with platinum, ruthenium, rhodium or iridium, when heated in air, produce a variety of oxygen-containing salts such as Sr_4PtO_6 and $Sr_3Pt_2O_7$. The technique involves heating in air, at 1000–1500°C, a 200 mesh powder of a platinum metal, after grinding the reactants thoroughly in an agate mortar. With the exception of the rhodium preparation, the reaction was rapid, and a pure product could be obtained in several hours with two intermediate grindings of the reaction mixture.

Low temperature sintering with sodium carbonate has been used with success for the corrosion of platinum metals concentrates from electrolytic refining processes. In one report,[25] the concentrate, after reduction with hydrogen to remove sulphur, was intimately mixed with sodium carbonate and heated to 700°C. The sintered mass was coherent and could be taken from the vessel as a solid dry body, and furthermore, the sintering of even large masses of concentrate could be accomplished in porcelain vessels with very little contamination. The sintered mass was readily dissolved by dilute acids, leaving only 2–3 per cent as a silica residue containing very small amounts of platinum metals, which could then be readily corroded by fusion with sodium hydroxide. The latter may also be used for low temperature sintering, and in some aspects the method is superior to the carbonate sintering. Inexplicably, such sintering processes were not effective for most of the platinum metals when treated separately.

Hydrated platinum(III) oxide has been isolated[26] following a sodium peroxide fusion. Because of the wide application of sodium peroxide fusions, various reports have been concerned with the degree of the resulting corrosion of platinum vessels. There has been general agreement that at low temperatures (about 400–600°C), in the absence of easily oxidizable substances such as sulphides etc., there is no significant corrosion of platinum vessels.[27, 28]

It is generally recognized that platinum vessels may be appreciably corroded by fusions with the following: alkali metal oxides, peroxides, hydroxides, nitrates and pyrosulphates, mixtures of easily reducible metal oxides such as those of lead, and particularly arsenides, phosphides, sulphides and mixtures which produce chlorine. Platinum vessels are particularly susceptible to corrosion by fused mixtures containing lithium oxide, peroxide or carbonate, or even by lithium silicates.[29] One finds, in otherwise reliable technical books, directions for the fusion of arsenical ores with mixtures of sodium carbonate and potassium nitrate in platinum crucibles. A single fusion of this type may destroy a platinum vessel.[30] In spite of the fact that analytical texts may direct the ignition in platinum crucibles of such precipitates as aluminium phosphate, this technique may also damage the crucibles.[31]

In general, it will be found that a caustic fusion followed by acid extractions is a useful technique for the dissolution of the more insoluble platinum metals, viz., ruthenium, osmium, iridium and rhodium. The obvious objections to caustic fusions include the certainty of at least some contamination from the vessel, the presence of high proportions of salts in the melt, and, because of the latter, the inapplicability of the technique to large amounts of metal. Although the low temperature sintering avoids a high degree of contamination, there remains the inconvenience of the high proportions of salt, and, more particularly, the application is restricted to certain physical forms of the metals. All of these detrimental factors can be avoided by certain methods of chlorination.

The Action of Chlorine

The use of chlorine to attack the platinum metals was known to the discoverers of each of these metals, and was applied in one form or another to produce platinum metal salts. In general, chlorinations are accomplished by any of three techniques, all of which require elevated temperatures. Perhaps the two most generally useful procedures from an analytical point of view are the direct chlorination in the presence of an alkali or alkaline earth metal chloride, or sometimes an arsenic or selenium salt, and the wet chlorination in a sealed tube containing hydrochloric acid and a suitable oxidizing reagent. A third method, less often used, but particularly useful for large amounts of metals, involves so-called dry chlorination, in which chlorine alone is passed over the metal or mixture in the absence of a salt. This method is invaluable for the separation of platinum from iridium.[32] In isolated instances chlorination has been accomplished by heating mixtures of sodium nitrate and magnesium chloride or iron(III) chloride to 300–350°C, so producing a corroding gaseous mixture of nitric oxide, chlorine and hydrochloric acid. This method[33] has been applied directly to ores, but recorded data are insufficient to predict its efficiency.

Hill and Beamish[34] examined the general behaviour of the platinum metals when heated in an atmosphere of chlorine, with and without admixtures of sodium chloride. The method used is described below (Procedure 8). The data from two sets of experiments are summarized in Table 1. In one series the pure metal was exposed to chlorine alone, whereas in the

TABLE 1. THE PRODUCTS OF CHLORINATION OF NOBLE METALS[34]

Element	Weight (mg)	State	NaCl added	Time (hr)	Temp. °C	Boat residue	Tube deposit	Receiving solutions Nos. 1 and 2
Ir	1·585	Reduction residue	No	24	660–720	Ir + + (v) (insol)	Ir + (s)	1st Ir – (s) 2nd Ir – (s)
	3·810	Sponge	Yes	8	680–720	Ir + (s) + + + (v)	Ir + (s)	1st Ir – (a), (s)[M] 2nd Ir – (a), (s)
Os	0·526	Sponge	No	67	650–710	None	Os – (b) (v) tr. (s)	1st Os + + (s) 2nd Os + (s)
	2·125	Sponge	Yes	5	640–670	Os + + + (s)	Os + + (s)	1st Os + (s) 2nd Os – (s)
Ru	14·403	Sponge	No	14	680–710	None	Ru + + + (v)	1st Ru + (c) 2nd Ru + (c)
	1·969	Sponge	Yes	8	670–710	Ru + (c)	Ru + + + (c)	1st Ru – (c), (s) 2nd Ru – (c), (s)
Rh	1·241	Sponge	No	18	600–710	Rh + + + (v) (insol)	Rh – (s)	1st Rh – (s) 2nd Rh – (s)
	1·918	Sponge	Yes	5½	620–710	Rh + + + (v)	Rh – (s)	1st Rh – (s) 2nd Rh – (s)
Pt	1·317	Sponge	Yes	8	680–710	Pt + + + (d)	Pt + (d)	1st Pt – (d) 2nd Pt – (d)
Au	3·049	Sheet	Yes	8	680–710	Au – (c)	Au + + + (c)	1st Au tr. (c) 2nd Au tr. (c)
Pd	1·499	Sponge	Yes	8	690–710	Pd + + + (f)	Pd – (f)	1st Pd – (f) 2nd Pd – (f)

Note—The identity of the qualitative test used is indicated in parentheses; the number of + signs roughly indicates comparative amounts; the – sign indicates absence of metal. [M] The contents of both receivers from a similar chlorination of 2 g of iridium also gave negative tests for iridium (a).

other it was first covered with dry sodium chloride. Qualitative examinations were made of the reaction products remaining in the boat. These had been deposited as a sublimate on the cooler end of the ignition tube, and had also been retained in the receivers. The tube deposit was easily removed by rinsing with dilute hydrochloric acid. The metals were detected by various tests, identified in parentheses in Table 1.

The Qualitative Tests Used Above

(a) *Iridium.* The solution was evaporated on a steam bath to 1 ml before applying Pollard's test,[35] using perchloric acid and lithium hydrogen sulphate (Procedure 120). The authors found it sensitive to 5 μg of iridium; the confirmatory test with dichlorobenzidine would detect 2 μg, but was less selective.

In connection with the iridium test (a), the authors' results were in disagreement with Pollard's, who claimed a superior sensitivity over the older nitric–sulphuric acid test. Evidently, the mauve colour formed with perchloric acid and the blue colour produced with nitric acid are both evidences of a higher oxidation state of iridium, and the authors found the methods equally sensitive. Furthermore, fuming with sulphuric acid, in the absence of added oxidant, invariably produced a strong violet colouration with iridium chloride solution.

(b) *Osmium.* The receiving solutions were concentrated separately, by evaporation over steam, to 1 ml. Then 1 ml of a thiourea solution was added, and heated for a few min. A pink colour developed when osmium was present. The thiourea solution was prepared by dissolving 25 g of thiourea in 250 ml of hydrochloric acid, and diluting to 1 l.

(c) *Ruthenium.* To the sample, concentrated to 0·5 ml by evaporation over steam, was added 1 ml of the above thiourea–hydrochloric acid solution, and warming was continued as in (b). The method was based on Wölbling's report.[36] The presence of ruthenium was indicated by a blue colour. If the test was negative, the procedure was repeated in the presence of tin(II) chloride.

(d) *Platinum.* The stannous chloride test as described by Tananaeff and Michaltschischin[37] was found to be the most sensitive, especially in the presence of other platinum metals.

(e) *Gold.* Feigl's procedure[38] using 5-*p*-dimethylaminobenzalrhodanine was used.

(f) *Palladium.* In the absence of other platinum metals, palladium was detected by the dark precipitate which formed on the addition of 1 ml of a saturated solution of tin(II) chloride in 6 M hydrochloric acid to the sample (previously concentrated to 0·5 ml on the steam bath).

(s) Spectrographic evidence.

(v) The colour of the residue and the nature of the tube deposit were considered sufficient proof of the presence of the metal, in some instances, without confirmation by a colour reaction.

General Conclusions of Analytical Interest on Chlorination

From these and confirmatory experiments, it was concluded that none of the platinum metals except osmium and ruthenium were ever carried out of the ignition tube. This information would facilitate subsequent analytical treatment of mixed chlorination products. Some gold was recovered from the receivers, however. In the absence of sodium chloride, conditions could probably be adjusted to drive all of the osmium out of the ignition tube and boat into the receiving solutions. The behaviour of ruthenium was not consistent in this respect.

The sublimate from ruthenium and from gold was heavy but was lighter from osmium, iridium and platinum. Palladium and rhodium were never detected in the tube rinsings. Osmium was sometimes deposited in a finely divided black form on ground-glass surfaces in the apparatus. This tendency was accentuated by the presence of organic matter, and when osmium was present it was never advisable to coat the flat adapter joint with wax, a device occasionally used to obtain a better seal.

Little difference was observed between the nature of the deposit obtained in the presence of sodium chloride and the product resulting from chlorination of the metal alone. Sodium chloride alone sublimed very slightly, most of it remaining unfused in the boat, with little decrepitation.

The boat residues were tested for solubility in 50 ml of 0·1 M hydrochloric acid. In the absence of sodium chloride, these were generally insoluble, but in its presence all residual chlorides dissolved readily, leaving no visible residue on filtering. There were indications that distinct complex chlorides with sodium choride had formed with iridium, platinum, palladium and rhodium. Osmium seemed to form a complex also, but it was apparently unstable and decomposed into sodium chloride and a volatile chloride of osmium. If any complex chloride of ruthenium was formed, it must have been unstable at 700°C.

RUTHENIUM

Published researches on the direct chlorination of ruthenium, though numerous, are frequently controversial in their conclusions about the extent of the reactions and the nature of the products. Claus[39] and, later, Howe, Howe and Ogburn[40] described conditions for the dry synthesis of $RuCl_2$, which were disputed by Joly,[41] Gutbier and Trenkner[42] and Kraus and Kükenthal,[43] who all found that these methods led to partially chlorinated mixtures containing $RuCl_3$. Wöhler and Balz[44] reported that $RuCl_3$ was the final product, but that its preparation was limited to temperatures below 845°C owing to the high dissociation pressure of the trichloride. By the direct high-temperature chlorination of ruthenium, Remy and Wagner,[45] and Morgan and Burstall[46] succeeded in preparing highly insoluble forms of $RuCl_3$. Wöhler and Balz[44] achieved chlorination at a lower temperature by mixing the metal with sodium chloride, which contaminated the product. Various investigators[44–47] have reported a variety of products, including carbonyl compounds, from chlorination in the presence of carbon monoxide.

The investigation by Hill and Beamish[48] was limited to the dry corrosion of pure ruthenium sponge by gaseous chlorine. Temperatures were chosen to achieve a reasonable rate of reaction and to maintain low dissociation pressures of ruthenium chloride. It was found that the complete conversion to the volatile trichloride could be made, yielding a pure product. Two distinct crystalline modifications were recovered.

The apparatus, more fully described in Chapter 7, Equipment No. 1.

consisted of a pre-heated silica chlorination chamber, into which a porcelain boat containing the metallic sample was introduced. This sample was weighed directly in a porcelain microboat, and sodium chloride was weighed on glazed paper and transferred to the boat so that it covered all of the metal. This microboat was placed into a larger boat and moved well to the back of the cold ignition tube, which was then flushed with chlorine and placed in the preheated muffle. A continuous current of chlorine gas throughout the ignition period served to expel traces of air and to sweep out volatile products. Spectrographically pure ruthenium sponge was used, and the chlorine was previously dried by passing it through concentrated sulphuric acid and over phosphorus pentoxide. Special precautions against the formation of volatile ruthenium tetroxide included flushing the reaction tube with chlorine just before and immediately after inserting the sample. On completion of each experiment, the reaction tube was disconnected and sealed, thus allowing the contents to cool in an atmosphere of chlorine.

Chlorinated products were recovered as non-volatile boat residues and as sublimates, which were generally deposited on cooler sections of the apparatus, but were occasionally carried over into dilute hydrochloric acid contained in a train of "bubbling towers ". Colorimetric and spectrographic tests indicated that only a small proportion of the ruthenium reached the receiving solutions. The relative amounts of residue and sublimate depended upon the extent of chlorination; prolonged treatment at about 700°C invariably caused complete conversion to the more volatile product, most of which crystallized on the walls of the reaction tube at room temperature.

The black residues from two incomplete chlorinations (2–3 hr at about 600°C) were analysed for ruthenium by reduction in hydrogen. A variation in the chlorine content suggested incomplete chlorination to ruthenium trichloride rather than the presence of lower chlorides.

Two distinctly different types of tube deposit were obtained, often simultaneously. One was a dark brown greasy layer and the other consisted of shiny black leaflets. The two were separated mechanically under a hand lens. The brown material was slightly hygroscopic but, after drying, both the brown and the black modification showed a ruthenium content within 0·2 per cent of the theoretical value for ruthenium trichloride.

The two substances differed greatly in chemical properties. Whereas the black crystals were negligibly soluble in water, hydrochloric acid or ethanol, these were solvents for the brown chloride. *Aqua regia*, which readily attacked the latter, had much less effect on the former. The brown trichloride formed a brown aqueous solution. Its hydrochloric acid solution was reddish brown: this was reduced to a blue solution by the addition of powdered zinc. The addition of ethanol to the brown chloride produced a brown liquid which, upon addition of zinc, became green, and finally yellow.

Complete conversion of metallic ruthenium to sublimed ruthenium trichloride usually required at least 48 hr at 700°C for a 50-mg sample. Some of the brown trichloride was always obtained, although the formation of the black crystals seemed to be favoured by conditions which retarded the reaction. A semiquantitative recovery of ruthenium as a sublimate was possible, the degree of solubility of the product depending on the relative amounts of the two forms of chloride.

Specimens of both the brown and the black varieties of sublimed ruthenium trichloride were examined by X-ray analysis. The samples were irradiated in the presence of beryllium. Definite and distinctive crystal structures were indicated for both materials.

Other researches have confirmed the existence of allotropic modifications of ruthenium(III) chloride. Kolbin and Ryabov[49] found that the complete chlorination of metallic ruthenium at 280–840°C yielded three modifications of the trichloride. The α allotrope, brilliant black discs, was insoluble in water and acids; the β compound was a brown powder which was insoluble in water and acids but soluble in organic solvents; the third modification was a dark brown, dense, hygroscopic, amorphous powder which was soluble in water. Contrary to the opinion of Hill and Beamish,[34, 48] the previous workers believed that incomplete chlorination yielded a mixture of metal and ruthenium(II) chloride. Products with a composition approximating to Ru_2Cl_5 were also formed. X-ray powder diagrams showed that the β modification was irreversibly converted to the α form on heating to about 500°C. In an earlier paper Ryabov and co-workers[50] postulated the formation of a volatile ruthenium(IV) chloride formed at 484–756°C in a current of chlorine and nitrogen. This conclusion has not been confirmed.

Westland and Beamish[51] found that the chlorination of mixtures of sodium chloride and ruthenium invariably produced some of the insoluble α modification, the presence of which introduced considerable difficulty into quantitative work. A method has been devised for the determination of micro amounts of ruthenium which involved a chlorination to produce chlorides which were completely soluble in aqueous media. The apparatus, described in Chapter 7, Equipment No. 2, is prepared by coating the cooler part of the chlorination tube with a layer of sodium chloride. Quantitative recovery depends upon avoiding the condensation of the ruthenium chloride on the hotter, glass surfaces. This condition is fulfilled if the dimensions shown for Equipment No. 2 are adhered to, and if the quantity of ruthenium in the sample is small.

In the chlorination of alloy samples weighing several mg, the presence of the other platinum metals apparently did not jeopardize the recovery of ruthenium by " saturating " the sodium chloride layer. The evidence for this consists of the failure to see any black ruthenium chloride residue on the filter through which the solution of chloride was passed. Although the extent of recovery from alloys was not determined, a duplicate analysis of an iridosmine mineral yielded satisfactory precision.[52] Various methods of coating the tubes with sodium chloride were investigated. In some instances appreciable amounts of the insoluble ruthenium chlorides were found after chlorination: when they constituted a large proportion of the ruthenium the methods of recovery met with little success.

Some effort was made to deal with these insoluble residues; they were separated from the extracting solution by filtration through a 0·8-cm circle of filter paper. The filter paper and residue were placed in a small nickel crucible, and were covered with a mixture of 2 parts of sodium hydroxide and 1 part of sodium peroxide, and the whole was fused and brought to a bright red heat. When known quantities of ruthenium salts were treated in this manner, the recoveries were not quantitative. It was thought that the difficulty was due, at least in part, to volatilization of ruthenium trichloride from the melt or from the mixture before the sample was entirely fused. There is some evidence that fusion in a nickel bomb results in small losses from volatilization and deposition on the bomb walls.

TABLE 2. RECOVERIES OF RUTHENIUM FOLLOWING ITS CHLORINATION[51]

Expt. No.	Ru taken (μg)	Source	Recovery (μg)			
			Soluble part	Insoluble part	Error (μg)	
1	208	Sponge	199	3	−6	Uniform NaCl coating. Formed by evaporating solution.
2	354	Sponge	186	..	..	Poor NaCl coating. Formed by evaporating solution. Insoluble chloride incompletely removed.
3	301	Sponge	236	..	..	Fair NaCl coating. Otherwise as 2.
4	856	Salt	804	17	−35	Fused NaCl coating.
5	1174	Sponge	784	240	−150	Fused NaCl coating. Much insoluble chloride.
6	60·0	Salt	59·7	..	−0·9	Fused NaCl coating. No visible insoluble residue.
7	132·0	Salt	128·4	..	−3·6	
8	318	Sponge	303	..	−15	
9	338	Sponge	330	..	−8	

The results of a study of the chlorination of ruthenium are summarized in Table 2. The insoluble matter was treated in a nickel crucible or bomb, as described above, then distilled, and the ruthenium was estimated photometrically as its thiourea complex. The insoluble residues were determined directly by distillation.

With samples 1, 2 and 3 (Table 2) the sodium chloride coating was formed by evaporating a film of salt solution on the glass. In the one instance in which the coating appeared to be uniform there was quantitative recovery, but in the other two the need for an unbroken coating is clearly evident. The quantities of ruthenium taken in samples 4 and 5 were too great for the size of apparatus employed. Of the remaining samples the smaller ones yielded the better accuracy. In considering the errors in samples 8 and 9, it should be borne in mind that the error in weighing ruthenium as sponge is greater than weighing as salt, as in numbers 6 and 7.

OSMIUM

Westland and Beamish[51] used chlorine to quantitatively dissolve micro amounts of osmium, ruthenium and platinum. The method is described in Procedure 39. The relatively volatile osmium chlorides were retained in the chlorination system by passing the chlorine stream into a train of receivers containing hydrochloric acid which was kept saturated with sulphur dioxide.

Osmium was attacked more easily by chlorine than were any other of the platinum metals. The reaction began at a lower temperature and proceeded much more rapidly, mg quantities of the metal being attacked completely in a few min at 575–600°C. A sublimate of osmium formed at various distances from the furnace. That nearest the furnace was often difficultly soluble in the wash solution, but when the reaction tube containing the wash solution was heated with a microburner, the deposit came free. This blue-black sublimate was entirely soluble in the hot sulphuric acid used in the distillation step. There appeared to be no advantage in covering pure osmium samples with sodium chloride.

RHODIUM

Rhodium metal also combines directly with chlorine, but relatively little is known about the optimum conditions for any analytical applications. The reaction presumably begins at about 250°C. the trivalent chloride being formed as a red powder insoluble in water and resistant to acids. There is some evidence for the existence of more than one form of chloride salt. In this respect, it is noteworthy that the trichloride formed in aqueous media. and subsequently isolated, behaves quite differently from the compound formed by direct chlorination. Although the former is quite soluble in water, it, too, becomes insoluble when heated. The analytical chemist may benefit from the knowledge that the brown solution of hydrated rhodium(III) chloride yields no precipitate with silver nitrate, whereas after boiling the solution becomes yellow, and all the chlorine may be removed as silver chloride. Undoubtedly, the quantitative chlorination of rhodium is best carried out in the presence of admixed sodium chloride, from which product the rhodium is readily dissolved by aqueous solutions.

IRIDIUM

Because of the exceptional inertness of this metal, the chlorination of iridium has received considerable attention. The powdered metal can be chlorinated directly at 600–700°C, giving an insoluble trichloride whose colour, varying from a dark green to a brown-black, seems to be somewhat dependent both upon the state of division of the iridium metal, and upon the chlorinating temperature. The initial chlorination may begin at 100°C; it continues to about 800°C. There is some evidence that chlorination is promoted by ultraviolet light.

A potentially useful method for chlorinating iridium in the presence of platinum was patented in 1913.[32] A separation of the two chloride salts is accomplished. The chlorination of the two metals is complete at about 600°C, under which condition the soluble and partially volatilized platinum chloride can be isolated from the relatively insoluble iridium chloride by treatment with *aqua regia*. The optimum temperature for chlorination is 600°C. By repeating the process, the metals can be separated to a high degree of purity. Undoubtedly this method could be extended to provide a separation of iridium from other metal admixtures.

While no data were found to encourage the hope for a general quantitative application, one cannot doubt that this method of selective dissolution of the chlorinated products will prove to be as effective for large scale separations as a refining procedure. However, because selective dissolution or selective corrosion techniques are fundamentally suspect, the use of such a method for the separation of small amounts of iridium and platinum would require the support of adequate data. One need only recall that even iridium metal, in a finely dispersed condition, is not inert to *aqua regia*.[53]

Direct chlorination in the presence of sodium chloride results in products which are quantitatively soluble in aqueous media. In a series of determinations, Hill and Beamish[34] covered iridium sponge with ten times its weight of reagent grade sodium chloride and exposed the mixture to chlorine in a heated silica tube for 8 hr at 700°C. The product was dissolved in 0·1 M hydrochloric acid, and filtered before determining the iridium content. No insoluble residues were obtained after 8-hr chlorination, but several preliminary trials showed 4 hr to be insufficient for the complete reaction of 5 mg of iridium. A pinkish grey sublimate, which also contained some iridium, was found in the cold end of the ignition tube. It was readily removed by rinsing with dilute hydrochloric acid. The iridium in the corroded product was determined gravimetrically.[34] No significant amount of iridium was found in the receiving solutions attached to the end of the chlorinating tube. Although the recoveries were on the average 0·7 per cent high, good precision was obtained.

PALLADIUM

Few quantitative data relevant to analytical chemistry have been recorded concerning the reaction of chlorine with palladium. The metal is readily converted to soluble salts by the action of single or mixed mineral acids. However, the chlorination of the platinum group recovered from natural sources does involve the chlorination of palladium because this metal is practically always an associate of platinum in natural deposits. Direct chlorination results in the formation of the red dichloride, which is readily soluble in water. Compared to the chlorination products of the other platinum metals, the palladium salts are relatively volatile, and dissociate perceptibly at 600–700°C, which is generally the optimum range for chlorination of the platinum metals. Undoubtedly the chlorination process used to separate platinum from iridium would be even more readily applicable to a similar separation of palladium from iridium.

In 1944, Plaksin and Shabarin[54] chlorinated palladium and platinum ores, ground to −28 mesh, in the presence of sodium chloride. They reported complete extraction of the palladium at 300–350°C. Platinum recovery was only 51–85 per cent at the same temperature.

PLATINUM

Although platinum, like palladium, is readily corroded by *aqua regia*, a considerable amount of data have been accumulated concerning its chlorination characteristics. Around the latter part of the nineteenth century many workers noted that hot chlorine gas attacked finely divided platinum. Schutzenberger[55] reported that some action took place at 240–250°C, yielding $PtCl_2$, but no greater yield was obtained at 300°C. Pigeon[56] reported a small yield of $PtCl_4$ at 360°C, together with some $PtCl_2$ and unreacted metal. He also found that heating admixtures of platinum, selenium and arsenic trichloride in a stream of chlorine resulted in the complete dissolution of platinum. Nogareda[57] studied the chlorination reaction, and concluded that between 600 and 850°C $PtCl_4$ was formed as a result of the collison of chlorine molecules on the hot platinum wire used. Above 1200°C, he considered it to be an atomic reaction which was governed by adsorption on the platinum. 850–1200°C was regarded as a transition range between the two processess. Troost and Hautefeuille[58] noted the volatility of the chloride in chlorine, as did Meyer[59] and Seelheim,[60] the latter two disputing the mechanism of the reaction. Troost and Hautefeuille[58] collected the $PtCl_2$ formed by attack at 1400°C at the cold end of the reaction tube. Wöhler and Streicher[61] studied the heat stability of the chlorides in an atmosphere of chlorine, and gave the temperature ranges over which the tetra-, tri-, di- and monochlorides existed, the latter being stable only over a 2°C range. If it was heated above this range it became metallic platinum.

Fraser and Beamish[62] investigated the nature of the platinum chlorination, both in the direct process and in the presence of various salts, with a view to its analytical applications. The powdered platinum was weighed directly in a Coors porcelain boat, covered with about ten times its weight of sodium chloride and placed inside a larger boat (Coors No. 2). The whole was inserted in a silica ignition tube of the same design as that described in Chapter 7, Equipment No. 1. The apparatus was identical except that no phosphorus pentoxide drier and only one sulphuric acid bubbler was used. Usually the chlorine was bubbled through the system at one bubble per second, and allowed to run overnight. The samples were cooled in an atmosphere of chlorine. The chlorination products in the boat were washed with water through a filter paper, and the residue was ignited at 800°C. The filtrate was treated to precipitate platinum sulphide. The receiver solutions were similarly treated. The results are summarized in Table 3.

Table 3 indicates that salts other than sodium chloride form soluble complexes with platinum, but not all with the same ease, calcium and barium oxide being relatively inactive, whereas potassium chloride is relatively active. At 720°C, all salts showed some volatilization of platinum chloride. Above 700°C, the reaction with sodium chloride was usually complete, but was invariably accompanied by volatilization of platinum chlorides. Below 600°C, volatilization did not occur in the presence of admixed salts. Reaction was only complete in this temperature range for two samples, 5·5 and 4·4 mg. For larger samples, the reaction at 600°C was incomplete, and increasing the time of chlorination from 14 to 40 hr did not complete the reaction. In order to determine the composition of the chlorinated product, it was separated from the salt by recrystallization as orange-red crystals analogous in physical appearance to $Na_2PtCl_6{\cdot}6H_2O$. After drying in an oven at 110°C, a yellow powder was produced similar in appearance to the original chlorinated product. The latter was reduced by hydrogen, and the platinum and chloride contents were determined gravimetrically. The data obtained indicated the formula of the yellow powder to be Na_2PtCl_6.

X-ray powder diffraction photographs of the dried salt and of a sample of " Baker's " sodium hexachloroplatinate were identical in appearance.

Chlorinations of platinum sponge were carried out with a view to their possible analytical application. The chlorination of 8·6 mg of metal at

TABLE 3. THE DISTRIBUTION OF PLATINUM AFTER CHLORINATION AT VARIOUS TEMPERATURES

Sample No.	Admixture	Wt. taken (mg)	Temp. (°C)	Time (hr)	Platinum content of					% reacted
					Insoluble boat residue (mg)	Tube deposit (mg)	Receiver solution (mg)	Recov. from soluble in boat (mg)	Total recov. (mg)	
1	None	9·11	735	10	6·99	+ + +	+	— — — — — — — — — —	— — — — — — —	23
2	NaCl	7·12	720	8	— — — —	1·02		7·21	8·23	100
3	KCl	6·99	720	10	·57	·17		6·74	7·48	92
4	CaO	9·18	720	7	8·42	·52		1·30	10·24	8
5	BaO	9·01	720	10	6·89	1·06		1·49	9·44	23
6	NaCl	8·52	720	15	·72	·33		7·50	8·55	92
7	NaCl	8·03	690	16	— — — —	·33		7·71	8·04	100
8	NaCl	10·31	720	14	— — — —	·57		10·20	10·77	100
9	NaCl	10·52	650	13	— — — —	·11		10·13	10·24	100
10	NaCl	10·20	720	17	— — — —	·49		9·89	10·38	100
11	$Ba(OH)_2$	9·11	720	16	6·35	+ +	·26	1·03	— — —	30
12	NaCl	10·27	720	13	— — — —	·81		10·34	11·15	100
13	NaCl	11·63	675	12	·53	·13	— — —	10·94	11·56	95
14	NaCl	9·22	650	10	4·58	·93	— — —	5·33	10·84	50
15	NaCl	10·60	595	14	1·39	·29	— — —	7·61	9·29	87
16	NaCl	9·73	535	16	·83	·08	— — —	9·01	9·91	91
17	NaCl	9·92	505	14	5·90	— — —		4·12	10·02	40
18	NaCl	12·66	480	15½	4·50	— — —		8·22	12·77	61
19	NaCl	9·12	495	49	1·64	— — —		7·65	9·29	82
20	NaCl	6·05	580	14	1·05	— — —		4·97	6·02	83
21	Discarded, leak in apparatus									
22	NaCl	4·81	455	41	1·92	— — —		2·78	4·70	60
23	NaCl	5·31	470	17	2·79	— — —		2·63	5·42	47
24	NaCl	3·53	560	14	— — — —	— — —		3·91	3·91	100
25	NaCl	4·70	610	19	·60	— — —		4·31	4·91	87
26	NaCl	4·39	595	18	— — — —	— — —		4·68	4·68	100
27	NaCl	9·89	535	24	·67	— — —		9·47	10·14	93

455–480°C for 8 hr resulted in a 55 per cent conversion to a volatile chloride, which deposited as a yellow film on the cold end of the tube, just outside the furnace wall. Immediately inside the furnace a slight black deposit was formed on the inside of the tube. The residue in the boat consisted of yellow hygroscopic material and grey metallic powder. At 525–535°C, 3·7 mg of the sponge was 78 per cent converted to a volatile powder after a 9-hr chlorination. The deposit was of the same colour and appearance as the previous one, but further removed from the boat, i.e. completely outside the furnace box. The residue in the boat was metallic in appearance, but contained 14–7 per cent chlorine. At 610–620°C, 5·3 mg of the sponge produced 48 per cent of the volatile chloride after a 7-hr chlorination. The boat residue was somewhat deliquescent, forming a yellow solution around metallic clumps in the boat. At 665–675°C, 8·8 mg of sponge produced 56 per cent of volatile chlorides after a 13-hr chlorination, these depositing in three distinct colours, viz., black, brown and yellow. After standing for 72 hr, they had all changed to a brownish yellow deposit. This suggested the existence of several forms of the same compound, their colours depending perhaps upon the state of division. The boat residue was completely metallic in appearance, and lost no weight on attempted reduction. The three, coloured chlorides were mechanically separated, and the platinum content was determined. The results are listed in Table 4.

In the above table, all results from the same chlorination have the same number, e.g., 21a, 21b and 21c. It can be seen that in all but No. 19 the data are almost identical for the three types of chloride deposit from the same chlorination. With the exception of the anomalous results in Nos. 14 and 15, the composition of the chloride tends towards a higher chlorine content with increasing temperature. Nos. 14 and 15 apparently yielded relatively pure $PtCl_4$, but attempts to duplicate the results were unsuccessful. No. 20 was almost pure $PtCl_2$. The other salts seemed to be mixtures of the two chlorides in proportions fixed by the temperature. The boat residue in No. 20 was a brownish powder, much denser than the volatile chlorides. Its composition, however, corresponded to that of partially chlorinated metal. X-ray examination of the three, coloured chlorides showed that they had identical crystal structures. Their composition varied between platinum(II) and (IV) chlorides. Low temperatures favoured the formation of the dichloride, and high temperatures, that of the tetrachloride. The reverse effect applied to the boat product. X-ray powder diffraction photographs showed the volatile chloride of intermediate composition to contain both the di- and tetrachlorides of platinum.

From the analytical point of view, the chlorination in the absence of a salt will have a restricted application. Undoubtedly this method may be of considerable use for mixtures of metals some of which form insoluble chlorides. A good example is the separation of platinum from iridium and ruthenium. A procedure of this type would require only the selective corrosion of platinum, with no restriction as to the composition of its chloride salts. The chlorination in the presence of salts will have wide applications, both for amounts of metals of the order of analytical requirements and for large scale corrosions.

Chlorination was applied quantitatively by Conrad and Evans[63] to the determination of platinum in petroleum conversion catalysts. They heated mixtures of the catalyst with a large excess of aluminium chloride at the "white hot" temperatures of an induction furnace. The unidentified volatile chloride was collected in purified water containing hydrochloric acid. The results compared favourably with those obtained by conventional methods.

TABLE 4. THE REDUCTION OF VOLATILE PLATINUM CHLORIDE

Sample No.	Colour of sample	Temp. of chlorination (°C)	Sample taken for reduction (mg)	% Cl	Ratio Pt : Cl
9	Black	675	3·231	32·97	1 : 2·71
10	Yellow-brown		7·479	31·15	1 : 2·49
14	Brown*	610–675	1·159	41·60	1 : 3·91
15	Black*		2·988	42·31	1 : 4·03
16	Yellow-brown	665	7·057	30·21	1 : 2·39
17	Black		7·171	30·25	1 : 2·39
18a	Brown	595–620	10·939	27·87	1 : 2·13
18b	Black		8·573	27·80	1 : 2·12
19	Yellow-brown	760	3·367	36·67	1 : 3·19
19b	Black		5·566	36·33	1 : 3·14
19c	Rusty-brown		4·927	40·50	1 : 3·75
20a	Yellow-brown	535–565	4·058	27·35	1 : 2·07
20b	Black		16·038	26·93	1 : 2·03
20c	Brown		4·375	27·11	1 : 2·05
20d	*Boat residue*		27·502	6·32	1 : 0·372
21a	Yellow-brown	525–550	5·051	28·78	1 : 2·22
21b	Brown		3·597	27·03	1 : 2·04
21c	Black		1·454	28·75	1 : 2·22
22a	Brown	455–470	5·595	27·88	1 : 2·13
22b	Black		3·725	27·95	1 : 2·14

* Very hygroscopic

The chlorination technique can be applied successfully to the most resistant of commercial platinum alloys—those containing high percentages of iridium—and to naturally occurring alloys such as iridosmines, the most resistant of which appear to be certain Tasmanian iridosmines.

THE CLOSED-TUBE CHLORINATION

In the present author's opinion the only other method of comparable efficiency to the above for analytical amounts of metals is the sealed-tube corrosion developed by Wichers, Schlecht and Gordon[64] at the United States Bureau of Standards. These authors recorded in excellent detail the character of the reactants, the optimum conditions for corrosion and the protective apparatus. In principle, the method is an adaptation of the Carius decomposition of organic materials, with much closer attention paid to the tube construction and to the oxidizing mixtures. The authors have successfully corroded both coarse and fine alloys of the platinum metals, and the method has been widely used with equal success as a routine procedure in various industrial and research laboratories.

The present author has experienced some difficulty, however, in its application to certain iridosmines[34] and to the more insoluble portions of some partially refined platinum metals.[25] It is not improbable, though, that these failures were due, not so much to the ineffectiveness of the method, as to failure to choose from the recommended procedures the optimum conditions for chlorination. Even so, the present author prefers, partly because of familiarity, the open-tube chlorination in the presence of a salt; very large as well as μg samples are readily attacked, and the products of the reaction are readily collected. Those residues which resist complete corrosion by the closed-tube method are readily converted to soluble forms by open-tube chlorination. On the other hand, where a salt is best avoided, the sealed tube is generally preferable. It is unfortunate, however, that dry chlorination in the absence of a salt has not been given sufficient attention. There can be little doubt that fruitful applications could be thus developed for the selective separation of iridium from both platinum and palladium.

When using a bomb chlorination, close attention must be given to the quantities of reagents, the ratio of hydrochloric acid to metal and to the chlorine equivalent. In general, the ordinary 36 wt. per cent hydrochloric acid is acceptable. No less than 4·2 g of hydrochloric acid should be used per g of platinum metal sample. Although 10 ml of acid is the minimum requirement, corrosion is hastened by the addition of about double this volume. For materials particularly resistant to chlorination, concentrations of hydrochloric acid up to 50 wt. per cent may be prepared by the distillation of the 36 per cent acid through a cold condenser with the collected acid cooled by ice. A more concentrated acid can be prepared by condensing dry hydrogen chloride on an ice surface.

The hydrochloric acid can be oxidized by various salts and acids. For practically all alloys and residues, the present author uses fuming nitric acid (*ca.* 90 wt. per cent HNO_3). A reasonable working rule for the more insoluble metals is the provision of 25 mg of chlorine per ml of internal tube volume. For each g of platinum, iridium or osmium, or mixtures of these, one may use either 0·22 ml of perchloric acid (70 wt. per cent $HClO_4$), 0·27 ml of nitric acid (70 wt. per cent HNO_3), 0·19 ml of fuming nitric acid (91 wt. per cent HNO_3) or 0·37 g of sodium chlorate. For the lighter platinum metals (ruthenium, rhodium and palladium), larger amounts of oxidant are required, in proportion to their smaller atomic weights. When the strongly associated nitroso compounds are to be avoided, nitric acid should not be used.

Perchloric acid should be avoided in the presence of organic matter or where low temperature chlorinations, e.g. below 250°C, are used, because the reaction is excessively slow. Furthermore, unless all the perchloric acid is reduced, losses of osmium and ruthenium tetroxides may occur on exposure of the reaction mixture to the atmosphere. This may also happen to osmium when nitric acid remains in the chlorinated solution. In general, perchloric acid is not recommended. Sodium chlorate is a suitable substitute for nitric acid, but sodium chloride remains as a dissolved constituent after the reaction.

The optimum temperature for quantitative chlorination varies with the identity and character of the metal. For the most refractory materials, 300°C is usually recommended. Certain metals, such as platinum–iridium alloys, may be effectively chlorinated at 100–150°C. Temperatures higher than 300°C are used by the present author for mg amounts of rhodium and iridium. In most instances the oxides of these and other metals, which are produced by various analytical techniques, are first reduced in the open tube by a stream of hydrogen. Subsequently, the end of the tube is sealed, the reactants are added as described below, and the temperature is maintained at 450–500°C, under which conditions the small amount of reduced iridium is chlorinated in 2 hr and the rhodium within 1 hr.

The hard glass tubes used by the author are 20 cm long, having a 9·52 mm outside diameter with a wall thickness of 2 mm. These have proved satisfactory for all chlorinations of 10 mg samples, with practically no incidence of explosions. Furthermore, no protective tube is required for the small tubes. Larger tubes are, of course, required for samples of 0·2–1·0 g or more (see Equipment No. 3A). In general, the tube should be no longer than is required to contain in two-thirds of its volume the amount of acid needed for the chlorination. These larger tubes, used by the author and certain industries, are about 20 cm long with an inside diameter of 15 mm and a wall thickness of 2 mm.

Each tube is sealed having a 10 cm stem of 4 mm inside diameter and 2 mm wall thickness. The author's experience has been confined to samples weighing no more than about 1 g. To accommodate larger samples, it is recommended that tubes of increased length rather than greater diameter be used. Samples of the order of 0·05–1·0 g are chlorinated in large tubes which are carefully protected to avoid explosions. The equipment used by the author is in general that recommended by Wichers *et al.*,[64] and described in Chapter 7, Equipment No. 3.

The sealed tubes are inserted into a steel cylinder fitted with a screw cap and gasket (see Equipment No. 3C). Calcium carbonate is added to the cylinder to remove acid should breakage occur. Solid carbon dioxide is also added in amounts calculated to compensate the pressure of chlorine derived from the hydrochloric acid. Prior to heating, the steel cylinder is immersed in water to test the screw cap for leaks. After the chlorination, the cylinder is air cooled, the tube removed, and then chilled in dry ice prior to opening. For the small tubes used by the author, the heating is accomplished without the protection of the steel cylinder etc. After cooling in dry ice, the opening is made by heating the seal to redness and then wetting it with a drop of water. A method of transferring the tube contents is illustrated in Chapter 7, Equipment No. 3B.

A bomb chlorination method used for the preparation of samples to be analysed spectrochemically is given in detail in Procedure 199.

Fusions with Base Metals

There is a variety of less generally applicable methods available for the preparation of solutions of the more resistant platinum metals. These involve a preliminary fusion with zinc, tin or bismuth, etc. to produce either intermetallic compounds soluble in mineral acids or to convert the platinum metals into a physical state more suitable for corrosion by mineral acids or oxidizing fusions.

FUSIONS WITH ZINC

Fusions with zinc are perhaps the most frequently used. In this process, a variety of intermetallic compounds may be involved. Compounds such as $RhZn_2$, Rh_3Zn_2 and hexagonal prisms of a ruthenium–zinc compound, have been reported. Fused mixtures of zinc and platinum have been stated to contain PtZn, $PtZn_2$, Pt_2Zn_3. Zinc alloys with both palladium and iridium have also been reported. Few of these products have been isolated as pure substances. It is noteworthy, however, that the reaction between fused zinc and certain of the platinum metals, e.g. platinum, may result in finely powdered metal which may be explosive on treatment with acids. The fusion may be accomplished in a quartz crucible at about 800°C. The metal is mixed with about 10 parts of powdered zinc, preferably free of lead, and covered with zinc chloride.

The progress of the fusion can be followed by stirring with a discarded carbon electrode. The time required for complete fusion is at least 1 hr, depending upon the identity and physical character of the alloy. Zinc fusions have been used for the determination of iridium in refined rhodium sponge (see Procedure 10). Certain types of iridosmines are thus converted to finely powdered metal after selective reaction with hydrochloric acid. The platinum metals residue is readily corroded by oxidizing fusions, and in some instances will explode upon ignition; in general, ignition should be avoided.

In 1955, Aoyama and Watanabe[65] used a zinc fusion to assist in the dissolution of an iridosmine. The residue from a hydrochloric acid treatment was heated in a current of oxygen to remove osmium prior to a fusion with sodium hydroxide and sodium nitrate. Presumably the authors experienced no difficulty from direct heating.

FUSIONS WITH BISMUTH

Molten fusions have also been used to provide limited separations. In this way, iridium may be freed from rhodium by fusion with bismuth. The iridium–rhodium powder is stirred into molten bismuth, and subsequent treatment with nitric acid isolates the rhodium.[66] Although the descriptive chemistry of the fusions with zinc or with bismuth have not been recorded, one may hope that these techniques will receive some attention as regards their analytical applications. Furthermore, one can expect them to have some usefulness in certain phases of refining processes.

FUSIONS WITH TIN

Fusions of the platinum metals with tin have been used successfully as an intermediate step in the dissolution of resistant metals by acids. A variety of tin–platinum metal compounds have been recorded, e.g. $RuSn_3$, crystallizing in cubes, and $RhSn_3$ and $IrSn_2$, which are residues from a hydrochloric acid treatment of fused tin and rhodium or iridium. Palladium is reported to form an alloy with tin, but no compound has been isolated; no report of an intermetallic compound with osmium has been found. A relatively large number of reports have been concerned with platinum–tin alloys. An examination of the thermal equilibria of this binary system[67–69] indicated an eutectic at 118°C, four discontinuities, and a maximum at 1281°C corresponding to PtSn. The components of the eutectic were reported as Pt_3Sn and PtSn. The discontinuity at 846°C corresponded to Pt_2Sn. This compound had been prepared by treating a fused alloy of 6 parts tin to 1 of platinum with hydrochloric acid. At 538°C, the composition of the solid corresponded to Pt_3Sn_8; other compounds reported were Pt_2Sn_3, $PtSn_2$ and $PtSn_4$. Presumably, alloys of tin with 0–30 per cent of platinum are readily attacked by dilute hydrochloric acid, but with increasing proportions of platinum, the attack is slower. With *aqua regia*, alloys containing as much as 80 per cent of platinum are readily attacked. When this is increased to 90 per cent, the alloy resists the attack even of chlorine.

Faye and Inman[70] prepared iridium–tin alloys, and subsequently purified the iridium by selective dissolution with acids and volatilization of the residual tin, finally removing traces of tin with ammonia. In this method, about 10–20 mg of iridium is alloyed with 3 g of tin by heating the mixture in a Vycor tube of 2·2 cm internal diameter and 10 cm length. Air is removed from the tube by nitrogen gas delivered over the mixture by a 1 × 15 cm Vycor tube. The melting tube is heated over an open flame, and the tube is vigorously swirled during the fusion. When fusion is complete, the hot metal is quickly poured into a litre of cold water. The water is then decanted, and the residue is dried on a hot plate. Any alloy frozen on the upper wall of the melting tube is scraped off, and is added to the dry residue. The mixture is transferred to a 300-ml beaker and 40 ml of concentrated hydrochloric acid are added followed by a 30 per cent hydrogen peroxide solution. The mixture is heated and further hydrogen peroxide solution is added; heating is continued until the residue is dissolved completely. The solution is then evaporated to about 5 ml, 10–20 mg of sodium chloride are added, followed by 10 ml of a 7 : 2 mixture of hydrochloric and hydrobromic acids, and the tin is removed by volatilizing over a flame. The solution is evaporated to 1 ml and the above volatilization is repeated six times. The solution is treated with 10 ml of a 1 : 1 mixture of hydrochloric acid and 30 per cent hydrogen peroxide solution to redissolve any iridium. Finally, the solution is evaporated to about 2 ml, diluted, and filtered. This iridium solution will contain traces of tin which, if necessary, can be removed by precipitation with ammonia. The hydrated tin oxide may contain traces of iridium. The above method is not recommended as a method of dissolution when mg amounts of iridium are to be determined.

A second method for the dissolution of iridium by fusion with tin was described by Pollard.[35] This method was integrated with a volumetric determination of iridium and is described in Procedure 120.

Methods for the analysis of the tin minerals have also been reported.[71]

The Effect of Oxygen on the Hot Metals

Contrary to general opinion, all the noble metals may undergo a change in weight when they are heated in oxygen or air at elevated temperatures. This is observed as a weight loss with platinum, iridium, ruthenium and osmium, and as a weight increase with rhodium, palladium and gold; alternatively the hot metals may incur both a loss of metal owing to the volatility of an oxide and a gain of weight resulting from the formation of a stable oxide. This simultaneous loss and gain may be experienced with iridium and ruthenium, and perhaps with others. It has been stated that the prolonged heating in air of all the platinum metals results in a more or less rapid loss in weight at temperatures above about 1000°C; because this loss does not occur in inert gas atmospheres, it has been attributed to the formation of volatile oxides.[72]

Although there is convincing evidence that at temperatures beyond those used in ordinary analytical processes each of the platinum metals forms some volatile metal–oxygen combination, the data accumulated by the author indicate that for the usual analytical applications, the changes in weight are significant only for platinum, iridium and ruthenium, and even for these the weight change is small at bunsen heat and may often be ignored, except in some instances of heating platinum ware. Osmium, of course, is completely volatilized by heating in oxygen.

None of the six platinum metals has the nobility of gold, although platinum is somewhat comparable to gold in its resistance to attack by single mineral acids and to the action of oxygen on the hot metal. Even with platinum, as the most noble of the six platinum metals, however, the analytical chemist who is seeking high accuracy must avoid prolonged heating of platinum crucibles or precipitates at temperatures of about 1000°C or higher.

Ruthenium, rhodium, iridium and palladium all form oxides when heated in air at the temperature of a bunsen flame. These oxides, however, are seldom used as weighing forms. The oxidation is usually slow, and there is superficial protection by the outer layers of oxides, e.g. the completed conversion of 200 mg of rhodium to the rhodium(III) oxide by heating in air with a bunsen flame has, on occasion, taken 3 days. Anyway, the mixtures of metal and oxides resulting from the precipitation and ignition of these four metals are always converted to the metal by heating in hydrogen. This gas, which is readily absorbed by some of the metals, is then removed by heating the metal in nitrogen.

Because of the variations in the analytical effects of air on the hot metals, these effects will be discussed for the individual metals. One must realize, however, that with those analytical processes which result in intermetallic alloys, either within the platinum group or with associated base metals, one cannot extrapolate the known effects of air for individual metals. Thus, although osmium metal will form the tetroxide on contact with air at room temperature, one cannot assume that the alloys and compounds of osmium will behave similarly, even at very high temperatures. The author has encountered silica residues from the acid treatment of a soluble osmate which retained traces of osmium even at red heat in air. It is also a fact that although certain alloys from platinum placer deposits may readily yield osmium tetroxide on heating, e.g. samples from Ethiopian placers, other types of natural alloys such as Tasmanian iridosmines yield no trace of osmium on high temperature treatment in air.

PLATINUM

It was recognized by some researchers at the beginning of the nineteenth century that platinum is not " indestructible " at elevated temperatures in air. The history of these investigations until 1942 has been reviewed,[73] with the conclusion that the volatilization from hot platinum proved to be an exceedingly complex phenomenon, from which there developed data not only of concern to the analytical chemist, whose interest is directed principally to significant changes in weight of platinum, but also to the whole area of mass communication by vacuum-tube techniques. While one may find differences of opinion concerning the mechanism of the volatilization expressed by such researchers as Deville, Debray, Thomas Eddison, Fresenius, Oliver Lodge, Sir William Crookes and Lord Kelvin, there can be no doubt that the bulk of the early evidence supported the conclusion that there was a loss of platinum at approximately 1000°C.

It was difficult to correlate some of the conclusions because researches were made under different conditions for example, platinum was heated in oxidizing and reducing bunsen flames, in the blast flame, in various types of electric furnaces and by an electric current. Failure to find a loss of weight when either pure or impure platinum was heated to temperatures of 1000°C is not easily explained, although it is possible that a high iron content may have masked the actual loss of metal. Undoubtedly much of the platinum used was impure, but except with rhodium and iron, the presence of some of the common impurities would accentuate the loss of weight.

TABLE 5. THE WEIGHT LOSS ON HEATING PLATINUM AND ITS ALLOYS[74]

Temperature (°C)	Weight loss			
	Pure Pt	1% Ir	2·5% Ir	8% Rh
900	0·00	0·00	0·00	0·00
1000	0·08	0·03	0·57	0·07
1200	0·81	1·2	2·5	0·54

The effects of oxygen on hot platinum crucibles etc. were discussed at some length by Burgess and co-workers.[74, 75] In 1916, Burgess[74] recorded losses of platinum with and without rhodium and iridium. These losses, expressed in mg/100 cm²/hr at various temperatures, are shown in Table 5.

For platinum crucibles[75] containing up to at least 3 per cent iridium or up to 8 per cent rhodium, the loss on heating was negligible below 900°C. Volatilization of platinum containing rhodium was less than that of pure platinum at all temperatures above 900°C, whereas the loss of weight of a platinum–iridium alloy increased with the iridium content.

Raub and Plate[76] measured a loss in the weight of some platinum at 900°C. Heating at 1000°C for 24 hr resulted in a loss of a few mg per dm². At 1100°C, the loss was 15 mg per dm². At 1200°C and at 1300°C, the losses were 65 mg per dm².

Figure 1 illustrates the loss of weight of platinum in oxygen at various temperatures.

Although the past century of research has clearly proved that a loss of platinum occurs at high temperatures, it has not necessarily enabled the chemist to estimate the loss which occurs in the ordinary laboratory routine of heating platinum crucibles. It has been stated that the data obtained by Burgess and Sale[77] permit a prediction of losses within limits close enough for analytical purposes. Their results were obtained under carefully controlled conditions, however, and they admitted that ignition over the blast lamp or in the ordinary muffle furnace with exposed metal parts did not produce consistently reliable results. Confirmation of the successful applications of the corrections suggested by Burgess and Sale would be welcomed by chemists. Weights of micro amounts of precipitates are particularly affected by the loss of weight of platinum crucibles. Only a slight difference between the weight of the empty crucible and the weight of the crucible when it contains the ignited precipitate may very appreciably affect the accuracy of the determination. A review of published microchemical procedures reveals the astonishing fact that this source of error is very often ignored.

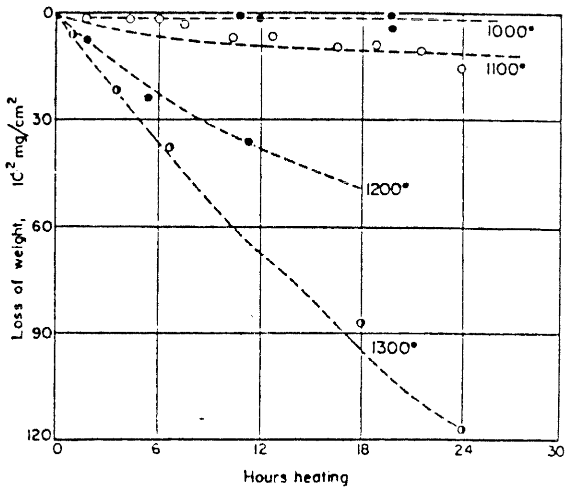

FIG. 1. Variation of weight loss of platinum with temperature.

It has been recorded[72, 76] that the volatility of platinum in oxygen at 900–1100°C is appreciably reduced by alloying it with palladium or rhodium.

A 10 per cent rhodium–platinum alloy loses about 240 mg per dm^2 in 10 days at 1100°C, and 90 mg per dm^2 at 900°C, whereas the corresponding figures are 190 and 0 for the 30 per cent rhodium alloy, 200 and 30 for the 10 per cent palladium alloy, and 110 and 10 for the 30 per cent palladium alloy. On the other hand, iridium–platinum alloys suffer much greater weight losses on heating in oxygen than does pure platinum, owing perhaps to the relatively high volatility of iridium in oxygen. Thus, even at 900°C, the 30 per cent iridium–platinum alloy loses about 400 mg per dm^2 in 24 hr, while the 20 per cent iridium alloy loses about 200 mg per dm^2 in 36 hr.

Regarding the explanation for the loss in weight of heated platinum, considerable progress has been made. The evidence cited in the above-mentioned review[73] indicates that the removal of the volatile impurities from platinum by heating does not ordinarily affect appreciably the weight of a platinum crucible as determined by sensitive balances. Any significant loss in weight of a good platinum crucible seems, then, to result from an actual loss of metal. This loss is relatively great when platinum is made incandescent in air or oxygen. In nitrogen, hydrogen or in a vacuum the loss is comparatively insignificant. These facts constituted almost the only early evidence for the existence of a volatile platinum oxide. It has been proved that platinum dioxide is present on the cooler walls of a vessel in which very hot platinum is exposed to oxygen: but synthetic platinum dioxide is not volatile at high temperatures. It decomposes considerably below red heat. Concerning the actual dissociation temperatures, there is little unanimity of opinion. Wöhler and Frey[78] made investigations to determine the oxygen dissociation pressure of platinum oxides. They admitted their failure to obtain a single equilibrium condition, owing to the tendency of the platinum oxides to form solid solutions, and also to the strongly delayed equilibria. They obtained indications that platinum dioxide dissociated into platinum and a solid solution of the monoxide or " sesquioxide " in the dioxide. Grandadam[79] found that platinum dioxide decomposes rapidly at 380–400°C under atmospheric pressure, giving the " more stable platinum monoxide ", which in turn decomposes at 560°C, producing platinum. The results indicated that prolonged oxidation of platinum black at 450°C under great oxygen pressures ought to produce pure platinum dioxide and that platinum monoxide was formed at lower pressures. The author stated that platinum monoxide " is isolated pure by direct oxidation of platinum black at 430°C under oxygen pressure of 8·25 kg/cm^2. The time of its formation is diminished when the fineness of the black is increased ".

Thus the loss of platinum at high temperatures, in contact with air or oxygen, was not necessarily explained by the formation of either volatile platinum dioxide or platinum monoxide. Wöhler and Martin[80] stated that there was no evidence to indicate a spontaneous oxidation of platinum to a trioxide; it had been anticipated that the oxygen dissociation pressure of the trioxide at ordinary temperatures would be greater than the partial pressure of atmospheric oxygen.

By a method comparable to that used to determine the identity of the volatile oxide of iridium,[81] and described below, Schäfer and Tebben[82] investigated the reaction between oxygen and platinum at temperatures of 1540° and 1338°C. Their data relating the partial pressures of the volatilized platinum oxide to the mole weight of platinum volatilized, the oxygen equilibrium pressure, and the mole weight of oxygen in contact with the platinum, together with corresponding isotherms, indicated the formula of the volatile products as Pt_xO_2. However, the authors' acceptance of x as unity is not yet experimentally acceptable,* and there remains the necessity for an explanation of the postulated stability of platinum dioxide at high temperatures, a situation comparable to that of heated ruthenium tetroxide. Anyway, their data on the platinum dioxide product indicated a mixture, one constituent of which was particularly resistant to reduction by hydrogen. Also, in contradiction to some of the early literature, they considered the solubility of oxygen in the platinum oxide as very small. Remy[83] has recorded that " it has not been possible to measure definite dissociation pressures over the platinum oxides owing to the formation of solid solutions, but it can be stated that no oxide of platinum is stable in oxygen under 1 atmosphere pressure above 500°C ". Schäfer and Tebben[82] used a temperature of about 1200°C and oxygen pressures of 0·127, 0·476 or 1·055 atmospheres to produce the postulated PtO_2.

Grube[84] investigated the electrical potentials between platinum oxide electrodes and hydrogen electrodes. He states: " Since platinum electrodes can be polarized up to 2 volts, it appears probable that an unknown tetroxide of platinum may exist ". Concerning the products of the direct oxidation of platinum by oxygen, Wöhler[85] stated that: " the grey coherent platinum sponge could be changed into a black oxide, and even smooth, polished platinum foil could be converted on the surface into platinum oxide ". Various researchers believed that the oxide formed between platinum black and oxygen was platinum monoxide or its hydrate.

Lacroix[86] studied the visible changes which occurred on the polished surfaces of platinum after heating to temperatures above 1000°C. The author believed that at these high temperatures in the presence of oxygen the mobility of the surface atoms was increased. He also stated that platinum did not volatilize below 1000°C in oxygen.

Lacroix found that the oxide produced by the volatilization of platinum in air had the empirical formula of Pt_2O. The rather low proportion of oxygen, however, was interpreted as being due to a partial dissociation of the oxide on the hot refractory upon which it was deposited.

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*Recent reports (by Alcock, *Platinum Metals Review* 1961, 5, No. 4, 134 and by Chaston, *ibid.* 1964 8, No. 2. 50) accept the composition PtO_2 over 1200–1800 C.

One must hope that the investigations of explanations for the effect of oxygen on hot platinum will continue.

PALLADIUM

Palladium metal, as a powder or in the massive form, is readily converted to the monoxide at the relatively low temperature of a bunsen flame. One cannot use the oxide as a weighing form, however, partly because of the excessive time required for quantitative oxidation. Furthermore, at about 875°C the oxygen dissociation pressure reaches one atmosphere and metal is rapidly formed. Raub and Plate[72, 76] found that palladous oxide dissociates completely at 870°C, whereas a sheet of palladium heated in oxygen at 1200°C gains about 0·1 per cent in weight in the first hour owing to the absorption of oxygen without the formation of a superficial film of oxide. On more prolonged heating at this temperature, there is a slow loss in weight owing to volatilization. At 1300°C in oxygen, the weight of a palladium sheet increases by about 0·08 per cent in the first half hour, and then decreases linearly with time, the original weight being reached in about 5 hr. At 1100°C there is a gain in weight of 0·05 per cent in 5 hr, after which time the weight remains almost constant. At both 900 and 1000°C, the increase in weight is 0·007 per cent in 1 hr and 0·015 per cent in 4 hr, and more prolonged heating at either of these temperatures produces no further change in weight. If the sheet is heated to 1200°C in oxygen until the maximum 0·095 per cent of oxygen is absorbed, and is then allowed to cool to 550°C, 0·037 per cent of the gas is still retained; on slow cooling to room temperature, 0·028 per cent of oxygen remains, but some of this may be combined with the traces of base metals present. Sheet quenched directly from 1200°C evolves oxygen very slowly at room temperature, and practically all the oxygen can be removed by heating the metal in a vacuum at about 800°C. These results indicate that the oxygen is present in solid solution, not as palladous oxide; this conclusion is confirmed by X-ray measurements of the lattice parameter after various heat treatments. Comparing the behaviour of palladium with rhodium and platinum in oxygen at high temperatures, the author concluded that platinum is the most, and palladium is the least volatile metal at temperatures up to 1200°C, whereas at 1300°C there is relatively little difference in the volatility of all three.

RHODIUM

Rhodium metal at high gas temperatures in air or oxygen oxidizes to form rhodium(III) oxide. In spite of early contradicting data suggesting the existence of lower oxides, there is little doubt that the only product of oxidation up to about 1000°C is Rh_2O_3. This oxide cannot be used as a weighing form, however, because even as little as 100 mg of rhodium sponge

may require many hours of heating to reach the composition of Rh_2O_3. Its dissociation temperature in air is not known accurately: according to Gutbier,[87] it is 1150°C. Raub and Plate[76] stated that at 1100°C rhodium sheet becomes coated with a thin film of oxide, the amount formed reaching a maximum of 8 mg per dm^2 after about 12-hr heating. Rhodium sheet, at 1200°C in oxygen, has an initial gain in weight for an hour or so, followed by a steady and practically linear loss in weight. At 1300°C, the linear loss is immediately evident. No adequate explanation has been provided for these phenomena.*

IRIDIUM

Iridium sponge or the precipitated metal can be oxidized to IrO_2. Whereas the oxygen dissociation temperatures of this oxide are not known with certainty, Schäfer and Heitland[81] prepared crystals of the dioxide by heating iridium foil in an oxygen–nitrogen atmosphere at 1130–1150°C, and cooling the resulting gaseous mixture containing iridium(VI) oxide. This caused decomposition to IrO_2, a crystalline deposit. It may be noted here that the data in Table 40 indicate that the composition Ir_2O_3 results from continued heating of iridium metal residues. These data should be interpreted merely as evidence that one cannot accept the oxides as weighing forms for an iridium determination. The most significant contribution toward an explanation of the effects of oxygen on iridium at high temperatures was recorded by Schäfer and Heitland.[81] These authors used temperatures appreciably above the dissociation temperature of iridium dioxide, and thus were concerned with the system: iridium, oxygen, volatile oxide of iridium. The equipment included a capsule containing rolls of iridium metal fitted into a tube through which passed an oxygen and nitrogen carrier gas to remove the volatile oxide from the capsule area. The weight of the unknown iridium oxide volatilized was determined by the difference in weight of the capsule before and after the heating period. The oxygen–nitrogen mixture was passed slowly over the iridium, the assumption that equilibrium had been established being based on observations made at varying flow rates and on other data.

In principle the method required the experimental determination of x and y in the relationship involving the following at equilibrium: the partial pressure of the gaseous iridium oxide, $p_{Ir_xO_y}$ the partial pressure of the oxygen, p_{O_2} which, because of the small quantity used, was taken as the applied partial pressure of oxygen; the number of moles of iridium metal volatilized as the oxide, n_{Ir}; the number of moles of oxygen present at equilibrium

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*Alcock, (*Platinum Metals Review* 1961, 5, No. 4, 134) attributed rhodium losses from a rhodium–platinum alloy at 1400 C to RhO_2.

n_{O_2}, which like P_{O_2} was accepted as the number of moles applied. Thus

$$x = \frac{n_{Ir}}{n_{O_2}} \times \frac{p_{O_2}}{p_{Ir_\alpha O_y}}$$

Applying a variety of possible reactions between oxygen and iridium and the experimental values of $p(Ir_xO_y)$, the resulting isotherms indicated the composition Ir_xO_3. In order to determine the value of x, the authors replaced iridium as the solid phase with iridium(IV) oxide, the partial pressure of oxygen being maintained at a value higher than the oxygen dissociation pressure of IrO_2 at the experimental temperatures. On the basis of three possible reactions between oxygen and IrO_2, the data indicated the reaction:

$$IrO_2 + \tfrac{1}{2}O_2 \rightarrow IrO_3$$

For example, only the values for the ratio of $p(IrO_3) : p(O_2)^{1/2}$ at 930°C and at 1030°C proved to be constant.

One must conclude that the authors have provided substantial evidence in support of the identity of IrO_3 as the constituent volatilized from iridium in oxygen at temperatures from 1034 to 1206°C, and partial oxygen pressures varying between 347 and 760·7 Torr. This would affect the long entertained expectation that a volatile tetroxide similar to OsO_4 would ultimately be identified for each of the six platinum metals. The authors have not precluded the presence of small amounts of other volatile gases associated with the IrO_3; the presence of these could account for the variation of about 5 per cent in the equilibrium constants at each particular temperature. These variations correspond to 0·6–5 mg of iridium for the 15–100 mg of iridium reported by the authors to volatilize as the oxide. The degree to which the losses of iridium by volatilization affect a determination of iridium is indicated by the discussion related to Table 40.

RUTHENIUM

It is presumably the analogous compositions and reactions of ruthenium and osmium compounds that have given rise to some confusion concerning the behaviour of these two metals when in contact with oxygen. There is little similarity. Unlike osmium, which forms the volatile tetroxide even at room temperature, there is no conclusive evidence that ruthenium forms a detectable amount of RuO_4 on heating the metal in air or oxygen with a bunsen flame. Both of these oxides are readily formed by the wet oxidation of aqueous solutions of their salts, but the oxide of ruthenium is by no means as readily formed by direct oxidation of the metal or its salts. In fact, the recorded data dealing with the oxides of ruthenium have indicated that the tetroxide may decompose with explosive violence at about 100°C, yet may also be produced at much higher temperatures by direct oxidation of the metal in air. While this apparent thermodynamic anomaly has received little attention, the explanation may be associated with the existence of various forms of RuO_4. By distillation, two types of osmium(VIII) oxides can be produced, one yellow and one brown. The yellow needles, an unstable form, can be produced by the condensation of a yellow distillate. By melting and then solidifying the yellow needles, the brown form appears; the latter can be sublimed, producing yellow crystals again. Whereas the tetroxide produced by distillation is unstable, particularly in the presence of organic compounds such as ethanol, when it is thoroughly dry, it can be kept in the dark in sealed tubes without any evidence of decomposition.

In the early nineteenth century, it was reported that heating ruthenium in oxygen at 958°C produced the tetroxide, which could be condensed in a flask cooled in ice. Similarly, in 1961 Campbell *et al.*[88] suggested that RuO_4 was formed above 1425°C in air. To account for weight losses when 0·2 g of metal was subjected to a differential thermal analysis, they stated: " Oxidation of RuO_2 to RuO_4 vapor must, therefore, occur at a rapid rate at 1400–1500°C accompanied by the gas phase decomposition of RuO_4 at temperatures above 1425°C ".

$$\text{i.e. } RuO_4(g) > 1425°C\ Ru(s, \gamma, \delta) + 2O_2(g)$$

It would thus seem that one must account for the existence of RuO_4 in air at temperatures as high as 1400°C, and at the same time explain the instability of RuO_4 at about 100°C. Schäfer[89] recorded that ruthenium wire at 1465–2090°C in an oxygen–nitrogen atmosphere produced volatile RuO_3. Remy[83] noted: " At high temperatures (above 600°C) ruthenium tetroxide is formed in traces, but decomposes in the course of cooling. The tetroxide is metastable at ordinary temperatures."

Campbell *et al.*[88] found no weight loss on heating the metal in air up to 1025°C, a slow weight loss from 1025 to 1400°C and a more rapid loss from 1400 to 1515°C. The failure to find a weight loss up to 1025°C may have been due to the fact that the weight measurements were made to an accuracy of about 0·5 per cent and it is not unlikely that a slight loss would have thus escaped detection. These data find support in Gilchrist's[90] conclusion, however, that samples of the order of weight used by Campbell do not lose weight on igntion in air. On the other hand, the present author has consistently found a significant loss of weight on heating mg amounts of the metal or its dioxide to 900–1000°C. Recently, Foreman[91] investigated the loss of ruthenium during the ashing of seaweed. He found no significant loss provided the temperature did not exceed 500°C. Pretreatment with nitric acid encouraged the loss.

Invariably, heating the metal in air at bunsen temperatures produces the dioxide; it is not a recommended weighing form because complete conversion of the metal is difficult, owing, perhaps, to the solubility of oxygen in the oxide, as well as to the usual failure to accomplish intimate contact of metal with oxygen. Very recently, Brandstetr and Vrestal (private communication) record the use of the dioxide as a weighing form in amounts of 50–100 mg. The hydrated oxide is precipitated by ammonium carbonate, and the oxide is ignited in air at about 600°C (see reference 581). Very early data have indicated that the condensate from very hot metal in contact with air contained the dioxide, and from this it had been assumed that the RuO_4 was formed at 1000°C, and then decomposed to form RuO_2; thus RuO_4 acted as a carrier. The oxygen dissociation temperatures and pressures recorded in many modern text-books have been derived from an early source. Re-determination could therefore be of some value because there is some evidence that the presence of metallic ruthenium affects the dissociation temperatures. Presumably the dioxide is stable in air at 950°C under an oxygen pressure of 50 mm of Hg. Campbell *et al.*[88] recorded a thermogram which showed an endotherm at 185°C, an exotherm at 1350°C and indications of a second endotherm at about 1450°C, the latter being ascribed to γ and δ transitions of ruthenium metal. There was no explanation for the low temperature endotherm, for no weight loss was evident and no crystalline or phase transitions occurred below 1000°C. The reaction postulated to explain the slow weight loss between 1025–1400°C included the decomposition of RuO_2 to metal and oxygen. However, the actual loss was about 40 per cent higher than the calculated value. Presumably no consideration was given to loss by volatilization of a ruthenium oxide.

OSMIUM

In 1855, Fremy stated that osmium could be oxidized to the volatile tetroxide at ordinary temperatures. Furthermore, there was some evidence to indicate that osmium tetroxide could be distilled directly from platinum metal residues by roasting them. Significantly, there are records to indicate that specimens of Siberian iridosmine at ordinary temperatures emitted sufficient of the tetroxide to stain a label sealed within the tube containing the mineral. On the other hand, Berzelius, Deville and Debray recognized the existence of an osmium metal whose metallurgical history resulted in resistance to oxidation at temperatures below the melting point of zinc. The present author has been able to distil some osmium directly from a native Ethiopian mineral, whereas Tasmanian iridosmine has always failed to yield osmium even after the most strenuous heating periods. At the present time, one of the most effective methods of preparing standard osmium solutions includes the direct oxidation of osmium metal at bunsen temperatures to produce osmium tetroxide quantitatively. No other product of the oxidation of osmium has been isolated. Krauss and Wilken,[92] however, supported the early observation by Berzelius that two forms of osmium tetroxide existed, viz., a white form melting at 39·5°C and a yellow isomer melting at 41·0°C. These could be produced alternately by melting and cooling, and each produced a distinct set of vapour pressures. Ogawa[93] disputed these findings with data which indicated that only one form was produced by distillation; it melted at 40·6°C. It was claimed that the pressures obtained by Krauss were in error owing to the non-establishment of equilibrium, and that a range of temperatures produced only one variety of the tetroxide. There is doubt therefore as to the existence of enantiotropes of osmium tetroxide. Further examination of the identity and behaviour of the osmium and ruthenium tetroxides produced by wet and dry methods could provide useful information and resolve this problem.

In a recent communication, Grimley *et al.*[94] used mass spectrometry and associated experimental techniques at 1373–2023°C, finding support for the existence of OsO_3^+ and OsO_4^+, ionized forms of OsO_3 and OsO_4 molecules respectively. Above 1973°C, there was evidence for the existence of a stable OsO_2 molecule. No lower oxide was detected.

ANALYTICAL SIGNIFICANCE

From the analytical point of view, one is generally concerned only with the results of heating each platinum metal in air at temperatures of about 1000°C or less. Even within this limitation one must bear in mind that the metallurgical history of each metal may appreciably affect the behaviour of the hot metal in air. Thus one may expect that prior reduction of the oxide in hydrogen, a process which frequently precedes gravimetric determinations, may introduce some variation in behaviour; for example, it has been stated that the oxidation of ruthenium is retarded by a prior reduction. The work of Lacroix[86] has demonstrated clearly the existence of surface changes on platinum sheet after heating the metal in air. Grooves, striations and surface coatings may appear. Whereas the explanation of these phenomena has not yet been provided, the suggestion that the mobility of the surface atoms is greater in the presence of oxygen may offer a partial explanation, not only of the reactions already recorded, but also of the divergent data obtained by various investigators. Whatever the explanation of volatility in air, and its absence in non-oxidizing gases, of the lack of agreement concerning dissociation temperatures of the various oxides, and of the apparent contradictions to accepted thermodynamic principles, the analytical chemist has available sufficient data to avoid significant experimental errors. Thus, one cannot, in general, use as weighing forms any of the oxidized forms of the platinum metals. Also one may expect significant weight losses when mg amounts of platinum, iridium and ruthenium are heated to high temperatures in air for prolonged periods. Invariably, continued heating of platinum crucibles will result in a continued loss of weight. In this connection, prior knowledge of the composition of the crucible material is important. Aside from the effects of variable composition, one cannot expect any platinum crucible to retain indefinitely its mechanical properties and thus its resistance to heating in air in the presence or absence of fusion mixtures.

GOLD

Gold is the most noble of all the elements. In contrast to the six platinum metals there is no evidence of its volatility in oxygen at high temperatures, and all the known oxides have a high oxygen dissociation pressure at bunsen temperatures. In some instances, however, heating in the presence of oxygen has resulted in a temporary gain in weight. Duval[95] found that precipitated gold may retain oxygen by adsorption, the amount varying according to the degree of subdivision, the nature of the precipitating reagent and the environmental atmosphere during heating. This gain may amount to as much as 1 per cent, and on continued heating exactly the same weight is lost as was gained initially. There is no evidence that gold crucibles have this property. Duval[95] provided a list of ten reducing agents which resulted in a gain of weight of 1–6·5 mg on heating 215–427 mg of the precipitated gold to about 950°C. An explanation of this phenomenon and its selective application would be a contribution.

CHAPTER 2

METHODS OF SEPARATING THE SEVEN NOBLE METALS

SECTION I

The Separation of Osmium from Ruthenium

The methods for isolating these metals from associated platinum metals and from base metals are included in Section II of this chapter. The methods discussed below are confined largely to the separation of osmium from ruthenium. Because some of these separational procedures are applicable also to the isolation of the two metals from complex systems, however, some repetition of techniques is inevitable.

The fact that both osmium and ruthenium in aqueous media form volatile tetroxides, in contrast to associated platinum and base metals, has been erroneously interpreted as indicating that their isolation is a relatively simple matter. Most of the common methods of dissolution of these metals involve either one or more treatments with *aqua regia*, chlorination in the presence of sodium chloride, or caustic oxidizing fusions with subsequent dissolution by hydrochloric acid. Unfortunately, the chloride complexes of osmium and ruthenium offer a peculiar resistance to the quantitative formation of the tetroxides. This is particularly noticeable with hydrochloric acid solutions of ruthenium. Consequently, with these dissolved constituents some preliminary treatment is sometimes required in preparation for the oxidation.

The choice of the dissolving medium cannot be made indiscriminately when the remaining platinum metals are to be determined, because serious interference may develop during the preparation of the residual or pot liquid for subsequent operations.

In general, for the simultaneous removal of both metals one may use oxidation with sodium bromate, bromic acid, perchloric acid, chlorine in caustic media, bismuthate, permanganate, ceric, lead dioxide, peroxydisulphate, etc.

In order to determine osmium and ruthenium in complex systems one may first selectively isolate osmium with nitric acid, or with sulphuric acid and hydrogen peroxide, and subsequently isolate ruthenium; or one may isolate both metals simultaneously using one of the above oxidants such as perchloric acid. A variety of methods has been proposed for the consecutive separation of osmium and ruthenium. These procedures employ oxidants and media which usually require rather prolonged pre-treatment before proceeding with the determination of associated platinum metals.

Procedures involving the prior simultaneous removal of osmium and ruthenium are only now being developed, but it is not unlikely that these methods will allow simplified subsequent separations. Among the large number of effective oxidants, perchloric acid has proved to be one of the most effective.

In addition to the problem of choosing a suitable oxidant, the analytical chemist must select wisely from the variety of proposed receiving liquids. This choice, of course, will sometimes depend upon whether it is necessary to collect the tetroxides consecutively or simultaneously.

RECEIVING SOLUTIONS FOR THE TETROXIDES

Sodium Hydroxide

For simultaneous collection, in so far as efficiency of collection is concerned, no better reagent than the classical caustic solution has been proposed. Ten per cent sodium hydroxide solutions were used as absorbants for ruthenium(VIII) oxide by Rogers *et al.*[96] In these instances the subsequent treatment involved acidification with hydrochloric acid, filtration, and an adjustment to 0·2 N in acid, followed by precipitation with thionalide. The results are acceptable but the method is tedious.

6 N sodium hydroxide solutions have been used to collect ruthenium(VIII) oxide from distillates obtained through oxidation by perchloric acid and sodium bismuthate.[97, 98] In this method the ruthenium is isolated from the caustic solution by precipitation with ethanol, using magnesium hydroxide as a collector, and is then determined colorimetrically.

Sodium hydroxide is now seldom used in analytical procedures, particularly for small amounts of metal, because the contaminants—silica, iron, etc.—become appreciable, and because of the detrimental effect of the large amounts of salts present on the subsequent operations.

Hydrochloric Acid

It is generally accepted that aqueous solutions of hydrochloric acid should not be used for the collection of osmium, whether or not any oxidant passes from the distilling liquid. Some tetroxide may volatilize from the hydrochloric acid receiving solution because its reduction to the lower valence state is not instantaneous. In general this is true also when ruthenium is to be collected, and whereas hydrochloric acid is frequently used as a collector, a reductant such as sulphur dioxide is usually added. However, 6 M hydrochloric acid has been used successfully for collecting ruthenium without either cooling, or adding any reducing reagent[99] (see Procedure 144). In this instance the ruthenium was quantitatively retained during the evaporation of 10 ml of receiving acid to 1 or 2 ml.

Hydrochloric Acid–Sulphur Dioxide

A much used receiving liquid for both osmium and ruthenium distillates consists of a 1 : 1 hydrochloric acid saturated with sulphur dioxide. This solution has been used successfully by Gilchrist[100] for 0·1 g quantities of osmium.

Recent investigations have provided pertinent data concerning the efficiency of this reagent and its applicability to the subsequent method of determination. With spectrophotometric methods which are dependent upon the identity of the dissolved osmium constituent, such as the thiourea method, the history of the receiving liquid is an important factor. With fresh distillates the thiourea reaction is satisfactory. If the distillates are several hours old the expected rose colour is less intense; after 24-hr standing, no colour is developed. These data have been interpreted as indicating that the fresh distillate contains the tetroxide, which is reduced to a low valence state on standing. This suggestion offered an explanation for Sandell's finding[101] that the evaporation of the sulphur dioxide receiving liquid required by Gilchrist's method[100] resulted in low values for osmium, which became significant when small amounts of the metal were to be determined. The fact that these evaporations yielded low results with the thiourea method was later confirmed and seemingly supported by the finding[102] that if the distillates were allowed to stand for 12–16 hr at room temperature no loss whatever occurred either during ageing or subsequently when the solution was concentrated by boiling.

However, a recent report by Geilmann and Neeb[103] indicates that osmium is not lost during the evaporation of either fresh or aged receiving solutions of hydrochloric acid–sulphur dioxide. This finding is not in disagreement with the explanation that low results obtained for μg amounts of osmium are possibly not due to losses by distillation from an evaporating solution of hydrochloric acid–sulphur dioxide but to a reduced sensitivity of the aged solution toward the thiourea reaction. Furthermore, it is now known that the thiourea method is inapplicable to aged distillates containing hydrochloric acid—sulphur dioxide.

Presumably Neeb[104] used tetraphenylarsonium chloride as the colorimetric reagent for osmium obtained from the evaporated receiving solution. This reagent reacts with osmium(IV) to produce a chloroform-extractable yellow complex.

One must conclude that the identities of the dissolved osmium constituents required for the thiourea reaction are unknown, and that their identification in the hydrochloric acid–sulphur dioxide solution could be most interesting and useful.

A second factor which may influence the choice of receiving liquid, particularly when gravimetric determinations are to be made, and relatively high accuracy is required, involves the presence of such compounds as silica, which may have been corroded from the container during evaporation or derived from the chemicals used. Certain absorbents, such as hydrobromic acid or sulphur dioxide–hydrochloric acid, require evaporation prior to the determination of the metal, in order to remove interfering constituents such as sulphur dioxide or to control the acidity of the solution. Strangely, the silica derived from some of the recommended receiving liquids has a strong affinity for osmium, to the extent that even ignition in air fails to remove the metal.[102] It has been reported that when sulphur dioxide–hydrochloric acid was used as the absorbing liquid, the silica removed during a hydrolytic precipitation did not contain osmium, and where the error owing to the presence of silica becomes significant, this absorbent is recommended, despite the necessity for the complete destruction of sulphur dioxide.

Hydrobromic Acid

Hydrobromic acid is used as a collector for both osmium and ruthenium distillates. The 48 per cent acid, analytical reagent, is twice distilled, discarding the first and last portions. In some instances it is preferred to sulphur dioxide absorbents because it is more efficient, easier to prepare and handle, and the resulting distillate requires neither evaporation to dryness to destroy sulphite complexes nor ageing before evaporation to a small volume. On the other hand, the silica derived from the evaporation of hydrobromic acid may contain osmium, and where this loss is a significant factor the acid should not be used. Chilling in ice-water is always desirable when hydrobromic acid is used.

Hydrochloric Acid–Thiourea

A solution of thiourea in hydrochloric acid was used originally as a receiving liquid for osmium(VIII) oxide in order to avoid the loss of the colour-producing constituent in distillates containing only hydrochloric acid and sulphur dioxide. Because thiourea is also a colorimetric reagent for ruthenium it would seem to be applicable for the retention of this metal as well as of osmium. No supporting data have been recorded, however, and, in the author's opinion, better absorbents are available. For the determination of μg amounts of osmium there is the advantage of increased speed and a simplification of procedure. The optimum proportions of thiourea required for the absorption, however, depend upon the amount of osmium to be distilled and upon the volume of the receiving solution. Sulphur may be deposited from the decomposition of the thiourea during the distillation. Generally, a single filtration will remove this interference. Care must be taken to completely wash the thiourea–osmium complex out of the receiving flasks. Thiourea solutions in hydrochloric acid and ethanol were used by Westland and Beamish[105] to collect osmium oxidized by perchloric acid. The receiving solutions were rinsed with 1 : 1 ethanol–hydrochloric acid into a measuring flask, from which the solution was filtered into the transmittency cell. These authors increased the amounts of thiourea from 2 to 5 per cent in those instances where the distilling liquid evolved oxidants such as chlorine.

Hydrogen Peroxide

A 3 per cent aqueous solution of hydrogen peroxide, maintained at a low temperature by immersion in an ice bath, was used initially by Rogers *et al.*[96] to collect the ruthenium(VIII) oxide formed by a bromate oxidation. The distillate required boiling to remove excess of hydrogen peroxide, because of its reaction with the precipitant, but evaporations were not necessary. One should not use the commercial 3 per cent hydrogen peroxide solution, which contains acetanilide as a stabilizer.

Thiers *et al.*[21] used chilled hydrogen peroxide solutions to collect ruthenium from a perchloric acid distillation. This solution could be boiled without loss of ruthenium, and gravimetric methods could be applied directly to the filtered distillates. Later, Westland[105] successfully used hydrogen peroxide as an absorbent for osmium and ruthenium distilled simultaneously from a perchloric acid medium. With these absorbents one must guard against a deficiency of hydrogen peroxide and even temporary heating of the distillates. The latter causes the decomposition of the peroxide, and is considerably accelerated by the catalysing action of the noble metals. This characteristic requires recognition during any transfer of the distillate containing osmium: the operation must be made as quickly as possible, and the transfer should preferably be made of the chilled solution to a chilled container.

The hydrogen peroxide solutions of osmium and ruthenium are not in general suitable for spectrophotometric methods. Any evaporation carried out to obtain a suitable concentration results in some loss of both metals, especially of the osmium. Furthermore, little is known concerning the identity of the dissolved constituents in the colourless solutions of either metal.

Other Receiving Solutions

A variety of reducing reagents can undoubtedly be used as receiving solutions for ruthenium(VIII) oxide. Hydroxylammonium chloride in hydrochloric acid has been used specifically for the application of 1,10-phenanthroline.[106] Receiving solutions containing colorimetric reagents and precipitants for ruthenium have been used, so far without much success. The single but questionable exception is the application of thiourea. The addition of thionalide, a precipitant for both osmium and ruthenium, to the receiving solution provides precipitates whose physical characteristics introduce precipitation and filtration difficulties.

OXIDANTS THAT PRODUCE THE TETROXIDES

So far, nitric acid and hydrogen peroxide are the only reagents that have been cited as being useful for the selective isolation of osmium. For the simultaneous oxidation of both metals, the following have been used more or less successfully, viz., sodium bromate–sulphuric acid, bromic acid, perchloric acid, sodium hypochlorite, ammonium peroxysulphate, ceric, permanganate and chromate.

Nitric Acid

The variety of equipment suitable for the distillation and collection of osmium and ruthenium is illustrated in Chapter 7.

Nitric acid is perhaps the most generally used oxidant for osmium. It is specific for that metal in the absence of trace amounts of other oxidants, sulphuric acid etc., and provided that the nitric acid concentration is less than about 5 N. It is particularly suitable for osmium compounds in caustic media or for ammonium bromosmate. For the chlorosmate, a nitric acid distillation frequently requires many hours of boiling, so other oxidants such as perchloric acid are preferred. Concentrated sulphuric acid can also be used effectively. The evolution of the osmium is accelerated significantly if a little nitric acid is added to the sulphuric acid solution. Under such conditions, however, ruthenium will co-distil appreciably. Indeed, it has been found that ruthenium is also evolved from sulphuric acid on strong heating.[53] Nitric acid is not a suitable reagent for the direct removal of osmium when it is present in the iron–nickel–copper alloys used for the collection of platinum metals from ores and concentrates,[107] nor is it directly applicable to iron–nickel meteorites.[108] In these instances, the osmium may be complexed by the oxides of nitrogen formed during dissolution. Sandell[108] avoided this error by dissolving the osmium in sulphuric acid, simultaneously dissolving the iron and nickel with hydrochloric acid, subsequently oxidizing the ferrous salt with potassium permanganate and then distilling from nitric acid. When hydrochloric acid is required to dissolve the alloy, the chlorides are converted into sulphates by fuming with sulphuric acid at as low a temperature as possible and in the presence of ferrous sulphate to prevent oxidation to osmium(VIII) oxide. The perchloric acid oxidation is particularly suitable for these base metal alloys.[109] The alloys are completely soluble, and both osmium and ruthenium are quickly removed; they may be collected in any of the above-described receiving solutions.

Nitric acid has been used successfully for the selective isolation of osmium in the presence of the other platinum metals. The subsequent removal of ruthenium, however, requires a prior evaporation to fumes with sulphuric acid in order to eliminate the nitric acid. During this process small amounts of ruthenium are lost, and these losses become significant when mg amounts

of metal are to be determined. Consequently, the method is not recommended in these instances, hydrogen peroxide being the preferred oxidant.

Hydrogen Peroxide

Hydrogen peroxide serves both as a selective oxidant for osmium and as a collector for osmium(VIII) oxide. As discussed above, a chilled 3 per cent solution is used as the receiving liquid, whereas as an oxidant a more concentrated solution, containing a small amount of sulphuric acid, is required, particularly for the hexachlorosmate. Up to the present time the hydrogen peroxide oxidation of osmium has been used following a simultaneous removal of both ruthenium and osmium tetroxides by using oxidants such as perchloric acid. In this instance the distillate is contained in a chilled solution of hydrogen peroxide. It is transferred to the distillation flask, and the osmium is selectively removed by heating the peroxide solution, to which has been added a small amount of sulphuric acid. As stated above, the fact that hydrogen peroxide will produce osmium(VIII) oxide makes necessary a careful transfer of the receiving liquid to the distillation flask. Furthermore, the selective removal of osmium will depend to some extent upon the amounts of the two metals present. It has been found that when the combined amounts of the metals present are much in excess of 15 mg, large excesses of hydrogen peroxide must be added to the distilling liquid because the catalytic action of the metal results in excessive decomposition of the peroxide, so that there may be some co-distillation of the ruthenium. This difficulty is always eliminated by adding more 30 per cent hydrogen peroxide solution and avoiding temperatures above 120°C. After removing the osmium, ruthenium can be volatilized by a further addition of sulphuric acid and the cautious addition of a 10 per cent aqueous solution of sodium bromate or bromic acid, followed by boiling.

Attention is directed again to the seemingly inexplicable effects of such reagents as sulphuric acid upon the choice of method for determining the platinum metals. When osmium is distilled from a sulphuric acid–hydrogen peroxide solution, the co-distillation of oxides of sulphur prevents the use of certain gravimetric reagents. Examples are osmium thionalide, which does not coagulate properly in the presence of sulphuric acid, and 2-phenylbenzothiazole, which requires the prior addition of hydroxylamine.[53]

Sodium Bromate–Sulphuric Acid

Solutions of sodium bromate and sulphuric acid have been used to produce ruthenium(VIII) oxide after the removal of osmium by nitric acid and the evaporation of the pot liquid to remove oxides of nitrogen. As was stated above, the direct fuming of the liquid with sulphuric acid may result in the loss of some ruthenium; this is avoided by prior evaporation with hydrochloric acid. One of the difficulties of this procedure concerns the subsequent removal of remaining platinum metals in the presence of the large amounts of salts derived from the sodium bromate. This factor becomes of some importance when small amounts of residual platinum metals are to be determined. Thus Westland[53] used bromic acid as an alternative oxidant. It should be noted that sodium bromate in the presence of sulphuric acid, without prior fuming, can be used to distil both osmium and ruthenium from solutions containing only small amounts of hydrochloric acid. The presence of sodium chloride, however, increases the resistance to the formation of the tetroxides. When larger amounts of ruthenium are distilled from a solution containing small proportions of hydrochloric acid, particularly if the heating is rapid, a black deposit of oxide may appear in the neck of the distillation flask. With mg amounts of ruthenium and careful distillation this should not occur. The deposit is difficult to remove, but in some instances chlorination in the presence of sodium chloride will remove the stain.

Perchloric Acid

Whereas perchloric acid has been used extensively as an oxidant in producing tetroxides of osmium and ruthenium, few quantitative data have been recorded. For the determination of these two metals in such base metal alloys as iron–copper–nickel no other known oxidant is more efficient. It is also a suitable oxidant for osmium and ruthenium present with small amounts of hydrochloric acid; in this instance it is superior to sodium bromate. Kavanagh[109] used 70–72 per cent perchloric acid to determine mg amounts of osmium and ruthenium in iron–copper–nickel alloys, and Sen Gupta[110] similarly determined these two metals in meteorites. In all instances the acid completely dissolved the alloys. Westland[51] used perchloric acid to recover osmium and ruthenium from distillates containing hydrochloric acid and sulphur dioxide after an evaporation to a small volume. Perchloric acid is a particularly suitable oxidant when osmium and ruthenium are to be distilled simultaneously and collected by hydrogen peroxide.

Perchloric acid containing a small amount of sodium bismuthate has been used as an oxidant. De Ford.[97] and Currah *et al.*[98] preferred this solution to perchloric acid alone, although one may expect added difficulty when determinations of other metals are to be made after the removal of ruthenium. Anyway, the quantitative data obtained by the method do not indicate superior efficiency of recovery.

It may be assumed that the sodium bismuthate which is added initially with the perchloric acid encourages the early oxidation to the tetroxide before the perchloric acid becomes an active oxidizing reagent, and perhaps it assists in the oxidation of the small amounts of chloride remaining from the earlier treatments. De Ford used sodium hydroxide as a receiving liquid, and precipitated the hydrated oxide by heating with ethanol, using magnesium hydroxide as a collector.

Despite the fact that perchloric acid is the preferable oxidant for ruthenium, no data are available which integrate this application within a general procedure for the noble metals. It is expected that such applications will be forthcoming in the near future.

Recently, solutions of perchloric and sulphuric acids have been used to distil ruthenium(VIII) oxide, which is then collected in a dilute hydrochloric acid solution containing hydroxylammonium chloride. The method described in Procedure 138 has been adapted to the use of 1,10-phenanthroline as a spectrophotometric reagent.

Sodium Hypochlorite

As compared to oxidation by sodium hypochlorite, oxidation in a sulphuric or perchloric acid medium has the advantage that entrainment of osmium or ruthenium in the pot residue is avoided. When using caustic solutions of hypochlorite, one may expect that as the distillation proceeds and the basic solution approaches neutrality, with the formation of chloride, some hydrolysis will occur to produce the voluminous hydrated oxides.

Nevertheless, the hypochlorite distillation can be a most useful method for specific purposes. Thiers *et al.*[21] used a chlorine–sodium hydroxide treatment of the ruthenium metal or residue to effect both dissolution of the metal and distillation of ruthenium(VIII) oxide. The procedure involves mixing the residue and filter paper in the still with a caustic solution containing 20 g of sodium hydroxide in 150 ml of water, passing in chlorine and nitrogen simultaneously until the former is no longer absorbed, and then boiling for 15 min. The chlorine quickly destroys the paper, and the ruthenium metal is rapidly attacked. The method used is described in Procedure 3, and is recommended for the production of ruthenium salts as well as for the quantitative determination of either osmium or ruthenium in finely divided residues etc. The procedure has not been tried with material containing other platinum metals, with complex mixtures involving base metals or with compact metals.

Peroxydisulphate

Peroxydisulphate has been used to distil ruthenium from nitric acid solutions. Thiers *et al.*[21] rejected this reagent as an oxidant for ruthenium in a nitric acid solution of the lead button. Nikolaev and Sinitsyn[111] were able to distil ruthenium from nitric acid solutions by oxidation with ammonium peroxydisulphate in the presence of silver ions. Under these conditions the recovery of the tetroxide was more effective than with bromate and sulphuric acid. The latter oxidation mixture failed to distil any ruthenium from solutions of $(NH_4)_2[Ru(NO)Cl_5]$, whereas the peroxysalt in the presence of silver ions produced more than 50 per cent of the metal oxide. Furthermore, an increase in the nitric acid concentration facilitated the separation of the tetroxide. It is assumed that the peroxy salt oxidizes the silver ion to Ag(II), which then reacts with the ruthenium.

It should be noted that whereas this oxidation may be useful for restricted separations, the addition of silver ions to the residual distillation liquid introduces difficulties if other noble metals are to be subsequently separated and determined.

Other Oxidants

Whereas all the oxidants described above have been used quantitatively, many other reagents exist which would adequately produce the tetroxides. Some have been used qualitatively and would no doubt serve for quantitative purposes. For example, permanganates and chromates will produce the osmium and ruthenium tetroxides. These and others may be used for specific purposes, but the indiscriminate use of an oxidant merely because the oxidizing potential is suitable should be avoided. Even though no subsequent determinations of the constituents of the residual pot liquid are to be made, one still has to avoid the co-distillation of interfering substances and their development in the liquid being distilled.

Geilmann and Neeb[103] have stressed the difficulties connected with the oxidation by permanganate in sulphuric acid solutions. It was rejected for the oxidation of μg amounts because of the retention of osmium by the manganese dioxide formed in the reaction. This retention was complete for 2–7 μg of osmium.

They also made an extensive examination of suitable oxidants for μg amounts of osmium and ruthenium. The proportions of the tetroxide lost on heating varied somewhat with the vessels used, being less from beakers than from evaporating dishes. It should be noted that an evaporation to 2 ml of the hydrochloric acid–sulphur dioxide solutions of both osmium and ruthenium, together with 0·5 ml of 60 per cent perchloric acid results in the almost complete retention of the metals.

Presumably these authors encountered difficulty with the perchloric acid oxidation to the tetroxides for they recommended the use of 0·5–1 g of chromium(VI) oxide for 25–30 ml of an osmium–ruthenium solution. This addition was particularly advisable when halogenides or organic materials were present. With chromium oxide there is a continuous regeneration of chromate. Undoubtedly reagents such as bismuthate and chromium oxides encourage the early and continuous formation of the tetroxides, but they are not necessary for the quantitative recovery of the two metals. In fact, their presence in the residual liquid complicates the determination of other platinum metal constituents.

In general, the osmium and ruthenium contained in the solid material

(excluding ores etc.), are put into solution by a caustic fusion or by some type of chlorination. In these instances, any of the oxidants described above may be used. With ores and concentrates the osmium and ruthenium, along with other noble metals, are concentrated by forming a lead or other base metal alloy. The perchloric acid dissolution and oxidation is the most suitable procedure for the alloys if osmium and ruthenium only are to be determined. Methods have not been recorded for the determination of the remaining noble metals in the residual perchloric acid. The most troublesome medium for the oxidation of osmium and ruthenium is hydrochloric acid. In this instance, it is advisable to saturate the solution with sulphur dioxide. This solution may then be evaporated to a small volume, and subsequently oxidized by perchloric or bromic acids.

The following separational methods deal with solutions of osmium and ruthenium in media of one or more of: sodium hydroxide, hydrochloric acid, hydrobromic acid, perchloric acid, sulphuric acid, hydrogen peroxide. Methods for the determination of these metals in more complex systems such as alloys with base metals or associated platinum metals are included in Section II of this chapter. These materials involve some preparatory treatment, but in each instance one or other of the above media is obtained.

THE ISOLATION OF OSMIUM USING NITRIC ACID AND OF RUTHENIUM USING BROMIC ACID

Procedure 1[100]

The isolation of osmium. Transfer the caustic solution containing osmium and ruthenium, or a mixture of their salts, or the evaporated hydrochloric acid solution, to the distillation flask described in Chapter 7, Equipment No. 4. Add to the receiver B, 150 ml of 1 : 1 hydrochloric acid freshly saturated with sulphur dioxide. Add 50 ml of the latter to each of the second and third receivers C and D. Add water to the distillation flask if necessary to increase the volume to about 150 ml. Then add through the inlet tube sufficient 1 : 1 nitric acid to make this solution about 5 N in this acid. Apply suction to create a slow regular stream of air or preferably nitrogen. Heat to boiling for at least 1 hr for the caustic solutions of osmium or for about 5 hr for the chloride solutions. In either instance ensure the complete removal of the osmium by further distillation followed by the transfer of the distillate to the precipitation beakers. If this is done, add about 50 ml of the sulphur dioxide–hydrochloric acid solution to the first receiver.

Evaporate the combined osmium distillates to a few ml, and repeat the evaporation four times, with intermittent addition of concentrated hydrochloric acid. Dilute the solution, filter through a porcelain filtering crucible, and treat for either a gravimetric or a spectrophotometric determination. A selection of these methods is described in the appropriate chapters.

The isolation of ruthenium. Transfer the liquid in the distillation flask to a suitable beaker, and evaporate the solution to dryness. Add a few ml of concentrated hydrochloric acid and again evaporate to dryness. Repeat this procedure four times. Add 10 ml of water and 10 ml of 1 : 1 sulphuric acid and repeat the evaporation on a steam bath. Heat the solution to fumes, cool, add about 3 ml of water and repeat the heating to fumes. Do not heat to above 120°C or for excessive periods. Dilute with water and transfer to the original distillation flask, being careful to avoid wetting the neck of the flask. Add 150 ml of the sulphur dioxide–hydrochloric acid solution to the first receiver and 50 ml of the same solution both to the second and to the third receiver. Add to the 50 ml solution in the distillation flask about 50 ml of a 5 per cent bromic acid solution, and boil for about 1 hr; then add a further 25 ml of the bromic acid and boil for another hr.

Combine the receiving solutions and evaporate them to a moist residue. Repeat the hydrochloric evaporations which were made with the osmium solution but not to dryness. Add a few ml of hydrochloric acid, warm, dilute, and filter through the porous porcelain crucible. Treat the solution to prepare for either a spectrophotometric or a gravimetric determination.

Note—The above procedure may be used for macro amounts of metal or for a few mg by appropriately adjusting the volumes of the constituents added to the distillation flask. Care should be taken, however, to ensure a sufficiently large volume of receiving liquid and a continuous supply of sulphur dioxide. The latter can be accomplished through the tube attached to the train of receivers. These volumes of receiving liquid cannot be less than 50 ml even for the distillation of mg amounts of osmium when the amount of nitric acid used for the oxidation is excessive, e.g. when a lead assay button or iron alloy is to be analysed for osmium. Furthermore the sulphur dioxide–hydrochloric acid solution can be replaced effectively by such absorbents as hydrobromic acid or hydrogen peroxide.

By using the above procedure the residual liquid from the ruthenium distillation can be treated for the determination of the remaining four platinum metals. These procedures are included below.

The Collective Distillation of Osmium and Ruthenium from Perchloric Acid, and their Subsequent Separation

Procedure 2[105]

The distillation apparatus is described in Chapter 7, Equipment No. 9 or No. 10.

The distillation of both metals. Transfer the solution (about 100 ml) containing a few μg up to about 20 mg of osmium and ruthenium, prepared in a caustic, hydrochloric, hydrobromic or sulphuric medium, to the distillation flask. A volume of about 100 ml is suitable. Add 100 ml of water to the trap and 30 ml of a 3 per cent hydrogen peroxide solution to the first receiver and 10 ml to each of the two following receivers. Add about 5 ml of a 5 per cent solution of thiourea in 1 : 1 ethanol–hydrochloric acid to the end bubbler. Apply gentle suction to produce about 3–6 bubbles per sec. Surround the three receivers with ice, and connect a stream of water to the condenser between the trap and the first receiver. Add 60 ml of 70–72 per cent perchloric acid for macro amounts of metal, or 20 ml for micro amounts, to the distillation flask. Boil for about 30 min after the acid is brought to fumes. A total of about 1 hr should be sufficient. Then add 15 ml of the perchloric acid to the trap through the attached funnel, and boil the trap solution for 25 min.

The separation of osmium. Transfer the receiving liquid to a fresh distillation flask, taking full precautions to avoid volatilization of osmium, by intermittent chilling of the receivers and the flask during the transfer. Wash the receivers and the delivery tube with 5 per cent sulphuric acid, then completely remove the cold acid from the tubes and receivers, because its presence interferes with the coagulation of osmium thionalide. Add 100 ml of water to the trap, 30 ml of hydrobromic acid (48 per cent, twice distilled) to the first receiver, and 10 ml to each of the two following receivers. Add some of the thiourea solution to the bubbler. Cool the receivers in an ice bath, and pass water through the condenser.

Add to the peroxide solution in the flask 40 ml of a 30 per cent hydrogen peroxide solution and 5 ml of concentrated sulphuric acid. Apply suction, and boil gently for 30 min (excessive heating results in frothing, and premature loss of hydrogen peroxide). Add 15 ml of perchloric acid to the trap, and boil the trap liquid for 25 min, applying very gentle suction to prevent perchloric acid from distilling into the receivers.

Methods for the subsequent determination of the osmium. If the osmium is to be determined gravimetrically by precipitation with thionalide, transfer the receiving liquid to a suitable beaker, taking the precaution indicated above, and rinsing with 10 per cent hydrobromic acid. Evaporate the contents of the beaker on a steam bath to 5 ml, and carry out the precipitation (Procedure 78).

If a spectrophotometric method is to be used, carry out the evaporation as required by the chosen method. This procedure is not required in the direct absorption of osmium tetroxide in a thiourea solution. The procedure is as follows:

Add 20 ml of a 1 per cent solution of potassium permanganate to the trap, and 15, 5 and 5 ml of a 2 per cent thiourea solution in 1 : 1 ethanol–hydrochloric acid to the three receivers, in order of distance from the trap. Otherwise repeat the above instructions for the separation of osmium. When boiling has been completed, boil the solution in the trap for 10 min. Disconnect the suction tube, and place three beakers containing water at 85 °C around the three receivers for 15 min. Transfer the receiving solutions to a 50-ml volumetric flask, rinsing with a 1 : 1 ethanol–hydrochloric acid solution and make up to the mark with the same solution. Filter through a 11-cm Whatman No. 42 filter paper into the transmittance cell. Measure the transmittance against a blank containing a 1 : 1 ethanol–hydrochloric acid solution (see Procedures 153 and 154). A standard curve should be made by taking known amounts of osmium through the complete procedure.

The removal of ruthenium from the pot liquid. No method has been applied successfully to the direct determination of ruthenium in the pot liquid.

To prepare for the ruthenium distillation, add 100 ml of water to the trap and 30 ml of a 3 per cent hydrogen peroxide solution containing 1 ml of concentrated hydrobromic acid to the first receiver, and add 10 ml of a 3 per cent hydrogen peroxide solution to the two remaining receiving liquids. Add thiourea to the bubbler, if desired. Pass water through the condenser. Apply a very gentle suction, to avoid frothing, and add 10 ml of concentrated sulphuric acid and an excess (usually 20–30 ml) of a 10 per cent solution of sodium bromate. Add the oxidant cautiously, a few ml at a time, or preferably 15 ml initially, with intermittent boiling before the addition of the remaining bromate solution, the total boiling period being 1 hr. Add 15 ml of perchloric acid to the trap, and boil the trap liquid for 30 min, applying very gentle suction to avoid any volatilization of perchloric acid. Add 8 ml of concentrated hydrobromic acid to the first receiver, and heat gently to remove any condensed ruthenium. Transfer the three receiving liquids to a beaker, and evaporate to about 1 ml or to a moist residue. Avoid evaporating to dryness, because ruthenium salts may resist redissolution. If dryness occurs inadvertently, add 5 ml of concentrated hydrochloric acid, boil under a cover glass, then evaporate to a moist residue.

Dilute, and determine the ruthenium by precipitation with thionalide or by applying a suitable spectrophotometric method.

A number of variations in the above procedures may be applied to separate osmium and ruthenium, or to isolate them simultaneously.

1. The simultaneous distillation may be accomplished using sodium bromate or bromic acid, and sulphuric acid, instead of perchloric acid. In this instance, the subsequent determinations of the remaining platinum metals may be accomplished by an evaporation to remove sulphuric acid followed by a conversion of the remaining four platinum metals to their chlorides. With perchloric acid distillations, the residual perchloric acid may be similarly removed, with the precaution that evaporations be made from a suitably constructed chamber in order to avoid danger from explosions.
2. The 3 per cent hydrogen peroxide receiving liquid for the retention of ruthenium may be prepared as a solution in 1 : 1 hydrochloric acid, in which instance the combined receiving liquids must be evaporated to remove most of the acid prior to the determination of ruthenium.
3. The hydrogen peroxide solution for the collection of ruthenium may be replaced by hydrobromic acid or by the hydrochloric acid–sulphur dioxide solution. In general, the former is preferred.
4. The simultaneous collection of osmium and ruthenium may be accomplished with a sodium hydroxide solution, in which instance the selective removal of osmium requires the acidification of that solution with sulphuric acid before the addition of the hydrogen peroxide. There is also the inconvenience of excessive amounts of salts in the pot liquid.

It should be noted, however, that caustic solutions can be most useful as collectors for either osmium or ruthenium when colorimetric methods are to be subsequently applied.

The Distillation of Ruthenium Using Hypochlorous Acid

The chlorine distillation from caustic solutions is most useful when the osmium or ruthenium is to be determined in mixtures of finely divided metals etc. In specific instances the method may also be preferred for solutions of the metals.

Thiers *et al.*[21] applied the method discussed below to the determination of the ruthenium metal remaining in the pot liquid after a perchloric acid distillation from lead alloys. When the method is applied to dry mixtures containing finely divided ruthenium, the sample, in a filter paper or as a solid, is transferred directly to the still.

Procedure 3[21]

The distillation equipment is described in Chapter 7, Equipment No. 5.

Prepare a standard filter stick by wrapping around the filtering end a No. 42 and a No. 50 Whatman filter paper, holding them in position with an elastic band. Arrange a trap to collect the filtrate, and use the filter stick to collect the residue from the suspension. If the filtered liquid still contains suspended particles, return it to the original vessel, and re-filter it. Wash the vessel with water, and filter until all the residue has been collected. Transfer the filter paper to the 250-ml still or, if the suspension was originally present in the still, remove the elastic band, and push the paper and residue into the still without removing them from the still at any time. Add a solution of 20 g of sodium hydroxide in 150 ml of water to the still. Also, add 25 ml of a 3 per cent hydrogen peroxide solution and 1 ml of a 42 per cent hydrobromic acid to the first solution and 5 ml of a 3 per cent hydrogen peroxide solution to each of the other receivers. Chill the receivers in ice. From opening C pass a steady stream of nitrogen through the solution, and through opening B, a stream of chlorine. The gas rate should be about 2–3 bubbles per sec. After 10 min or so, depending on the chlorine flow rate, the temperature rises and a rapid effervescence occurs. At this point, control the rate of flow by turning off the gases, and placing one's finger over the mouth of the last receiver. This raises the pressure in the system, and markedly slows the effervescence. Then judiciously release the escaping gases to allow the effervescence to occur without any overflow. Pass in the chlorine until it is no longer absorbed, and then boil the liquid for 15 min. By this stage, the chlorine will have destroyed the paper and dissolved the metallic ruthenium.

Disconnect the receivers from the still, but not from each other, and add 8 ml of 45 per cent hydrobromic acid to the first receiver, which should contain most of the ruthenium. Place a ground-glass stopper in this receiver, and boil the contents of the vessel, thus ensuring the reduction of ruthenium salts and avoiding losses during the subsequent heating. Transfer the receiving liquids to a suitable beaker, boil for 10 min, and precipitate ruthenium with thionalide (Procedure 72).

Notes—The above method can be applied with equal efficiency to a caustic fusion or to the sodium peroxide fusion in a silver crucible of a residue containing ruthenium.

Distillations such as these can be made in less than 1 hr. Samples of the order of 10–20 mg of ruthenium have been used in the above method, but much larger weights may be used with appropriate variations in reagents and equipment.

The Distillation of Ruthenium Using Perchloric Acid

Procedure 4[106]

The distillation equipment is described in Chapter 7, Equipment No. 6.

The ruthenium solution containing 10–50 μg of ruthenium must be free of chloride ion. This may be accomplished as follows:

Evaporate with hydrochloric acid if nitric acid is present, then fume with sulphuric acid at as low a temperature as is feasible. Transfer the ruthenium solution to the distillation flask.

Pour into the receiving flask 30 ml of 0·2 N hydrochloric acid and 4 ml of a 5 per cent solution of hydroxylammonium chloride. Add to the bubbler 3–4 ml of the hydrochloric acid and 1 ml of the hydroxylammonium chloride solution. Fit the delivery tube into the receiver flask and place a little water into the flared top of this flask. Add 1 ml of concentrated perchloric acid to the distillation flask, and quickly connect the delivery tube. Add 0·5–1 ml of the perchloric acid to the flared top of the distillation flask, and, by holding the neck of the flask, move the delivery tube so as to work some perchloric acid into the ground-glass joint, thus making a good seal and preventing the joints from freezing. Pass cold water through the condenser, and a slow stream of dry air through the system. Heat the solution, and distil until perchloric acid is refluxing well up in the neck of the distillation flask. Then remove the heat source, and after 1 min disconnect the air flow. Cool the pot liquid (during which period the solution in the receiving flask rises into the delivery tube, and the solution in the bubbler is forced into the receiver flask). Rinse the bubbler with several small portions of 0·2 N hydrochloric acid, the large diameter of the delivery tube permitting the bubbler to be emptied in this manner before the solution in the receiving flask rises even half-way up to the delivery tube. Connect the air stream to prevent the receiver solution from passing into the distillation flask.

Remove the delivery tube, and rinse with several small portions of 2 N hydrochloric acid. Add the rinsings to the receiver solution, and transfer the contents to a 250-ml beaker. Evaporate on a steam bath to 20–30 ml and continue according to Procedure 138.

Note—The above method must be followed carefully to avoid the co-distillation of perchloric acid. The latter causes the slow precipitation of the insoluble tris-(1,10-phenanthroline) ruthenium(II) perchlorate. With proper care little perchloric acid should pass into the receivers.

The Solvent Extraction of Osmium Tetroxide

Osmium tetroxide can be extracted from aqueous solutions by either chloroform or carbon tetrachloride. Because very few inorganic substances are soluble in these organic media, these extraction methods can be useful.

The solvent extraction method is particularly suitable for amounts of osmium in the range of 5–1000 μg. Compared to the distillation methods, there is perhaps less effort expended in retaining a small volume for spectrophotometric purposes. A proper choice of receiving liquids, however, can virtually eliminate this claimed advantage.

As would be expected, ruthenium tetroxide is simultaneously extracted, but separation from osmium can be effected by reduction to a lower valence state and the far easier re-oxidation of osmium. Ruthenium is maintained in a reduced state by ferrous sulphate while osmium is selectively oxidized by 5 N nitric acid. Tests have shown that the effectiveness of the method depends upon the rate of reduction of the two tetroxides by iron(II) salts in acid solution. Prolonged reduction results in the formation of excessive amounts of Os(IV), with the result that the re-oxidation by nitric acid is retarded.

The extraction is impractical in the presence of hydrochloric acid and particularly in the presence of chloride salts. The chlorosmates are not quickly oxidized by nitric acid, and the extended time allows the production and thus the extraction of some ruthenium(VIII) oxide. If proper care is exercised, however, the chloride may be removed by fuming with sulphuric acid in the presence of iron(II) salts.

The method is applicable to solutions of osmium containing as much as 500 mg of copper(II), and 1 mg each of platinum(IV) and palladium(II).

The following procedure is applicable to solutions containing osmium in valence states lower than VIII.

Procedure 5[112]

Add to the chloride-free osmium solution, containing more than 5 μg of osmium, 5 ml of 6N sulphuric acid and 2·5 ml of 85 per cent phosphoric acid to obtain approximately 25 ml of solution. The total volume of the osmium solution should not exceed 50 ml. Add dropwise a 5 per cent solution of potassium permanganate to the appearance of a pink colour. (If much ferrous iron is present in the initial solution, add the potassium permanganate as a finely ground solid to keep the volume of the solution as small as possible.)

Discharge the permanganate colour with 25 mg of ferrous ammonium sulphate, added as a solid or in solution. If the colour is not completely discharged add a similar amount of ferrous ammonium sulphate. The solution should now contain no suspended material. Do not allow the solution to become warm during the oxidation lest some osmium tetroxide be volatilized.

Transfer the solution to a separatory funnel, and add 15 ml of concentrated nitric acid (or enough to make its concentration in the final solution 5 M). Cool the solution to 20–25°C, add 10 ml of reagent-quality chloroform (less preferably carbon tetrachloride), and shake vigorously for 2 min. Allow the phases to separate, and deliver the chloroform layer into a dry glass-stoppered flask. Repeat the extraction with two or three 10 ml portions of chloroform, depending on the recovery desired.

To the combined chloroform extracts add 5·00 ml of a 0·1 M solution of thiourea in 1 N sulphuric acid (freshly prepared daily) and shake vigorously for 5 min (a mechanical shaker operating at 180 c/min is convenient). Allow the phases to separate, transfer the clear aqueous layer to an absorption cell (1-cm is satisfactory), and measure the transmittance at 480 mμ using a spectrophotometer or filter photometer. If the red colour is too strong, dilute the solution with water to an appropriate volume before reading. Establish the standard curve by treating known amounts of osmium tetroxide in water with thiourea; the final concentration of the latter should be about 0·1 M in 1 N sulphuric acid, but the concentrations are not critical.

Note—Whereas the above procedure does not allow for the subsequent determination of ruthenium in the aqueous extract, this, no doubt, could be accomplished by an evaporation with sulphuric acid to destroy the organic matter followed by a perchloric acid distillation.

The Solvent Extraction of the Ruthenium–Diphenylthiourea Complex

Very few analytical procedures have been described for the solvent extraction of ruthenium. Techniques for the chloroform extraction of ruthenium analogous to the osmium method described above are hindered by the slow removal of the ruthenium(VIII) oxide into the aqueous phase.

Solvent extraction methods for the determination of osmium in the presence of large proportions of ruthenium and the determination of ruthenium in the presence of large proportions of osmium have been described by Geilmann and Neeb.[113] These procedures involve the formation of a complex with either diphenylthiourea or with 2,4-diphenylthiosemicarbazide for ruthenium determinations, or a tetraphenylarsonium complex for osmium determinations. In the first instance the complex is extracted into chloroform, followed by distillation to remove the chloroform, then by an oxidizing distillation to isolate the ruthenium(VIII) oxide. Whereas attempts to remove the ruthenium from the organic layer into aqueous sulphuric acid have proved successful, the subsequent determination is somewhat difficult. The sulphuric acid extract, however, can be subjected to distillation from perchloric acid etc. as described below (Procedure 6).

Procedure 6[113]

The distillation equipment is described in Chapter 7, Equipment No. 7.

The solution of the metals as hexachloro salts may contain as much as 10 mg of osmium and about 30 μg of ruthenium. Adjust the acidity of 5–20 ml of the solution to 5–7 N in hydrochloric acid, and add 2 ml of a saturated methanolic solution of diphenylthiourea. Heat for 30 min at 80°C. Cool, and transfer the solution to a separatory funnel. Make three extractions with 10 ml amounts of chloroform. Filter the extracts through a small filter paper into the distillation flask A. Distil off the chloroform, and to the residue add 20 ml of concentrated sulphuric acid, 5 ml of 60 per cent perchloric acid and 3 g of chromium(VI) oxide. Connect the flask to the distillating train, and add to flask B, 10–20 ml of 6 M hydrochloric acid saturated with sulphur dioxide. To each of the two receivers add 10–15 ml of the same absorbing solution. Connect the pump, and draw a slow stream of air through the system. As a precaution moisten the ground-glass joints of the distillation flask with concentrated sulphuric acid. Heat to gentle boiling, avoiding the distillation of sulphuric acid. After 1–1·5 hr, disconnect the receiving train; combine the solution from flask B with the two receiving liquids, rinsing well with water. Evaporate on a steam bath, adding more hydrochloric acid–sulphur dioxide solution if the odour of sulphur dioxide disappears during the evaporation. Treat the evaporated residue as is required for the spectrophotometric or gravimetric determination of ruthenium.

Notes—When very small amounts of ruthenium are to be determined in the presence of very large proportions of osmium, so much of the latter may appear in the distillate as to make necessary further extractions and a second distillation.

When osmium is to be determined simultaneously with ruthenium, the aqueous extract of the former from the chloroform–ruthenium separation is evaporated on a water bath and gravimetric or colorimetric determinations made using suitable reagents.

In those instances where osmium is to be determined in the presence of much smaller amounts of ruthenium, it is advisable to treat 30–60 ml of a 6 M hydrochloric acid solution of the mixed chloro salts with 3–5 ml of the methanolic diphenylthiourea solution, and heat for 45 min at 80°C. After cooling, the blue ruthenium complex is extracted with 20–30 ml of chloroform and then with 5-ml portions to attain a colourless aqueous phase. The latter is evaporated, and the osmium determined using di-*o*-tolylthiourea or thiourea (Procedure 153).

While no data have been recorded to indicate the accuracy obtained for the simultaneous determination of ruthenium and osmium, presumably the proportion of the latter carried into the chloroform layer may be regarded as insignificant, at least in those instances when the ratio of osmium to ruthenium is not excessively great.

The Solvent Extraction of the Osmium–Tetraphenylarsonium Complex

Osmium may also be separated from ruthenium by a chloroform extraction of the tetraphenylarsonium–osmium complex. Concerning the chloro complex, the osmium compound is readily soluble in chloroform whereas the ruthenium complex is not extracted. Strangely, with the bromo salts, the reverse tendency is true. Thus the separation requires a chloride solution, the maximum recovery being obtained only in a weak acid solution.

Procedure 7[113]

The distillation equipment is described in Chapter 7, Equipment No. 7.

The solution of the mixed hexachloro salts may contain up to 200 μg of osmium and up to 5 mg of ruthenium. Add to a separatory funnel 15–20 ml of the metal ion solution, and adjust the acidity to 0·1–0·3 M with hydrochloric acid. Add 2 ml of a 1 per cent aqueous solution of tetraphenylarsonium chloride, shake thoroughly, and extract 3 times with 10-ml amounts of chloroform. Filter the extracts through a filter paper into the distillation flask. Evaporate the chloroform on a steam bath, and add to the flask sulphuric acid, perchloric acid and chromium(VI) oxide, as described in Procedure 6. Also distil and collect the osmium(VIII) oxide in the hydrochloric acid-sulphur dioxide solution as described in that procedure. Determine the osmium colorimetrically or gravimetrically.

Note—The ruthenium in the aqueous layer may be determined simultaneously, although a small loss will result from the chloroform extraction. It should be noted that the latter co-extraction may also produce errors in the osmium determination.

Other Solvent Extraction Methods of Isolating Ruthenium

A method for the separation of ruthenium and palladium by solvent extraction has been reported by Wilson and co-workers.[114] The procedure involves the formation of the pyridine thiocyanate complex of palladium in an alkaline solution at room temperature, and its subsequent extraction into hexone. The alkaline aqueous phase is then acidified, heated and cooled, and the ruthenium complex extracted with hexone, spectrophotometric measurements being made directly.

The details of a thiocyanate method are recorded in Procedure 145.

Solvent extraction methods have also been used for the separation of ruthenium from iron, titanium etc. The acetylacetone complex of ruthenium(III) chloride can be extracted into chloroform at room temperatures, at pH 1·8–2. The method is recorded in Procedure 140.

The Separation of Rhodium from Iridium

In most analytical schemes involving either wet and dry extractions or both techniques, rhodium and iridium are isolated simultaneously. In fire assay extractions these two metals constitute most of the so-called insolubles, and are usually contaminated by traces of base metals and some of the other platinum metals such as ruthenium. Rhodium and iridium are resistant to the usual acid dissolutions, but solutions may be obtained through chlorination in the presence of sodium chloride,[34] by a bomb technique[64] or by a fusion with sodium peroxide in a silver crucible.[115]

The separation of rhodium from iridium presents the most difficult aspect of platinum metals analysis. Until recently no acceptable method was available. During the past decade a good variety of methods has been recorded, all of which are capable of producing accurate results in the hands of experienced analysts Some of the methods are intricate and time-consuming: some are limited to small amounts of metals and, of course, all of them require a prior isolation of the two metals. It is a reasonably safe guess that the next decade will provide new and improved methods for this separation.

One of the earliest separatory methods for rhodium involved a fusion of the mixed platinum metals with sodium hydrogen sulphate, the rhodium being preferentially dissolved by aqueous extraction of the fusion. This

method has recently been recommended by Ubaldini[116] for the separation of rhodium from platinum catalysts. This type of method, however, is subject to the common defects of selective dissolution in that with admixtures some platinum is simultaneously dissolved, and unless dissolution is complete some rhodium remains unattacked. The Gibbs method of separation using sodium sulphide[117] has recently received attention also,[118] but it appears to be applicable only to small amounts of rhodium. The classical separation of iridium from rhodium as ammonium hexachloriridate is insufficiently accurate for analytical work. It has been stated that reprecipitation is not effective for purifying the precipitate.[119]

A number of quantitative separations of rhodium from iridium using selective reductants have been proposed. Among these reductants are copper, antimony, titanium(III) chloride, chromium(II) and vanadium(II). In all of these instances the respective reduction potentials compared with those of iridium indicate that iridium should be reduced to the metal simultaneously with rhodium. When magnesium and zinc in 1·0 M hydrochloric acid are applied as reductants of iridium to the metal, only part of the iridium is precipitated even after boiling for 1 hr and warming on a steam bath for 24 hr. Undoubtedly some solutions of iridium contain unusually stable complexes. This view is supported by the general analytical behaviour of iridium e.g. the difficulty of arriving at complete precipitation using hydrogen sulphide etc. Peculiarly, the reduction of iridium seems to be encouraged by the presence of palladium. The problem seems to be a kinetic one; its interpretation would provide a distinct contribution to the chemistry of the platinum metals.

REDUCTION BY COPPER

Copper metal has been used by various authors for the general precipitation of the platinum metals. Mukhachev[120] thus determined the sum of these metals. The method involved the introduction of a copper wire into the hydrochloric acid solution of the platinum metals. The solution was boiled for 5 hr, and then the supernatant liquid was decanted. Water was added to the residue and the deposit on the copper wire was dislodged by boiling the water. The wire was removed and the residue in the water was treated with an aqueous ammonia solution, followed by hydrochloric acid to selectively remove any copper contamination. The mixture was filtered, the residue was ignited in hydrogen, and then weighed. The method is simple, but inaccurate because the final residue may contain appreciable amounts of impurities such as silica.

Aoyama and Watanabe[121] used copper powder to separate iridium from gold, platinum and rhodium. After the reduction the iridium in the filtrate was precipitated as ammonium chloriridate. Procedures were also recorded for the complete precipitation of palladium, ruthenium and rhodium using copper powder. In 3 N hydrochloric acid at 61°C, these metals could be quantitatively reduced. At this acidity the copper dissolved (with the evolution of hydrogen), and the rhodium metal floated as a sponge. At a similar acidity platinum could be separated from iridium. The precipitate of platinum was treated with an aqueous ammonia solution for 2 hr, and further traces of copper were removed by nitric acid. The platinum was dissolved in *aqua regia*, and precipitated using sodium hydroxide and hydrazine. The filtrate, containing iridium and copper, was evaporated, the residue ignited in hydrogen, and the iridium purified by treatment with nitric acid. Where high accuracy is not required, copper is thus a good precipitating and separatory reagent for iridium. The selective removal of base metal impurities using mineral acids is not recommended for the reasons discussed in Chapter 1.

Tertipis and Beamish[122] have used copper powder to separate both mg and μg amounts of rhodium from iridium. The procedure requires the precipitation of the rhodium in 1·0 M hydrochloric acid using an excess of copper powder. The rhodium is separated from admixed copper by cationic exchange after dissolution by *aqua regia* and then by dry chlorination. Gravimetric and colorimetric methods can be used to determine the rhodium. The iridium in the filtrate is separated from copper by cationic exchange, and can also be determined either gravimetrically or colorimetrically.

THE SEPARATION OF RHODIUM FROM IRIDIUM USING COPPER

Procedure 8[122]

Apparatus

Large ion-exchange column. A borosilicate glass tube 2·3 cm inside diam., joined to a draining tube 5 mm inside diam., and containing a resin bed 16–17 cm deep.

Small ion-exchange column. A borosilicate glass tube 1 cm inside diam., joined to a draining tube 4 mm inside diam., and containing a resin bed 5–6 cm deep.

Ion-exchanger. Dowex 50X cationic resin in the sodium form, 20–50 mesh, supported in the column by a small plug of glass wool. Regenerate the exchanger just before use with 3 M hydrochloric acid until the eluents are colourless and are free from iron and copper, as shown by spot tests with potassium thiocyanate and rubeanic acid, respectively. Remove the excess of acid from the exchanger by washing with water until the eluant is neutral to litmus paper.

Chlorination apparatus. A Vycor tube 19 mm inside diam. and 50 cm in total length, with an elongated end (outlet) to allow its connection to a rubber tube, and heated by an electric furnace, 9·53 cm long.

Procedure. For 10–20 mg of metal, make the rhodium–iridium solution, in a 150-ml beaker, 1·0 M in hydrochloric acid, and a total volume of 30 ml. For μg amounts the total volume should be 20 ml. Add 0·5 g of freshly reduced copper (prepared by reducing copper(II) oxide powder in hydrogen at 400–420°C, and grinding in an agate mortar). Cover the beaker tightly with a watch glass, and heat to the gentle evolution of bubbles (91–93°C) for 1 hr, with swirling at intervals of 1 min.

Keep the volume constant by the addition of water. Add an additional 0·29 g of copper powder after the solution has been heated for 30 min, to prevent any possible redissolution of metallic rhodium, and also to complete the reduction of rhodium. Filter the warm solution through a 3-ml, A2 filter crucible by suction, and decant thrice. Transfer the residue to the filter crucible using a water stream, and wash it into the crucible; 18 such washings are recommended.

Note—When copper is added, the solution instantaneously changed from dark red to light pink, iridium being reduced to a low valence state.

The recovery and determination of rhodium. Place the filter crucible containing the residue in the original beaker, and treat it with 24 ml of *aqua regia* (3 : 1) on a steam bath until the reaction ceases, the beaker being well covered with a watch glass. Filter the resulting solution through the original filter crucible and wash the beaker several times using a water stream to transfer any residue into the filter crucible (filtrate A). Dry the residue in the crucible in a steam cabinet, cover it with finely ground sodium chloride, and chlorinate for 7 hr at 700°C.

Dissolve the chlorination product in 0·1 M hydrochloric acid, filter the resulting solution through a glass-wool stem, and combine the filtrate with filtrate A. Evaporate the combined solutions almost to dryness. Repeat a few times with concentrated hydrochloric acid, dilute with water, then treat again with concentrated hydrochloric acid. Evaporate to dryness to expel any nitric oxide, and to convert the metals to their chlorides. Dissolve the salts in 50 ml of water, adjust the pH of the solution to 1·3–1·5, and remove the copper by passing the solution through an appropriate cation-exchange column at 1 drop per sec. Wash the large and small columns with 550 and 170 ml respectively of dilute hydrochloric acid (pH 1·3–1·5).

The determination of the rhodium in the effluent solution. For mg amounts of rhodium, add 3·5 ml of concentrated hydrochloric acid to each sample, and determine the rhodium gravimetrically using thiobarbituric acid (Procedure 82).

For μg amounts, reduce the effluent volume, transfer to a 30-ml beaker, and evaporate to dryness in the presence of 2 ml of a 2 per cent sodium chloride solution. Destroy organic matter by digestion with concentrated nitric acid and a 30 per cent hydrogen peroxide solution, and convert the metal to its chloride using concentrated hydrochloric acid. Determine rhodium spectrophotometrically using a solution of stannous chloride in 2 M hydrochloric acid, the absorbance being measured at 470 mμ (Procedure 158). For 2 to 100 μg of rhodium, make the final volume of the solution 25 ml and use a 5-cm cell, whereas for more than 100 μg, make the volume 50 ml and use a 1-cm cell. In all instances, carry a reagent blank through the entire procedure. Use standards directly from the rhodium stock solution.

The recovery and determination of iridium. Evaporate the filtrate and washings from the rhodium precipitation to dryness in a 400-ml beaker, and dissolve the residue in 50 ml of water. Eliminate copper from the resulting solution by the cation-exchange procedure described above in the recovery and determination of rhodium. Evaporate the effluent from the small column to dryness in the presence of 2 ml of a 2 per cent sodium chloride solution, in order to remove mineral acids which interfere in the subsequent precipitation of iridium using 2-mercaptobenzothiazole.

When mg amounts of iridium are to be determined, dissolve the residue in 30 ml of water, and determine the iridium gravimetrically using 2-mercaptobenzothiazole, in the presence of one or two glass beads to prevent bumping (Procedures 89 and 90).

When μg amounts are to be determined, dissolve the residue in water, and transfer the resulting solution to a 30-ml beaker. Destroy the organic matter by digestion with a few drops of concentrated nitric acid and a hydrogen peroxide solution, evaporate to dryness, treat the residue with concentrated hydrochloric acid, and determine the iridium colorimetrically, using a modification of the Berman–McBryde method (Procedure 163).

In both procedures carry a reagent blank through the entire procedure. Use standards directly from the iridium stock solution and, for the μg amounts, analyse them simultaneously with the unknown samples.

Because the recorded redox potentials for iridium systems indicate that copper should precipitate iridium, it is of interest to know the amounts of iridium that can be precipitated by copper under the conditions of the above procedure. Table 6 indicates the amounts which may be expected to precipitate.

THE SEPARATION OF RHODIUM FROM IRIDIUM USING THIOACETANILIDE

Recently, Jackson[123] recorded a method for the selective precipitation of a rhodium–organic complex in the presence of iridium. The procedure requires the evaporation to fumes of a sulphuric acid–lithium sulphate solution of the two metals, and additional heating with perchloric acid. Rhodium is then selectively precipitated by thioacetanilide after using a fresh chromium(II) chloride solution to reduce both species to the divalent state.

TABLE 6. IRIDIUM REDUCED BY COPPER[122]

Iridium	
Added (mg)	Found (µg)
9·15	32
	30
	33
4·60	8
	9
	8
	9
	8
	9
1·84	5
	4
	5
0·459	1·8*
0·459	
0·459	
0·092	1·4*
0·092	
0·092	
0·046	0·3*
0·046	
0·046	

* After reduction by copper, the three residues were combined, and analysed for iridium.

Iridium in the filtrate is precipitated as its sulphide by thiourea in the presence of chromium(II). The method has been applied successfully to 0·5–100 mg of metal.

Procedure 9[123]

Reagents

Sulphuric acid–lithium sulphate solution. Add 266 g of lithium sulphate to 1 l. of concentrated sulphuric acid, and warm until dissolution is complete.

Thioacetanilide solution. Dissolve 2 g of thioacetanilide in 100 ml of glacial acetic acid, and filter the solution.

Chromous chloride solution. Approximately 1·0 N.

Hydroquinone solution. Dissolve 0·1424 g of hydroquinone in 500 ml of dilute sulphuric acid (1 + 99).

3,3′-*Dichlorobenzidine indicator solution.* Warm 0·1 g of 3,3′-*dichlorobenzidine* with 10 ml of dilute sulphuric acid (1 + 2), and dilute the solution to 100 ml.

Procedure. Evaporate the chloride solution of rhodium and iridium in the presence of 10 ml of concentrated nitric acid and 10 ml of the sulphuric acid–lithium sulphate solution until fumes are evolved. Heat strongly, and add 0·5 ml of perchloric acid to ensure complete dissolution. Allow the reaction to subside, and then cool. Dilute, boil, and cool to room temperature.

Dilute to 200–300 ml with cold distilled water, and add approximately 0·5 ml of thioacetanilide solution per mg of rhodium present, followed by 2–5 ml of chromous chloride solution. During this addition stir the solution, and take care to avoid atmospheric oxidation of the chromous chloride. Set aside for 2–3 hr, stirring the solution occasionally. Filter the solution through an 11-cm Whatman No. 44 filter paper, wash the rhodium precipitate thoroughly with dilute hydrochloric acid (1 + 99), and ignite gently. Heat in a stream of hydrogen, cool, treat with hydrofluoric acid in a platinum dish, and evaporate to dryness. Moisten the residue with dilute hydrochloric acid (1 + 99), filter through a 9-cm Whatman No. 44 filter paper, wash with hot water, ignite and reduce as above. Heat to 650–700°C in a current of chlorine, cool, treat with dilute *aqua regia* (1 + 4), and filter through a 9-cm Whatman No. 44 filter paper. Ignite the rhodium precipitate, reduce to metal as above and weigh.

Add to the filtrate containing the iridium 25 ml each of concentrated nitric and sulphuric acids. Heat on a hot plate to 250°C (indicated by a 360°C thermometer in the solution), and, without delay, oxidize by adding a few drops of concentrated nitric acid followed by perchloric acid. When the reaction has subsided, add 2–4 g of thiourea, and remove from the hot plate when the iridium sulphide has flocculated (after a few sec). Cool, dilute to 250 ml, and filter the precipitate onto an 11-cm Whatman No. 41 filter paper. If no iridium sulphide can be seen, dilute the filtrate, boil (Note 1), and then filter. Wash the precipitate thoroughly with hot water, then carefully ignite the residue. Treat with hydrochloric acid and boil. Filter the resulting suspension through a 9-cm Whatman No. 44 filter paper, ignite the precipitate, reduce to metal using hydrogen, and weigh.

If the amount of iridium sulphide is extremely small, return the precipitate obtained from the thiourea treatment to the beaker, and decompose it with 20 ml of concentrated nitric acid and 2–3 ml of the sulphuric acid–lithium sulphate solution. Evaporate to fumes, and oxidize any remaining carbon with nitric acid followed by perchloric acid. Dilute and filter the solution. Evaporate the filtrate, and, after oxidation, determine the iridium by titration with a hydroquinone solution using the 3,3′-dichlorobenzidine solution as indicator (Procedure 120).

Note—Boiling the filtrate causes sulphur to precipitate, which carries down small amounts of iridium sulphide.

THE DETERMINATION OF IRIDIUM IN REFINED RHODIUM SPONGE

Procedure 10[123]

Fuse 100 mg of the sponge with 10 g of zinc and a small amount of ammonium chloride in a covered porcelain crucible. Remove the zinc by dissolution in dilute sulphuric acid (1 + 9), and filter the suspension. Destroy the filter paper with nitric acid, then dissolve the residual, finely divided rhodium in 10–15 ml of the sulphuric acid-lithium sulphate solution, and heat to fumes.

Dilute, cool, then precipitate the rhodium using thioacetanilide as described in Procedure 9. Add a little filter paper pulp, set aside for 2–3 hr, stirring occasionally during this period. Filter the suspension through a pad of filter paper pulp, wash the residue, and determine the iridium in the filtrate titrimetrically (Procedure 120) after a separation using thiourea as described in Procedure 9.

THE SEPARATION OF RHODIUM FROM IRIDIUM BY PRECIPITATION WITH ANTIMONY

For separating small amounts of rhodium from iridium, Westland and Beamish[124, 53] reduced rhodium by boiling a sulphuric acid solution of that metal with antimony dust. The antimony in the iridium-containing filtrate can be removed by distillation as the trichloride; with large amounts of iridium, however, the antimony gives little or no interference. The method has not been applied to more than 200 μg of rhodium.

Serious losses of rhodium may occur if the antimony is not thoroughly mixed by vigorous boiling. These losses can be minimized by keeping the volume as low as is convenient. Antimony of a fine grain size should be used, the mixture then becoming opaque when the suspension is boiled.

Procedure 11[124]

Evaporate the sulphuric or hydrochloric acid solution of rhodium and iridium to 0·5 ml, keeping the temperature below 200°C. Dilute to 8 ml with water, add 75 mg of antimony dust, and boil vigorously for 30 min, adding water to maintain a constant volume. Filter through a 4·25-cm Whatman No. 42 filter paper, and wash the residue with 5 ml of water.

Return the paper and residue to the original beaker, and place it in a muffle furnace at 400–450°C for 10 hr. Cool, break up the ash with a glass rod, and add, in this order, 0·5 ml of concentrated sulphuric acid, 1 ml of a 30 per cent hydrogen peroxide solution and 2 ml of concentrated hydrochloric acid. Cover with a glass, and evaporate to 1 ml.

Spectrophotometric determinations may be made using tin(II) chloride (Procedure 158) or 2-mercapto-4, 5-dimethylthiazole (Procedure 161). If the former is used, add 1 ml of hydrochloric acid, and dilute to 5 ml (Note 1). Prepare the standard curve with samples containing the same amount of antimony as was used for the rhodium separation. If 2-mercapto-4, 5-dimethylthiazole is used, first acidify the sample with 10 ml of hydrochloric acid, then treat it in the usual way (Procedure 161), except to add twice the recommended quantity of reagent and to boil the solution for 2 hr. With either reagent for rhodium, good sensitivity can be obtained by diluting to only 50 ml, and measuring the absorbance of a solution 5-cm thick.

To the iridium–antimony filtrate, in a flask fitted with a dropping-tube and a thermometer well, add 10 ml of concentrated sulphuric acid and 0·5 g of hydrazine sulphate. Pass a current of nitrogen through the flask, and simultaneously heat the contents until fuming. While the temperature is maintained at 160–200°C (Note 2), add dropwise 75 ml of concentrated hydrochloric acid, allowing the antimony chloride to escape. Fume the solution to about 2 ml, at which point a brown colouration, not due to iridium, may be observed (Note 3). Dilute to about 50 ml, and add 50 mg of nickel chloride and 5 ml of a 10 per cent sodium bromate solution. Add a sodium hydroxide solution to approach neutralization, and finally adjust to pH 6·7–7·5 using a dilute sodium hydrogen carbonate solution and dilute hydrochloric acid, the nickel hydroxide turning black in this pH range. Boil the mixture for 30 min, and filter through a porous-bottomed 5-ml crucible. Wash with a few ml of a 1 per cent ammonium chloride solution, and return the crucible to the original beaker.

Dissolve the precipitate in 8 ml of *aqua regia*, and then evaporate to 2 ml. Add 2 ml of concentrated hydrochloric acid, and again evaporate slowly to 2 ml. Transfer the solution to another beaker, and leach any residue in the crucible, on the steam bath, with 5 ml of slightly acidified water. Then add this leach liquid to the main bulk of the solution, and similarly leach the crucible a second time. Dilute the total solution to 100 ml, and pass it through a 10-cm bed of Dowex 50-X cation-exchanger at about 2 ml per min. Wash the column with 50 ml of water, and add 10 ml of concentrated hydrochloric acid and 2 ml of a 2 per cent sodium chloride solution to the effluent. Evaporate this to dryness, and treat the residue with *aqua regia* and hydrochloric acid as described above. Then determine the iridium spectrophotometrically according to Procedure 163.

Notes—1. The dense precipitate of antimony oxychloride re-dissolves on heating.
2. Temperatures in excess of 200°C are to be avoided because low recoveries may result.
3. This colouration causes no difficulties when the iridium is subsequently precipitated.

THE SEPARATION OF RHODIUM FROM IRIDIUM USING METAL SALTS

The first acceptable analytical separation of rhodium from iridium was recorded by Gilchrist.[119] He converted the metals to their sulphates, and then selectively reduced rhodium by using titanium(III) chloride. Two precipitations provide a quantitative separation from iridium. The most serious criticism of the method is that it is necessary to remove excess of titanium from the filtrate before determining the iridium. This is done by precipitating the titanium with cupferron. The precipitate, being bulky, encourages adsorption of iridium. Re-precipitation is difficult and time-consuming, although with care very acceptable results can be obtained if the amounts of iridium are about 100 mg or more.

Better methods, however, are available for the separation of very small amounts of iridium and rhodium. A procedure for the separation of rhodium from iridium using titanium(III) chloride is included in an analytical scheme for the determination of noble metals in decorative alloys (see Procedure 29).

Pollard[35] recorded a separation of very small amounts of rhodium and iridium which involved the reduction of rhodium by titanium(III) chloride in the presence of 2-mercaptobenzothiazole, giving a reddish-brown insoluble complex of rhodium. The filtrate was treated with thiourea to give iridium sulphide. This was filtered, converted to sulphate by various acid treatments, and then titrated with hydroquinone as described in Procedure 120. The method requires the prior formation of the sulphate solutions.

No procedure is included for the determination of rhodium. Also the tendency to low results indicates adsorption of iridium by the rhodium complex or reduction to iridium metal by the titanium(III) salt. The substitution of a molybdenum salt reduction offers few advantages.

Chromous chloride has been used as a separatory reagent, and whereas the recorded methods[125] for this reduction are not acceptable where high accuracy is required, this reagent is potentially useful because the subsequent separation of chromium from iridium should be comparatively simple.

Modifications of early methods are recorded from time to time; in one of these[118] rhodium is precipitated by sodium sulphide, ignited, reduced to the metal, and weighed. Iridium in the filtrate is oxidized to the quadrivalent state, and may be precipitated as the hydrated dioxide. None of these methods is recommended for small amounts of rhodium and iridium.

ION-EXCHANGE METHODS OF SEPARATING RHODIUM FROM IRIDIUM

Many ion-exchange methods have been proposed for the separation of rhodium from iridium. Whereas most of these are useful under specific circumstances, only a few have been developed to a generally useful degree. In some instances these methods involve separations of platinum from palladium as well as of rhodium from iridium, and in other instances separations of a variety of combinations of metals. The procedures recorded below for the separation of rhodium from iridium have in some instances been extracted from the more widely applicable methods.

Various anion-exchange methods for the separation of rhodium from iridium were proposed by McBryde and co-workers. Cluett, Berman and McBryde[126] used the anion-exchanger IRA-400 to adsorb the rhodium(III) and iridium(IV) chlorides; the latter valence is maintained by the addition of bromine water to the 0·1 M hydrochloric acid and 2 per cent sodium chloride solution of the metals. Rhodium is eluted by the latter solution, iridium then being eluted by a 5 M ammonium hydroxide–1 M ammonium chloride solution, then with either 6 M hydrochloric acid or 8 M nitric acid. The method proved acceptable for weights of the order of 10 mg, but was objectionable because the determination of iridium required the prior removal of much of the large amount of salts and acid used for its elution. Also, losses of iridium in the feed solution indicated that attempts to use the procedure for smaller quantities of the metal would lead to appreciable quantities of iridium remaining with the rhodium. Furthermore, the author's early use of bromine was rejected because for small amounts of the metals any procedure which would recover rhodium quantitatively resulted in a loss of about 1 per cent of the iridium present: and because the loss was more or less an absolute one, it thus became significant when μg amounts of metals were to be separated.

An interesting exchange method for the separation of rhodium from iridium was proposed by MacNevin and McKay,[127] who precipitated rhodium by using sodium hydroxide, and dissolved the hydrated oxide as a species which was largely cationic. Berman and McBryde[128] applied this method by precipitating with 7 M ammonia solution, and subsequently dissolving in 2 M hydrochloric acid. The dissolved rhodium constituent was only partially retained on a cationic resin. Separations of rhodium from iridium, however, were accomplished by treating the mixed solutions containing 500 μg of each metal with ammonia, followed by dissolution in hydrochloric acid, and finally feeding into a column of the anion-exchanger Amberlite IRA-400. The feed and water-wash effluents contained the rhodium: the 50 ml of 6 M hydrochloric acid eluant contained the iridium. Inexplicably, however, this quantitative separation failed when applied to freshly prepared rhodium and iridium solutions. Complete recovery of the rhodium from the iridium extract required the repeated passage of the iridium fraction through the exchanger after the evaporations of the iridium extract. This method is worthy of further examination.

Berman and McBryde[128] preferred their later method (described below) which involves the use of Amberlite IRA-400, freshly converted to the chloride form, and which can be applied to μg amounts. The samples, in hydrochloric acid containing sodium chloride, are passed through the resin, which has been previously treated with cerium(IV) solution to counteract its reducing effect. The rhodium(III) is eluted with 2 M hydrochloric acid; the iridium(IV) is subsequently obtained by soxhlet extraction of the resin with 6 M hydrochloric acid, which process can be accomplished in about 1·5 hr.

An Anion-exchange Method for Separating Rhodium from Iridium

Procedure 12[128]

Equipment. A conventional column, 5 mm internal diam. and 12 cm long, adequate for a flow rate of 50 ml per hr.

Amberlite IRA-400, analytical grade, ion-exchange resin. Convert to the chloride form by stirring the resin for several hr with a large excess of 3–4 M hydrochloric acid. Then soxhlet extract the resin for 1–2 hr with 6 M hydrochloric acid, to avoid the colour throwing of a fresh solution, and to extract contaminating ions. This extraction is important if good accuracy and precision is desired. Whereas the resin can be used without grinding, as originally recommended, a column 3 cm deep is preferable to that of 2·5 cm recommended. Store the resin in 2 M hydrochloric acid.

A microextractor, Corning No. 3860.

Make a thimble by blowing a small hole in the bottom of a soft-glass test tube, cutting the tube to the appropriate length, and pulling some glass wool through the hole so that liquids will pass through but not resin particles.

Procedure. Evaporate to dryness the hydrochloric acid solution of rhodium and iridium, containing 6 mg of sodium chloride. Dissolve the residue in 2 ml of 0·8 M hydrochloric acid, and add this solution by means of a dropper to a 3-cm bed of resin which has been previously washed with 10 ml of water followed by 10 ml of a solution containing 1 ml of 0·1 M cerium(IV) sulphate per 100 ml of 0·8 M hydrochloric acid (Note 1). Rinse the beaker with 2 ml of 0·8 M hydrochloric acid, and transfer to the column. Elute with 90 ml of the above cerium solution. Evaporate the effluent to a few ml, and determine the rhodium using tin(II) chloride in 2 M hydrochloric acid, measuring the absorbance at 479 $m\mu$ (Procedure 158). To eliminate the slight interference from cerium, use blanks which have been carried through the complete process.

Wash the column with 0·8 M hydrochloric acid to complete the removal of cerium ions. Remove the upright part of the column, and allow the bed to drain. Invert the column, and, using a stirring rod, shove out the resin bed, along with the glass wool supporting pad, into a specially prepared glass thimble. Place the thimble in a small extractor, add 15 ml of 6 M hydrochloric acid to the pot, and extract for 1 hr. Transfer the pot liquid to a 30-ml beaker, evaporate almost to dryness, and determine the iridium spectrophotometrically, using the tin(II) chloride–hydrobromic acid method (Procedure 163) (Note 2).

Notes—1. Failure to wash with water may result in low iridium results.

2. Under normal conditions the iridium solution should contain no organic matter. When this is present, it may be destroyed in the usual way with nitric acid and a 30 per cent hydrogen peroxide solution followed by evaporation in the presence of hydrochloric acid. Six evaporations of this type will ensure the absence of such interfering substances.

A Cation-exchange Method for the Separation of Rhodium from Iridium[129]

Dowex 50-W-X8 was used by Berg and Senn[129] to retain rhodium selectively in the presence of iridium. The method involves the formation of the iridium(IV)–thiourea anionic complex and the corresponding rhodium(III)–thiourea cationic species. After the passage of the iridium-containing anion, the rhodium-containing cation is eluted with 6 M hydrochloric acid at 74°C. The method has been used for mg amounts of the two metals. The supporting data concerns solutions containing 3 mg of rhodium and 6 mg of iridium.

Procedure 13[129]

Treatment of the resin. Wash the cation-exchange resin, Dowex 50-W-X8, in successive operations as a batch process, with water, 3 M hydrochloric acid, and finally with more water. Then slurry the resin and pack it in a column so that the bed is 17·5 cm by 1·4 cm diam. Wash the column with 3 M hydrochloric acid, and wash out the excess of acid with water. The above treatment serves to remove iron and other contaminants, and leaves the resin in the hydrogen form. The treatment is unnecessary after the initial separation, which involves a treatment with 6 M hydrochloric acid.

Procedure. Evaporate the rhodium–iridium solution to a few ml, and add a few ml of *aqua regia*. Fume to a moist residue on a steam bath, re-dissolve in 0·3 M hydrochloric acid, and return to the steam bath. Add sufficient thiourea, and continue heating for 1 hr with adequate additions of 0·3 M hydrochloric acid to keep the volume constant, the extended heating period being required to ensure the complete formation of the rhodium–thiourea complex. Cool the sample, and transfer the solution to the ion-exchange column at 2–3 ml per min, the rhodium(III)–thiourea complex appearing at the top of the column as a sharp reddish-orange zone. Collect the first colourless fractions of the effluent, which contain the iridium(IV)–thiourea complex. Wash the column with 100 ml of 3 M hydrochloric acid at room temperature to ensure the complete removal of the iridium complex.

With the column maintained at 74°C, elute the rhodium complex with 6 M hydrochloric acid.

Add 5 ml of *aqua regia* to both the rhodium and the iridium solutions, boil for 15 min, and fume to a moist residue. Repeat these treatments until the destruction of the thiourea complexes is complete. To both solutions then add 12 M hydrochloric acid, and fume to dryness. Dissolve the resulting metal chloride in 1 M hydrochloric acid. Determine the rhodium gravimetrically using thiobarbituric acid (Procedure 82) or spectrophotometrically using tin(II) chloride (Procedure 158). Determine the iridium gravimetrically using 2-mercaptobenzothiazole (Procedures 89, 90) or spectrophotometrically using tin chloride in hydrobromic acid (Procedure 163).

THE SOLVENT EXTRACTION SEPARATION OF RHODIUM AND IRIDIUM

While a variety of casual references have been made to the use of liquid-liquid extractions for rhodium and iridium, only two have approached the status of analytical separations.

The Tin(II) Bromide–Isoamyl Alcohol Method

This method for the separation of rhodium from iridium requires isoamyl alcohol as a solvent for rhodium complexed with tin(II) bromide in a perchloric–hydrobromic acid medium at room temperature. Microgram quantities, 10–100 μg of rhodium and 7·5–73·8 μg of iridium, can be separated and subsequently determined. Rhodium and iridium are determined spectrophotometrically directly in the organic and in the aqueous phase respectively. Accurate and precise values can be obtained, and in the present author's opinion, the method is superior to all hitherto published methods from the point of view of time required and simplicity of operation.

Procedure 14[130]

Reagents

Tin(II) bromide–hydrobromic acid. Dissolve 3 g of mossy tin in A.R. 48 per cent hydrobromic acid, and evaporate the solution to dryness. Cool the residue, and dissolve it in 17·0 ml of redistilled hydrobromic acid. Dilute with water, filter into a 50-ml volumetric flask, and make up to volume with water. This solution should be freshly prepared each week.

Perchloric acid. Dilute 19·5 ml of 70 per cent ($d = 1{\cdot}66$) perchloric acid to 50·0 ml with water.

Procedure. Transfer to a 30-ml beaker the solution of rhodium and iridium chloride salts, containing no more than 100 μg of each metal. Evaporate to dryness on a steam bath in the presence of 2 ml of a 2 per cent sodium chloride solution. Add 4–5 drops of redistilled hydrobromic acid, allow to stand to effect dissolution, and then transfer the solution to a 75-ml pear-shaped separatory funnel with 5 ml of water. Wash the beaker with 5 ml of the tin(II) bromide–hydrobromic acid solution, and then with 5 ml of the perchloric acid (Note 1). Allow to stand for 30 min, with frequent shaking, to produce the yellow rhodium complex. Add 25 ml of isoamyl alcohol, and shake for 2·5 min, thus leaving the iridium in the colourless, aqueous phase. Drain this aqueous layer into a 25-ml volumetric flask. Then add 3·3 ml of the tin(II) bromide–hydrobromic acid solution to the separatory funnel, shake, and drain into the 25-ml volumetric flask (Note 2).

Drain the organic phase into a 50-ml volumetric flask, and wash the separatory funnel 3 times with isoamyl alcohol. Add the washings to the 50-ml flask. Add isoamyl alcohol to the mark, and determine the rhodium immediately by measuring the absorbance of the solution at 429 mμ in matched 1-cm silica cells (see also Procedure 159).

To the iridium-containing aqueous phase in the 25-ml volumetric flask add 3·3 ml of perchloric acid, shake thoroughly, and place the flask in a boiling water bath for 3 min. Remove, cool the flask in air for 5 min, and then under the tap, and make up to the mark with water. Determine the iridium spectrophotometrically by measuring the absorbance of the solution at 403 mμ in matched 1-cm silica cells (Procedure 163). Determine standards for rhodium and iridium simultaneously.

Notes—1. These washings, placed in the separatory funnel, should produce a 15 ml solution, 0·17 M in tin salt, 1·5 M in hydrobromic acid, and 1·5 M in perchloric acid.

2. This washing removes residual traces of iridium, cleans the organic phase, and washes the stem of the separatory funnel.

The Tetraphenyl–Phosphonium–Chloroform Extraction Method

In the absence of other platinum metals, iridium may be determined in the presence of rhodium by a chloroform extraction of the brown tetraphenyl phosphonium chloroiridate(IV). From 30 to 80 μg of iridium can be determined in the presence of 1–2 mg of rhodium.

Procedure 15[131]

Add 3 ml of a 2 per cent aqueous solution of tetraphenylphosphonium bromide to 15–20 ml of an iridium(IV) solution 0·1 M in hydrochloric acid. Add the same volume of chloroform and shake for 3 min. Separate, and filter the chloroform layer through a dry fluted filter paper. Measure the absorbance at 500 mμ or with appropriate filters. Prepare standards similarly. See page 418, for the details of the spectrophotometric method.

Other Solvent Extraction Methods

It has been stated that the ammonia-type compounds formed by chlororhodites and chloroiridites with pyridine can be extracted to provide for the separation of these two elements.[132] This method involves the prior separation of other platinum metals and a **variety of** base metals, then fuming to produce a perchloric acid solution of rhodium and iridium. The acidity is adjusted to 4 N, and pyridine is added followed by strong sodium hydroxide to separate the dark blue pyridine layer. The latter is washed three times with dilute hydrochloric acid, and intermittently separated with 6 N sodium hydroxide. The pyridine layer is then isolated, treated with a few drops of 6 N sodium hydroxide and the pyridine is evaporated. Hydrogen sulphide is passed into the residual basic solution, acidifying with hydrochloric acid during the process. The sulphides of rhodium and iridium are dissolved in *aqua regia* and the solution is fumed with sulphuric acid. Finally, the rhodium is separated using titanium(III) chloride, and iridium is determined after the removal of titanium by cupferron. This method is cumbersome and no data are available to ascertain its effectiveness. Anyway, any other of the above methods is preferred for general analytical practice.

The Separation of Gold, Platinum and Palladium

PRECIPITATION SEPARATIONS

Practically all of the conventional methods of separating and determining the seven noble metals involve the initial removal of osmium and ruthenium, followed by the consecutive isolation of gold, palladium and platinum, or, as in the hydrolytic separation, the removal of osmium and ruthenium by distillation, followed by the isolation of platinum from solutions containing palladium, rhodium and iridium, in which scheme gold may be isolated along with base metal impurities by the prior hydrolytic precipitation in the presence of nitrite. The applications of both approaches to such complex materials as native alloys and natural alloys obtained by fire assay techniques will be discussed in the second section of this chapter. In the older schemes, platinum was almost always separated by precipitation with ammonium chloride; for the separation of large quantities, or in instances where the highest accuracy is not required, this method is undoubtedly effective. In a few instances, palladium and platinum have been removed simultaneously as the hexachloride,[133] but this procedure is not recommended for quantitative determinations.

Maynard[134] used tetraethylammonium chloride to precipitate gold in the presence of small amounts of platinum and palladium.

Pshenitsyn and co-workers have recorded various procedures for the separation of platinum and palladium. When dealing with copper–nickel slimes Pshenitsyn and Yakovleva[135] used calomel at 90–95°C. A second procedure[136] required reduction by acetylene following a period of boiling with tartaric acid. Repeated treatments with acetylene were necessary. Neither of these two methods is recommended for analytical application.

One of the earliest applications of the hydrolytic separation of platinum from the remaining platinum metals was described in 1835 by Dobereiner[137] who used lime water to isolate platinum in an analytical scheme involving osmium, rhodium, iridium, palladium and copper. Moser and Hackhoffer[138] used hydrolytic methods for the separation of platinum from iridium. The method involved hydrolysis from a nearly neutral solution to which is added successively sodium bromate and sodium bromide. Gilchrist recorded procedures some fifteen years earlier[139, 140] for the analysis of alloys, minerals and solutions in which the platinum metals were the major constituent. After the removal of osmium and ruthenium, the four remaining platinum metals, oxidized to their highest valence state, were hydrolysed by sodium hydrogen carbonate (to pH 6–8), resulting in the selective precipitation of palladium, rhodium and iridium.[140] Ryan[141] used the hydrolytic separation of platinum to remove as little as 5 μg of platinum from solutions of palladium, rhodium and iridium.

The separational characteristics of precipitants for gold, palladium and platinum are discussed immediately below. The gravimetric procedures for these precipitants are included in Chapter 3.

PRECIPITANTS FOR THE SEPARATION OF GOLD

Hydroquinone

Hydroquinone is an effective separating precipitant for quantities of gold of the order of 1–50 mg. With larger samples the accumulation of the organic reaction products in the filtrate becomes inconvenient when residual metals are to be determined. For solutions containing up to 50 mg of gold and 2 mg or more of palladium, the gold–hydroquinone filtrate may be treated directly for palladium by the addition of dimethylglyoxime. Strangely, for less than 2 mg of palladium, the precipitation may be incomplete. Table 7 illustrates the deleterious effect of the hydroquinone reaction product on the subsequent precipitation of traces of palladium.

Concerning the effect of hydroquinone on 1·2 M solutions of hydrochloric acid containing rhodium, iridium, osmium and ruthenium, it has been found that precipitation does not occur on standing for at least several days. With platinum solutions at pH 6, there is also no evidence of precipitation.

X

However, with palladium solutions which have been adjusted to pH 6, and to which just sufficient hydrochloric acid has been added to dissolve the brown hydrated oxide, a grey precipitate will appear after the addition of hydro-quinone, and subsequently boiling. Presumably this precipitation is complete.

As indicated below, hydroquinone selectively precipitates gold from acid solutions also containing copper, nickel and zinc, and it is therefore useful for the determination of gold in alloys containing these base metals.

The determination of platinum in the gold–hydroquinone filtrate may present some difficulties. The reduction products of the hydroquinone reaction interfere to the degree that even precipitation by sodium formate or hydrogen sulphide is incomplete. As indicated below, the filtrate may require evaporation and then some method of removing organic matter. However, while no data are available to indicate the efficiency of the direct ignition of the evaporated residue obtained from the prior separation of gold using hydroquinone and then palladium using dimethylglyoxime, one may expect some loss of platinum because its complex with dimethylglyoxime may ignite with explosive violence. In the presence of this complex it is advisable to use a wet oxidation prior to ignition. An alternative and perhaps preferable method for the determination of platinum after the initial removal of palladium, and gold as above, allows the precipitation of platinum by zinc without the necessity of removing organic matter (see Procedures 35 and 103).

TABLE 7. THE DETERMINATION OF PALLADIUM IN THE HYDROQUINONE SOLUTION FROM THE GOLD PRECIPITATION[142]

No.	Palladium added* (mg)	Loss of palladium (mg)	Precipitate formation
1	0·2	0·2	None
2	0·4	0·3	
3	0·6	0·6	
4	0·8	0·6	
5	1·0	0·3	After considerable stirring
6	1·5	0·1	
7	3·0	0·05	Immediate
8	10·0	0·0	
9	35·0	0·0	
10	75·0	0·0	
11	150·0	0·0	

* 25 mg of gold added in each instance.

Sulphur Dioxide

The isolation of gold by using sulphur dioxide is one of the most effective separatory methods, because the precipitation need not involve the presence of a salt. In the presence of palladium and platinum, however, these metals contaminate the precipitated gold. In this respect hydroquinone is the preferred reagent. As might be expected, this contamination occurs both with sulphur dioxide and sodium sulphite. Table 8 indicates the error which can be expected.

However, in those instances noted above when traces of palladium are present with large amounts of gold, the hydroquinone precipitant for the latter is not acceptable, sulphur dioxide being recommended. There is less interference in such a situation with the dimethylglyoxime precipitate from sulphur dioxide solutions than from hydroquinone treatments. It is common practice to treat the filtrate from gold–sulphur dioxide precipitations with a few drops of nitric acid, after having boiled the solution vigorously, to aid in the removal of sulphites. In so far as palladium is concerned, the addition of nitric acid to the sulphur dioxide filtrate does not make the precipitation of the dimethylglyoxime more complete. In accurate analyses, the filtrate should be evaporated to remove sulphites.

TABLE 8. THE OCCLUSION OF PLATINUM AND PALLADIUM DURING THE PRECIPITATION OF GOLD[295]

Reagent	Added			Gold	
	Gold (mg)	Platinum (mg)	Palladium (mg)	Recovered (mg)	Error (%)
Sulphur dioxide	33·79	—	—	33·78	−0·03
	33·79	25·75	—	34·15	+1·07
	33·79	—	25·00	33·81	+0·06
	33·79	—	50·00	33·86	+0·21
Hydroquinone	33·79	—	—	33·81	+0·06
	33·79	50·00	—	33·80	+0·03
	32·19	23·41	22·95	32·30	+0·34
	36·07	23·27	21·04	36·09	+0·06
	33·57	22·93	24·48	33·55	−0·06
	33·79	—	50·00	33·78	−0·03
	168·97	25·75	—	168·73	−0·15

Oxalic Acid

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In some respects reduction by oxalic acid ought to be the most suitable method for the precipitation of gold in the presence of other noble metals. However, the sensitivity of the reduction to the presence of nitroso compounds, and the resistance to complete reduction by oxalic acid of very small amounts of gold salts previously treated with *aqua regia* and sodium chloride are deterrents to its application. The gold precipitated by oxalic acid is finely divided, which makes quantitative filtration difficult and uncertain. Re-precipitation is also necessary because of the persistent tendency of palladium to co-precipitate.

It is sometimes an acceptable practice to use oxalic acid as a precipitant following an initial isolation of gold by using sulphur dioxide. In this application, the gold is redissolved in *aqua regia*, treated carefully with hydrochloric acid to remove the nitric acid, and the residue is then dissolved in hydrochloric and sulphuric acids. An oxalic acid solution is finally added to precipitate the gold.

Tetraethylammonium Chloride

This was recommended by Maynard[134] as a substitute for oxalic acid for use following the initial sulphur dioxide precipitation. The small amounts of platinum and palladium accompanying the latter precipitation do not interfere. Presumably the method requires less time for the determination of gold in dental alloys, but the precipitate is impure, and its ignition to gold requires a special treatment with sucrose in a sodium hydroxide solution.

Sodium Nitrite

Reduction by sodium nitrite has also been recommended for the precipitation of gold previously isolated by using sulphur dioxide. This method is particularly suitable for a gold solution containing other noble metals, and modifications of the method have been recorded for the determination of gold in the presence of copper, nickel, etc., as well as in the presence of platinum metals. The efficiency of the method is associated with the ease of formation of the nitrite complexes of the platinum metals, which resist the formation of hydrated oxides even at boiling temperatures.

When base metals are present, they precipitate with gold in the basic medium, and are removed by selective dissolution with mineral acids. The subsequent determination of platinum metals in the nitrite–gold filtrate requires the prior removal of nitrite.

This may be accomplished by boiling with hydrogen peroxide,[143] which simultaneously ensures the oxidation of platinum to the quadrivalent state, in which condition the co-precipitation of platinum dimethylglyoximate with the corresponding palladium complex is avoided.

Ferrous Salts and Other Precipitants

Whereas ferrous sulphate is a very acceptable reductant for gold, the presence of iron in the filtrate may be an unnecessary inconvenience, for many alternative separatory reagents are available. Of these, however, none has proved to offer advantages over those cited above when subsequent determinations of platinum metals or base metals are required.

THE SEPARATION OF PALLADIUM BY PRECIPITATION

The effects of acceptable reductants for gold on the subsequent determination of palladium and platinum have been discussed above.

A variety of oximes may be used for the separation of palladium from platinum. In most instances the reports of new applicable oximes contain little or no data concerning the efficiency of the platinum recovery from the palladium filtrate. With many of these oximes, also, one may expect a reaction with platinum comparable to that occurring between that metal and dimethylglyoxime. When using the latter, platinum may interfere with the separation of palladium.

Dimethylglyoxime forms a complex with platinum(II). The crystals appear either bronze or blue, apparently depending upon the conditions under which they are produced. Under the microscope, they are prismatic and distinctly pleochroic. In reflected light the crystals are yellow to bronze when the vibration of the light is perpendicular to the long axis of the crystals, and dark blue to bluish purple when the vibration is parallel to the long axis. Its extinction is parallel. These anisotropic crystals, of composition $C_8H_{14}N_4O_4Pt$, may be admixed with the yellow, palladium dimethylglyoximate, giving a flocculent, green precipitate when the contamination is excessive. This admixture almost always occurs when there has been a prior fuming with sulphuric acid. In general a single precipitation of palladium dimethylglyoximate carried out in the presence of platinum is found to be contaminated with platinum. If there has been a prior treatment with *aqua regia* this contamination may be slight, and due perhaps largely to occlusion or adsorption by the flocculent yellow palladium complex. Anyway, for an accurate determination, a re-precipitation is advisable, and this is most certainly necessary if there is any green tint in the palladium precipitate. It should be stressed again that a mere dissolution of palladium dimethylglyoximate in *aqua regia* is seldom effective. The complex should be treated to remove organic matter completely.

When palladium is to be separated from gold it is generally advisable to remove the gold initially as indicated above. However, whereas dimethylglyoxime will precipitate an unstable complex with gold, this reagent has been used for the prior removal of palladium from gold which is then subsequently precipitated by hydroquinone. The method (Procedure 35) requires a precipitation from a chilled solution by the addition of sodium dimethylglyoximate. The contamination by gold is insignificant, and there is no platinum contamination.

The Separation of Platinum by Precipitation

As stated above, the determination of platinum usually follows the separation of gold and palladium. One or both of the latter may be removed by organic reagents, in which instance the precipitation of platinum may require the prior destruction of organic matter. If oximes have been used it is advisable to evaporate the filtrate at low temperatures, followed by the addition of a wet oxidant such as nitric or sulphuric acid, followed by evaporation to dryness, and then ignition within the beaker to produce an ash. Subsequently, dissolution is accomplished with *aqua regia*, and evaporation with hydrochloric acid.

In general such precipitants as hydroquinone and the oximes provide a filtrate containing platinum with organic products which do not interfere with a direct precipitation using zinc. The application of zinc as the reductant, however, requires careful attention to the amount of excess, the method of addition, the acidity of the solution, etc. For maximum accuracy with small amounts of platinum, re-dissolution and re-precipitation are advisable. It may be repeated that despite the relatively long analytical history of platinum there is still a scarcity of good platinum precipitants. The most effective are hydrogen sulphide, which tends to produce high results, formic acid, which suffers from poor precision with small amounts of metal, thiophenol, which is unstable and has an offensive odour, and zinc, which requires a perfected technique.

The details of precipitational procedures for the separation of gold, palladium and platinum from one another, and from other metals are included in the comprehensive methods for complex materials discussed in Section II of this chapter. In principle, one method (Procedure 34) involves the precipitation of gold by hydroquinone, then the precipitation of palladium by dimethylglyoxime, the removal of organic matter by wet and/or dry methods, and subsequently the precipitation of platinum by a suitable gravimetric reagent.

A second method (Procedure 35) involves the initial removal of palladium using dimethylglyoxime, then of gold, using hydroquinone, and finally the precipitation of platinum by zinc without the prior removal of organic matter.

In a third method (Procedures 29 and 30),[143, 144] gold is first removed by using sodium nitrite, which complexes the palladium and platinum. After the destruction of the nitrite in the filtrate by evaporation with hydrochloric acid, the palladium is precipitated by dimethylglyoxime, and then the platinum by zinc or by hydrogen sulphide; the latter method requires the destruction of the organic matter in the palladium filtrate. Alternatively, when rhodium and iridium are present, the platinum may be isolated from those metals by its oxidation to platinum(IV), followed by hydrolysis to form the hydrated oxides of rhodium and iridium.

The relative efficiency of the separation of platinum, rhodium and iridium as directed by Gilchrist's hydrolytic method (Procedure 30) and Payne's absorptiometric method (Procedure 52) was discussed by Lloyd and Morris.[145] This examination was made with the aid of iridium-192 as a tracer. They found that in some instances the weights of the precipitates obtained through the formation of the hydrated oxides were 3 per cent higher than were expected from the weights of the elements taken. This error was reduced somewhat by leaching processes. Furthermore, the chromatographic method of separation devised by Rees-Evans *et al.* (Procedure 51), and modified by Payne (Procedure 52), proved to be simpler than the titanium method used by Gilchrist.[119]

In connection with researches which claim to compare the efficiency of hydrolytic methods with other methods, there exists the alternative viewpoint that what is really being examined is the ability of the analytical chemist to use the method with the maximum efficiency. The effective precipitation of the hydrated oxides, particularly with small samples, requires a good degree of analytical skill and experience.

The Separation of Gold, Palladium and Platinum by Solvent Extraction

The isolation of gold, platinum or palladium by extraction into selective, immiscible solvents is frequently recommended for the removal of a single metal. Few extractive procedures are available for the consecutive separation of the three metals when they are present together or associated with the remaining platinum or base metals. A considerable variety of these extractions have been used for restricted separations of metal complexes prior to the application of spectrophotometric methods for their determination.

Gold

The possibility of extracting gold from the platinum metals by using immiscible solvents was initially suggested by Mylius and co-workers.[146, 147] These authors showed the effects of acidity on the efficiency of some extractions, noting that a decrease in the efficiency of these extractions occurred at low acidities. Lenher[148] found that gold chloride could be completely separated by solvent extraction from the alkaline earths and many other base metal chlorides such as chromium, manganese, nickel, lead, etc. Ethyl acetate was considered to be the most efficient extractant. Lenher and Kao[149] used ethyl acetate to extract gold from 21 base metals in a 10 per cent hydrochloric acid solution. All of this early work involved 0·1–1·0 g of gold. Recently Ducret and Maurel[150] used a trichlorethylene extraction of the gold chloride–methyl violet complex. In the absence of platinum the optimum pH is 1, and in the presence of platinum 1 M hydrochloric acid is used. Nitrates interfere if their concentration exceeds 5×10^{-2} M in 1 M hydrochloric acid. The effects of other platinum metals and base metals are not known. The organic phase is used directly for spectrophotometric determinations.

The most effective solvent extraction is that of bromauric acid rather than of chlorauric acid. The hydrobromic acid concentration in the aqueous phase should be 2·5–3 N. At this acid concentration the efficiency of extraction is practically independent of the gold concentration. Isopropyl ether is the recommended extractant, and with equal volumes of the ether and aqueous phase, a single extraction removes 98–100 per cent of the gold from solutions containing 0·1 mg in 10 ml of solution.

There is very little interference from the platinum metals except from osmium. The latter, of course, need not be present because its removal as the tetroxide is usually relatively simple. The co-extraction of iron is an objectionable feature of this procedure, and this contamination increases with the hydrobromic acid concentration. In the presence of iron it is advisable to operate at hydrobromic acid concentrations of 2·0–2·5 N. Because small traces of iron result in a relatively intense colouration of the gold extract, a few drops of phosphoric acid are added to the aqueous solution used to extract the gold from its isopropyl ether solution. This final aqueous extraction is made to facilitate the spectrophotometric measurements of the bromoaurate ion.

Continued experience with this method of extraction and the subsequent spectrophotometric measurement has revealed considerable difficulty in the application of the determination to the aqueous extracts from the isopropyl ether phase. The unacceptable precision and accuracy seem to arise from unknown impurities in the isopropyl ether. No degree of purification from reducing constituents has eliminated the errors. The large decrease in the colour intensity of the final aqueous phase is not an indication of incomplete recovery of gold because an evaporation of the aqueous extract and a subsequent gold determination reveals the complete recovery of the gold. The data accumulated have proved that the extraction is effectively complete. Because of this difficulty, the procedure proposed by McBryde and Yoe[151] has been modified to permit the complete removal of the solvent prior to a determination. By this method the extraction to separate gold from platinum, palladium, rhodium, iridium and copper is quantitative and complete. The modification (Procedure 16) involves the evaporation of either the ether phase or the final aqueous extract. In general it seems advisable to eliminate the final aqueous extraction. By either method the evaporated residue may contain iron, so phosphoric acid is added to complex the iron after the dissolution in *aqua regia* and removal of nitrate.

The Solvent Extraction of Gold Bromide by Isopropyl Ether

Procedure 16[151]

48 *per cent hydrobromic acid*, reagent grade, distilled to remove bromine.

Isopropyl ether. If it contains peroxides, it produces a yellow colour in both phases which obscures the boundary between the two phases. To eliminate interferences the ether is shaken with ferrous sulphate, and distilled over this salt. Isopropyl ether which contains reducing alcohols may sometimes be made satisfactory by treating it with sodium wire. There can be little doubt that the commercially available isopropyl ether contains a constituent which interferes with the spectrophotometric bromide method when applied to the aqueous extract as directed by McBryde and Yoe.[151] Despite the various methods of purification adopted by the present author, this interference has not been removed.

Procedure. Add 5 ml of concentrated hydrobromic acid to 10–12 ml of the gold solution containing a minimum amount of hydrochloric acid. Extract twice with 15 ml portions of isopropyl ether. Combine the extracts, and shake with 5 ml of 4 M hydrobromic acid. Discard this acid. Evaporate the isopropyl ether to dryness on a steam bath. Add a few ml of *aqua regia*, evaporate, then add 2 ml of a 2 per cent sodium chloride solution and a few drops of concentrated hydrochloric acid, and evaporate. Repeat the addition of hydrochloric acid and the evaporation in order to remove nitrate. Add 1 drop of hydrochloric acid and 10 ml of water. Transfer, with suitable washing, to a volumetric flask of an appropriate volume, add 5 ml of hydrobromic acid, and dilute to volume. For samples known to contain iron the solution should contain 5–10 drops of concentrated phosphoric acid. Measure the transmittance at 380 mμ.

The Solvent Extraction of Gold by Ethyl Acetate

Ether and ethyl acetate were used by Yoe and Overholser[152] to separate gold from palladium. The method was designed for the ultimate determination of palladium, although gold can be determined simultaneously. The separation can be made from proportions of 10,000 of gold to 1 of palladium. Ether appears to be the more suitable extractant, and gives the more accurate recovery of palladium. Ethyl acetate, however, effects a more complete removal of gold with a lesser number of extractions.

Procedure 17[152]

Add sufficient hydrochloric acid to the solution containing gold and palladium chlorides to give a final acid concentration of *ca.* 3 N. Transfer to a small separatory funnel, add 10 ml of ethyl acetate or ether, shake for a few sec, and drain off the acid layer. Shake the organic layer with a few ml of 3 M hydrochloric acid and combine the wash solution and the first acid extract. If necessary repeat the extraction with another 10 ml of ether or ethyl acetate. Evaporate the organic layer to dryness on a steam bath, dissolve in *aqua regia*, treat with hydrochloric acid as described above, and apply the appropriate analytical method for gold. Repeat this evaporation process for the determination of palladium.

Table 9 indicates the efficiency of the palladium recovery as indicated by the *p*-nitrosodiphenylamine method.

Other Applications

Various schemes of separation for application to complex materials include the use of immiscible solvents for the extraction of gold along with other constituents. To isolate gold along with thallium, Wada and Ishii[153] used an ether extraction from 1 M hydrobromic acid. An ether extraction for some 20 constituents, including gold, was used by Yosida.[154]

For the determination of traces of heavy metals in water, Abrahamczik[155] separated them initially by adsorption on permutite, and then used chloroform to extract the dithizone complexes of gold and other metals.

Palladium

The Solvent Extraction of Palladium Oximates

As would be expected, the high selectivity of dimethylglyoxime and other oximes for palladium has encouraged the use of these reagents for extractive purposes. Strangely, these extractions have not been systematically studied, and even the extraction constants for palladium dimethylglyoximate are not known.

Young[156] used a chloroform extraction of this oxime complex to isolate palladium from the sulphuric acid parting solutions of a silver–platinum–palladium–gold bead (Procedure 36).

TABLE 9. THE RECOVERY OF PALLADIUM BY SOLVENT EXTRACTION[152]

No. of extractions	Au added (mg)	Pd added (μg)	Pd found		Au/Pd
			Ethyl acetate (μg)	Ether (μg)	
One	1	5·0	4·5	5·0	200
One	5	10·0	10·0	11·0*	500
Two	10	20·0	19·0		500
One	5	5·0	5·0	6·0*	1000
Two	10	10·0	9·5	9·5	1000
Two	10	5·0	4·5	5·0	2000
Two	15	5·0	4·5	5·0	3000
Two	20	5·0	4·5		4000
Three	50	5·0	5·0	5·5	10000

* High results were due to the interference of gold.

Ayres and Tuffly,[157] however, failed to apply successfully the method used by Young, who dealt with small amounts of palladium. It was found that with 10–20 mg of palladium, the extraction by chloroform or amyl acetate of either palladium dimethylglyoximate or of palladium dithiooxamide resulted in the collection of most of the precipitate at the liquids' interface.

By using large amounts of chloroform, Fraser *et al.*[158] were able to extract completely up to 1 mg of palladium as the dimethylglyoximate from solutions containing as much as 15 g of lead. The chloroform was evaporated, and the organic matter was destroyed with nitric and sulphuric acids. Prior to the spectrophotometric determination as the iodide complex, the nitric acid was removed by fuming several times, with the intermittent addition of water. Three extractions with chloroform were usually sufficient for the complete removal of palladium. With more than 250 μg of palladium, a precipitate of palladium dimethylglyoximate appeared, but this did not hinder the extraction. This method of extraction is applicable to both lead buttons and silver beads obtained from fire assay collections.

There is no interference from platinum, nickel or copper, iron being the only associated metal to interfere. As little as 3 mg of iron prevents the extraction of 60 per cent of the palladium present. This interference is avoided by the addition of sodium ethylenediaminetetra-acetate, 0·5 g of this reagent being required to complex 50 mg of iron. The method, as applied to a lead button, is described in Procedure 40.

The palladium complex of phenyl-α-pyridyl ketoxime can be extracted by chloroform. This separates palladium from a wide variety of metals (see Procedure 177), including zinc, mercury(II), lead, manganese(II), iron(III), ruthenium(VI), rhodium(III), osmium(VI), iridium(III), platinum(IV) and silver. Interference from copper(II), iron(II), cobalt(II) and nickel(II) is eliminated by the addition of 0·1 M EDTA solution. Iron(III) and bismuth(III) cause some difficulty through the formation of hydrated oxides which collect at the interface of the two phases. Gold interferes, and must be removed.

Methylglyoxime[159] has also been used to form a palladium complex extractable by benzene or chloroform. The extraction is free of interference from platinum(IV). The interference of iridium can be eliminated by reduction with hydroxylammonium chloride. Whereas cobalt and nickel do not interfere when present separately, their presence with iridium produces low results.

Salicylaldoxime[159] may also be used to form a benzene extractable complex free of interference from platinum(IV), nickel and cobalt. Iridium(IV) interferes.

The Solvent Extraction of the Palladium–Nitrosonaphthol Complexes

The dimethylglyoxime extraction was rejected by Pantani and Piccard[160] in favour of the extraction of the palladium complex with 1-nitroso-2-naphthol. Acidities of 2 or 3 N were recommended.

Pollard[161] also preferred 1-nitroso-2-naphthol to dimethylglyoxime for complexing the palladium. The naphthol complex can be extracted into toluene to give an orange solution. The 2-nitroso-1-naphthol complex of palladium gives a violet toluene extract. These extracts are recommended for the spectrophotometric measurement of palladium.[162]

An extraction with isoamyl alcohol has been used with tin(II) bromide. The results were 5–7 per cent low.

The Solvent Extraction of the Palladium–Phenylthiourea Complex with Amyl Acetate

The extraction of the slightly soluble palladium–phenylthiourea complex from slightly acid solutions into ethyl or amyl acetate may be applied to

10 to more than 20 mg of palladium. When mineral acids other than hydrochloric acid are used to acidify the solution prior to the extraction, the amount of palladium recovered is considerably less, for example, 50 per cent less from sulphuric acid. The extracts cannot be used directly for spectrophotometric measurements, a prior evaporation being required.

Table 10 indicates the degree of interference which may be expected from associated metals.

TABLE 10. THE EFFECTS OF DIVERSE IONS ON EXTRACTIONS OF PHENYLTHIOUREA COMPLEXES INTO AMYL ACETATES[157]

Ion	% extracted (in absence of Pd)	Tolerance of 100 ppm of Pd (ppm)
Platinum(IV)	40	300
Iridium(IV)	< 1	150
Rhodium(III)	< 1	400
Ruthenium(III)	0	—*
Osmium(IV)	0	—*
Gold(III)	Trace	10
Iron(III)	< 1	500
Cobalt(II)	0	1000
Nickel(II)	0	4000
Copper(II)	16	2500
Chromium(VI)†	< 1	4000

* Lost as volatile tetroxide during acid evaporation, hence no interference.

† Chromium(VI) reduced by phenylthiourea, but then oxidized by nitric and perchloric acids.

Column 3 indicates the tolerance to a foreign ion of 100 ppm of palladium when they are present together and co-extracted when only one extractor into the organic phase is made.

Procedure 18[157]

Add to the palladium(II) solution in a separatory funnel 20 ml of an 0·5 per cent phenylthiourea solution (2·5 g in 25 ml of ethanol, and diluted to 500 ml with water). Then add 25 ml of a 20 per cent ammonium chloride solution, and dilute to 100 ml with 0·2 M hydrochloric acid. Add 25 ml of amyl acetate and shake vigorously. Remove the water layer, and wash the organic layer with 25 ml of the 20 per cent ammonium chloride solution (this reagent hastens the separation of the two phases). Evaporate the amyl acetate and bake the residue at 150°C. Slowly add 6 M nitric acid to this residue until the vigorous reaction ceases, then fume with a few ml of perchloric acid. Dilute to a known volume, and determine the palladium gravimetrically.

The Solvent Extraction of the Palladium p-Nitrosodimethylaniline Complex

The orange to red colour formed by the reaction of a large excess of *p*-nitrosodimethylaniline and a palladium salt may be quantitatively ex-extracted into chloroform. Because regular chloroform contains unknown interfering constituents the latter must be of purified (C.P.*) grade. The extraction can be applied successfully to solutions containing μg amounts of palladium, but for amounts exceeding 1 mg the method is not recommended. Under these circumstances a red film may collect at the chloroform–water interface. By this method small amounts of platinum may be separated from large proportions of palladium. The aqueous phase is used for the platinum determination, after evaporation to dryness, ashing with nitric acid and hydrogen peroxide solution and applying the *p*-nitrosodimethylaniline method (see Procedure 183).

The chloroform layer is similarly evaporated and treated, and the palladium is determined using the same reagent. It should be noted that *p*-nitrosodimethylaniline has not been used successfully for the quantitative solvent extraction of platinum; presumably the reaction is incomplete. This method requires the prior isolation of other platinum metals.

Yoe and Kirkland[163] provide a second method (Procedure 20) which simultaneously separates platinum and palladium from the commonly associated elements which interfere with the colorimetric determinations.

Procedure 19[163]

Place in a small separatory funnel the 10-ml sample of pH 2–5, containing not more than 0·5 mg of palladium. Add 0·5 ml of a 5 mg per ml ethanolic *p*-nitrosodimethylaniline solution and 5 ml of 95 per cent ethanol. Shake for 5 min. Extract the orange to red colour with 10 ml of chloroform. Re-treat the aqueous phase with 0·5 ml of reagent and 5 ml of ethanol. Allow to stand for 5 min, and extract with another 10 ml of chloroform. (If more than about 0·5 mg of palladium are to be extracted, two additional extractions may be required.) Transfer the chloroform layer to a small beaker and the aqueous layer to a second beaker. Evaporate both to dryness on a steam bath. If the residues, particularly that from the aqueous phase, contain large amounts of reagent, heat carefully on a hot plate to eliminate green fumes. Add to the residues 5 ml of fuming nitric acid, and heat almost to dryness. Add a further 5-ml portion of fuming nitric acid, and evaporate to 2 ml. If the solution is pale yellow or amber, add dropwise a 30 per cent solution of hydrogen peroxide to the incipient boiling mixture until it becomes colourless. Evaporate almost to dryness and treat with three successive 5-ml portions of concentrated hydrochloric acid, with intermittent evaporations.

To ensure the complete removal of oxidizing constituents, add to the evaporated residue 5 drops of a 1 per cent sodium bisulphite solution, and again evaporate to dryness. Dissolve the residue in a few ml of distilled water, with careful heating, then cool, and add water to adjust to almost the desired volume. Adjust to pH 2–3 with a buffer prepared by mixing 50 ml of a 4 M sodium acetate solution and 53 ml of 4 M hydrochloric acid, and make up to the final volume with distilled water.

Note—Whereas the authors used *p*-nitrosodimethylaniline to determine both platinum (Procedure 183) and palladium (Procedure 168), other spectrophotometric methods are applicable.

The Solvent Extraction of Palladium Diethyldithiocarbamate

The simultaneous extraction of platinum and palladium from associated platinum metals may be accomplished by a chloroform extraction of the metal complexes formed with sodium diethyldithiocarbamate.[163] This

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*Chemically Pure.

reagent was first used by Pollard[161] to produce a benzene extractable product when added to a palladium chloride-tin(II) chloride solution. Pollard used the carbamate as a titrant for the palladium-tin(II) complex in a benzene medium. Yoe and Kirkland[163] used a modification of this method, which involved the addition, to a strong hydrochloric acid solution of palladium, of an amount of potassium iodide sufficient to form soluble iodide complexes of both platinum and palladium. The addition of sodium diethyldithiocarbamate then produced a chloroform extractable brownish-yellow complex. This simultaneous extraction particularly lends itself to the additive absorbance technique (Procedure 185).

Gold must be removed before the simultaneous separation. Osmium and ruthenium are readily removed during the dissolution processes. A preliminary separation of palladium is necessary when it is desired to determine very small amounts of platinum in the presence of large amounts of palladium and more than traces of rhodium and iridium. In the presence of large amounts of rhodium and iridium (10–20 times the palladium concentration), it is advisable to provide the necessary amount of iodide by adding solid potassium iodide. A large quantity of iodide is also required if more than 10 ppm of palladium are to be extracted. In the presence of 1 mg of each of rhodium and iridium the extraction capacity for palladium is reduced from 100 μg to about 60 μg, in 5 ml of solution. Up to 200 μg of platinum in 5 ml of solution are completely extracted. The influence of the associated base metals on the efficiency of extraction is not known quantitatively.

Whereas the method described in Procedure 20 is particularly suitable for the application of the additive absorbance method, variations may be used to allow for the separation and determination of both platinum and palladium.

Procedure 20[163]

Transfer to the separatory funnel about 5 ml of the solution, containing 200 and 100 μg of platinum and palladium respectively, and free from organic or oxidizing species. (If rhodium and iridium are present in large proportions, the amount of palladium in the 5 ml solution should not exceed 60 μg.) Large proportions of palladium to platinum require the prior separation of the palladium. Add 5 ml of concentrated hydrochloric acid and 4 ml of a 2 per cent potassium iodide solution; if the sample contains more than 50 μg of palladium or large amounts of rhodium and iridium, add sufficient potassium iodide, as a solid or in solution, to prevent the precipitation of palladium iodide. Allow the rose-brown mixture to stand for 5 min. with frequent shaking. Add 2 ml of a 1 per cent aqueous sodium diethyldithiocarbamate solution, and allow to stand for 5 min. with frequent shaking.

Extract the white or cream mixture with two 5-ml portions of chloroform. Repeat the reduction and extraction procedure with 2 ml of a 2 per cent potassium iodide solution, 2 ml of a 1 per cent sodium diethyldithiocarbamate solution and two 5-ml portions of chloroform. Combine the chloroform extracts, add 5 ml of fuming nitric acid, and evaporate almost to dryness. Add a further 5 ml of the nitric acid, and evaporate to 2 ml. If the solution is then darker than a pale yellow, repeat the treatment with fuming nitric acid. Then add to the amber liquid a few drops of a 30 per cent hydrogen peroxide solution, and warm carefully until the liquid is colourless. Evaporate to a moist residue, and remove nitrogen

oxides by at least three successive evaporations with concentrated hydrochloric acid. If there is any indication of oxidizing constituents remaining, add a few drops of a 1 per cent sodium hydrogen sulphite solution, and again evaporate to incipient dryness. Add distilled water, and apply the additive spectrophotometric method with *p*-nitrosodimemethylaniline as described in Procedure 185.

If it is desired to separate platinum and palladium, the hydrochloric acid solution obtained from the above ashing process is treated with dimethylglyoxime, and the palladium is extracted with chloroform as described above. Alternatively, the palladium may be extracted by the *p*-nitrosodimethylaniline method described in Procedure 19.

Other Extraction Methods for Palladium

Among the complexes potentially useful for the solvent extraction of palladium are those formed with 8-mercaptoquinoline and thiocyanate. Bankovskis and Ievens[164] used the former in 4–6 M hydrochloric acid, and extracted with chloroform. Platinum was masked by thiourea. Thiocyanate was used by Przheval'skii *et al.*[165] to produce the red $[\mathrm{Pd(SCN)_4}]_2^{2-}$ extractable into isoamyl alcohol or butanol, at a pH below 5. There is no interference from platinum(IV). Excess of thiocyanate prevents interference from iridium; iron is masked by adding disodium hydrogen phosphate.

Corresponding to the large number of known, coloured palladium–organic complexes, there exists a wide variety of solvent extraction methods for these palladium complexes. Unfortunately the efficiency of these extractions as separatory methods in the presence of other platinum and associated base metals has received relatively little attention. In many instances the problem of co-extraction has been related to the degree of interference with the colorimetric measurements, with little or no attention to the completeness of separation from the other constituent(s) or to the subsequent isolation and determination of these constituents.

Thus, in view of the substantial number of colorimetric reagents for most of the noble metals, one may expect with confidence that good separations of the platinum metals by a complete solvent extraction procedure will be forthcoming.

Platinum

As indicated above the extraction methods for palladium frequently accomplish a simultaneous extraction of platinum. When using diethyldithiocarbamate, the two metals are retained in the organic layer. With such reagents as the oximes, the platinum remains in the aqueous layer and the required wash solutions. Although few of the recommended procedures include detailed techniques for the determination of platinum in the aqueous phase, the process requires only the usual evaporations, decompositions of organic matter, etc. Very few extraction methods for the direct and specific isolation of platinum by the organic phase have been proposed.

The Solvent Extraction of Platinum Applied to Platinum Reforming Catalysts

Recently, Conrad and Evans[63] used a solvent extraction to isolate platinum from platinum-reforming catalysts. The method involves the chloroform extraction of the iron–cupferron complex, with a recovery of the platinum from the aqueous phase. The recommended weights of platinum are 25–150 μg. It may be suggested here that for the specific purpose of this extraction ion-exchange techniques may prove at least equally efficient (see Procedure 47).

Procedure 21[63]

Filter the chloride solution into a 100-ml volumetric flask. Make up to volume with de-ionized water, and transfer an aliquot containing 25–150 μg of platinum to a separatory funnel. Add 2 ml of concentrated hydrochloric acid, 15 ml of C.P. chloroform, and 10 ml of a 6 per cent aqueous cupferron solution, in this order. Extract immediately, shaking vigorously for 30 sec, and relieving the pressure several times. Draw off the lower, chloroform solution of the iron–cupferron complex. Add 15 ml of chloroform, and extract vigorously for 15 sec to remove excess of cupferron. Run off the lower layer, and discard it. Add 2 drops of concentrated hydrochloric acid, and repeat the extraction with 15 ml of chloroform.

The *p*-nitrosodimethylaniline method (Procedure 183) is recommended for the spectrophotometric determination of platinum: the necessity of adjusting the pH to 2·2 ± 0·05 is stressed.

The Solvent Extraction of the Platinum–Tin(II) Chloride Complex

A solvent extraction method for the determination of platinum in cathode slimes has been reported by Struszyński and Chwastowska.[166] After dissolving in *aqua regia*, and the removal of nitric acid by evaporations with hydrochloric acid, then of lead chloride by crystallization, the platinum is treated with tin(II) chloride. The solution of the yellow complex is extracted into ethanol; the extract is then evaporated to dryness and taken up with hydrochloric acid, and the tin(II) chloride spectrophotometric method applied (Procedure 179).

The Solvent Extraction of Palladium and Ruthenium as their Thiocyanate–Pyridine Complexes

A series of researches which may provide potentially useful methods of separating and determining platinum metals was initiated by Wilson and his associates.[167, 114] These methods involved the replacement of chloride by thiocyanate in the pyridine complexes of the platinum metals. Thus, by the addition of pyridine to a solution of palladium(II) chloride at pH 4–6 containing an excess of thiocyanate, a complex was formed whose composition was $[\mathrm{Pd(py)_2(SCN)_2}]$. Extractions with hexone (iso-butylmethyl ketone) or chloroform produced a yellow solution whose absorption spectrum shows a maximum at 345 mμ.

With the chloro complexes of ruthenium in 0·1 N acid solutions, an excess of thiocyanate produced a red colour which on heating became a blue complex of unknown structure. The authors postulated the existence of ruthenium(II) in the form of $[\mathrm{Ru(SCN)_4}]^{2-}$ or $[\mathrm{Ru(SCN)_3}]^{-}$ because presumably some reduction took place, as suggested by the evolution of hydrogen sulphide during the formation of the blue complex, and because the complex was held by an anion-exchanger, but not by a cation-exchanger. In conformity with the earlier acceptance of the formula $[\mathrm{Ru(SCN)}]^{+2}$ for the blue complex, the authors suggested that with lower thiocyanate concentrations the composition tends to that of the above cation, because under these conditions the blue complex was not completely held by an anion exchange column.

The following procedures were recommended for the separation and determination of ruthenium and palladium. The absorptiometric methods are relatively insensitive and are not applicable to less than 25 μg each of palladium and ruthenium.

Procedure 22[114]

To 20 ml of the solution, which should not contain less than 25 μg of palladium and 25 μg of ruthenium, and should have a pH of 1·5–2·0, add a 10 M sodium hydroxide solution rapidly until the pH is 11–12 (Note 1).

Transfer the solution to a separatory funnel, and use an 0·05 M sodium hydroxide solution to rinse the beaker, adding these washings to the main solution. To this pale green solution add 0·5 ml (excess) of a 40 per cent solution of potassium thiocyanate, followed by 5 drops of pyridine, the solution becoming pale yellow owing to the formation of the pyridine–thiocyanate complex of palladium.

Extract the solution twice with 10-ml portions of hexone, and make up the organic extract to 25 ml (Note 2).

Filter the hexone extract into the absorption cell of the spectrophotometer, in order to remove tiny globules of air or water which may be present. Measure the absorbance of this solution at 345 mμ against hexone as a reference, and read off the palladium concentration from the prepared calibration curve.

Transfer the pale green aqueous solution remaining after the extraction of the palladium to a 50-ml beaker (Note 3). Add rapidly, and with stirring, 1 ml of concentrated hydrochloric acid, and heat the solution to about 90°C, when hydrogen sulphide is smelt. The time taken to reach this temperature should be about 4 min. While still hot, pour a further 5 ml of concentrated hydrochloric acid down the sides of the beaker, in order to intensify the colour of the blue complex and, allowing for wash liquor, to make the solution approximately 2 M in hydrochloric acid. Cool the beaker and its contents to about 20°C.

Transfer the solution to a separatory funnel, extract twice with 10-ml portions of hexone, and make up the extracts to 25 ml (Note 4).

Filter the hexone extract into the absorption cell of the spectrophotometer. Measure the absorbance of this solution at 570 mμ, against hexone as a reference, and read off the ruthenium concentration from the prepared calibration curve.

Notes—1. It is essential that this adjustment should be made quickly with a strong alkali solution.

2. The hexone solution contains all of the palladium present in the original aqueous solution. Under these conditions a thiocyanate complex of ruthenium is either not formed, or, if it is formed, is not extracted.

3. This solution contains potassium thiocyanate (excess), a trace of pyridine, ruthenium, if present, and has a pH of approximately 11.

4. This solution contains all of the ruthenium present in the original aqueous sample.

5. It is necessary to carry out the extraction of $[\mathrm{Pdpy_2(SCN)_2}]$ at a pH above 11, because it is not formed below pH 4, whereas at pH 4–8 a hydrous oxide of ruthenium precipitates. It cannot be emphasized too strongly that the initial adjustment of the ruthenium-palladium mixture to pH 11 must be made very rapidly, using a concentrated alkali solution, under which conditions no precipitation is observed. The same precaution is also necessary on later acidification, i.e. the concentrated hydrochloric acid must be added rapidly.

The Solvent Extraction of Palladium, Platinum and Rhodium as their Thiocyanate–Pyridine Complexes

By methods similar to those used for the separation of palladium and ruthenium, Wilson and co-workers[167] separated palladium, platinum and rhodium. The lower limits of applicable concentrations are 25 μg of palladium, and 50 μg each of platinum and rhodium.

Procedure 23[167]

To about 20 ml of the solution for analysis, which should contain not less than 25 μg of palladium, 50 μg of platinum and 50 μg of rhodium, and should have a pH of 2·5, add pyridine dropwise, with stirring, until the pH reaches 6·0–6·5.

Transfer the pale yellow solution to a separatory funnel, add 0·5 ml (excess) of a 40 per cent potassium thiocyanate solution, swirl the mixture, and allow to stand for 2 min. Extract the solution twice with 10-ml portions of hexone, and make the combined extracts up to 25 ml (Note 1).

Filter the hexone extract into the absorption cell of the spectrophotometer, in order to remove tiny globules of air or water which may be present. Measure the absorbance of this solution at 345 mμ against hexone as a reference, and read off the concentration of palladium present from the prepared calibration curve.

Adjust the pH of the remaining aqueous solution (Note 2) to 2·0–2·5 using hydrochloric acid, and heat the solution, taking 4 min to reach the final temperature of 90°C (Note 3). Cool the beaker and its contents to about 20°C.

Transfer the solution to a separatory funnel, extract it twice with 10-ml portions of hexone, and make up the combined extracts to 25 ml (Note 4). Filter the hexone extract into the absorption cell of the spectrophotometer. Measure the absorbance of this solution at 385 mμ against hexone as a reference, and read off the concentration of platinum present from the prepared calibration curve.

To the yellow aqueous solution remaining after the extraction of palladium and platinum add 0·5 ml (excess) of a 40 per cent potassium thiocyanate solution, followed by concentrated hydrochloric acid until the acidity of the solution is 3–4 N. Cool the beaker and its contents to about 20°C.

Extract the solution twice with 10-ml portions of hexone and make up the combined extracts to 25 ml (Note 5). Filter the hexone extract into the absorption cell of the spectrophotometer. Measure the absorbance of this solution at 380 mμ against hexone previously saturated with 2 M hydrochloric acid as a reference and read off the concentration of rhodium present from the prepared calibration curve.

Notes—1. The hexone solution contains all of the palladium present in the original aqueous solution. Under these conditions, thiocyanate complexes of platinum and rhodium are either not formed, or if they are formed, they are not extracted.

2. The colourless solution remaining after the extraction of palladium contains potassium thiocyanate, a little pyridine, platinum and rhodium, if initially present, and has a pH of 6.

3. On first heating, a cloudiness appears at about 40°C, a golden yellow colour being developed. The reaction is complete at 90°C.

4. This hexone solution will contain all of the platinum present in the original aqueous sample. Under these conditions the rhodium thiocyanate complex, although present in solution, is not extracted.

5. This hexone solution will contain all of the rhodium that was present in the original aqueous sample.

The Solvent Extraction of Palladium, Ruthenium and Rhodium as their Triphenylmethylarsonium Iodide and 8-Quinolinol Complexes

A solvent extraction method for the separation of palladium, ruthenium and rhodium was recorded by Jasim, Magee and Wilson.[168] In this method only palladium reacts with triphenylmethylarsonium iodide, to produce a red constituent extractable by chloroform. Rhodium and ruthenium, in the aqueous phase, are separated through the formation of their 8-quinolinate complexes and a chloroform extraction. The aqueous phase, which contains the ruthenium, is re-treated with butylcellosolve to remove traces of rhodium. The lower concentration limits are 25 μg each of rhodium and palladium, and about 12 μg of ruthenium.

The absorbance measurements can be made directly on the organic extracts. It should be noted that osmium does not interfere with the determination of ruthenium.

Since 8-quinolinol is an analytical reagent for a wide variety of metals, many of the associated base metals must be removed prior to the separation.

Procedure 24[168]

To about 5 ml of the solution of palladium, rhodium and ruthenium, contained in a separatory funnel, and adjusted to be 0·1 M in hydrochloric acid, add 2 ml of a 1 per cent aqueous solution of triphenylmethylarsonium iodide, then 0·4 ml of a 3 M sodium chloride solution. Extract with two 5-ml portions of chloroform, the chloroform extract containing the palladium and the aqueous layer containing the rhodium and ruthenium.

Transfer the red chloroform layer to a separatory funnel, add 5 ml of a 5 per cent chloroform solution of 8-quinolinol, and shake vigorously. Loosen the stopper of the funnel, and warm the vessel in a water bath at 40°C for 10 min. Filter the solution through a filter paper holding 2 g of anhydrous sodium sulphate. Collect the dried filtrate in a 50-ml graduated flask, and make up to the mark with chloroform. Measure the absorbance of this solution in 1-cm cells at 430 mμ. Determine the palladium concentration from a calibration curve.

Add 5 ml of a 10 per cent chloroform solution of 8-quinolinol to the aqueous layer from the palladium separation, and shake vigorously for 3 min. Adjust the pH of the aqueous layer to 6·4 with a 10 per cent ammonium acetate solution, shake for a further 3 min, allow the layers to settle, and separate them. Add a further 5 ml of reagent to the aqueous layer, and repeat the extraction. Combine the organic extracts, and set them aside for the determination of ruthenium. To the aqueous layer add 3 ml of butylcellosolve, and shake vigorously for 3 min. Then extract with three 5-ml portions of the 8-quinolinol solution, and combine the chloroform extract with the previous extracts, giving Solution A.

To the aqueous layer, containing the rhodium, which should have a volume of 5 ml, and should contain not less than 25 μg of that metal, add 6 ml of a 2 per cent acetic acid solution of 8-quinolinol. Adjust the pH to 6·0–8·0 with a 10 per cent ammonium acetate solution. Warm for 30 min on a boiling water bath. Cool, and transfer to a separatory funnel. Extract with three 5-ml portions of chloroform, to remove all the colour from the aqueous layer. Filter the combined extracts through a filter paper holding about 2 g of anhydrous sodium sulphate. Collect the clear liquid in a 50-ml graduated flask, and dilute to the mark with chloroform. Measure the absorbance of the solution at 425 mμ, and determine the rhodium from a previously obtained calibration curve.

Filter the combined chloroform and cellosolve extracts (Solution A) through a good grade of quantitative filter paper, holding about 2 g of anhydrous sodium sulphate. Collect the green filtrate in a 50-ml graduated flask, and make up to the mark with chloroform.

Measure the absorbance of the solution at 410 mμ in 1-cm cells. Determine the ruthenium from a previously obtained calibration curve.

Adsorption and Ion-exchange Methods for the Separation of Gold, Palladium and Platinum

The techniques involved in the separation of all noble metals by ion-exchange and adsorption processes are of very recent origin. The methods so far proposed have, by and large, been developed through empirical approaches. This is largely the result of the lack of information concerning the identity of the dissolved noble metal constituent, and to a degree, to ignorance of the character of the exchange mechanisms. The effects of acidity, salt content, temperature, time of standing, order of addition of reagents, character of the containing vessel, degree of prior exposure to air, etc., may become significant under specific circumstances. It is surprising that despite the long history of researches with gold compounds one cannot predict with assurance the identity of the dissolved gold constituent as one changes the acidity of the solution. These deficiencies in knowledge of descriptive chemistry not only mitigate against an intelligent approach to ion-exchange separation, but they also retard the development of new spectrophotometric reagents and, in some instances, new chromatographic methods. An outstanding example is the ion-exchange separation of gold.

The Separation of Gold by Ion-exchange

Perhaps the earliest adsorption methods for gold involved the use of some form of carbon. As might be expected, the chief interests in the application of such processes were concerned with monetary aggrandizement. The removal of gold from sea water was accomplished by contact with bone-black and wood charcoal.[169] The mechanism of this adsorption was discussed by Koch.[170] The rate of adsorption of gold was found to be rapid, but its determination was complicated by a disturbance of the equilibrium owing to some reduction to metal. Finely divided wood charcoal was found to be the most satisfactory adsorbent. Kropachev[171] also recommended wood charcoal for the adsorption of gold from sea water and gold solutions prepared from animal and vegetable organisms.

For the determination of gold and other heavy metals in water, Abrahamczik[155] applied an exchange reaction with permutite, and removed the adsorbed metals by eluting with a sodium chloride solution. Alternatively, a combination of resins could be used for the simultaneous adsorption of cations and anions. The extraction of the adsorbed metals could be made with chloroform or carbon tetrachloride solutions of dithizones.

One of the latest applications of ion-exchange resins to the determination of gold in waste cyanide solutions was described by Fridman,[172] who used the chloride forms of the resins An-2F and EDE-10. The dissolved gold constituent is $[Au(CN)_2]^-$ and the gold concentrations were less than 0·2 μg per ml. The process involves mixing 10 g of the anionite for 2 hr with 3 l. of the gold solution. The ion-exchange proceeds well at pHs 3–6 and 8–10. The method is said to be superior to precipitation using zinc dust.

Concerning the quantitative separation of gold from associated base and noble metals there seems to be a dearth of information. It is probable that gold, along with platinum, palladium, rhodium, iridium and ruthenium, may be separated from certain base metals by a cation-exchange resin such as Dowex 50W-X or Dowex 50W-X8. Published data suggest that while platinum metals may be thus separated from very large proportions of iron, copper and nickel, a similar separation of gold is adversely affected by the presence of iron. In the presence of the latter the recovery of gold is low by several per cent. This may be due to the presence of iron(II) salts, although the simultaneous use of various oxidants gives little improvement in the completeness of the recovery.

The Separation of Gold from Iron, Copper and Nickel by Cation-exchange

In general, the conditions for the recovery of gold by cation-exchange require a pH of 1·0–1·5. At the lower pH limit there is some compromise between improved recovery of the noble metals anions and some leakage of base metals; for example, one may expect at pHs less than 1·0 some contamination of the eluate with traces of iron and nickel. The chloride concentration should be about 0·2 M.

The gold chloride solution may contain 0·5–10 mg of gold per 400 ml. Undoubtedly these concentrations may be extended. The exchange column of 1 in. diameter should contain sufficient resin to retain 5 g of base metal. When a separation of larger amounts of base metals is required the length of the column and the amount of resin can be increased appropriately.

Procedure 25[173]

Adjust the solution of gold and base metals to pH 1 with hydrochloric acid or a solution of sodium carbonate. Transfer the solution to the exchange tower containing Dowex 50W-X8 resin and collect the eluate in a 1-l. beaker. Wash the resin with about 500 ml of water adjusted to pH 1 with hydrochloric acid. Evaporate the combined eluate and washings to dryness, and destroy organic matter with a 30 per cent solution of hydrogen peroxide, and fuming nitric acid. Add 2 ml of a sodium chloride solution, and evaporate to dryness. Remove nitric acid by several evaporations on a steam bath with a few ml of strong hydrochloric acid. Add water and acid to prepare for a spectrophotometric or gravimetric determination. For a gravimetric determination the hydroquinone method is recommended (Procedure 105); for a spectrophotometric determination, the gold bromide method is recommended (Procedure 16).

The Separation of Platinum Metals by Ion-exchange

In the present author's opinion, a major contribution of ion-exchange technique in the field of platinum metals separations will lie in the area of the *en masse* isolation of associated base metals in ores, concentrates and natural and artificial alloys. The applications to separations within the platinum group can be expected to supply new procedures, but in general they will not, in the foreseeable future, displace the existing chemical and chromatographic procedures. On the other hand it is not impossible, and perhaps not improbable, that certain aspects of fire assay extractions will find serious competition, particularly for ores in which the amounts of platinum metals are sufficiently small to require some method of mechanical concentration.

The ion-exchange methods for the separation of rhodium and iridium have been described above.

At the present time few exchange methods are available which will efficiently separate each of the platinum metals. The increasing variety of exchange methods are directed toward restricted separations among the platinum metals or toward the removal of some or all of the latter from base metals. A few procedures, however, allow for the selective isolation of platinum or palladium. The latter, alone amongst the noble metals, is predisposed toward cation formation, and advantage has been taken of this property for its separation. On the other hand this same property introduces difficulty when one wishes to separate *en masse* the noble metals from solutions containing base metals; such procedures require conditions for the formation of noble metal anions. With some of the few relatively effective ion-exchange methods, platinum is isolated initially by the hydrolytic precipitation of the associated platinum metals.

To separate platinum from palladium, rhodium and iridium, Stevenson *et al.*[174] added nitric and perchloric acids to the solutions of the four metals, and evaporated to near dryness. This was repeated to remove all traces of chloride, finally giving a volume of 0·2–0·5 ml of fuming perchloric acid. The solution was diluted to 10 ml, and passed through a column of Dowex-50 resin. Platinum was carried through as an anion, and the retained palladium, rhodium and iridium were washed with distilled water to remove all the platinum. Palladium was stripped with 0·05–0·5 M hydrochloric acid, then rhodium was eluted slowly with 2 M hydrochloric acid, and finally iridium was removed by 4–6 M hydrochloric acid. The report of the method included no data, but the method may well find useful application where perchloric acid has been used to remove osmium and ruthenium from alloys of noble and base metals.

The separation of platinum from palladium can also be accomplished with the hydroxide form of the basic exchanger Permutit (E.T.). Blasius and Wachtel[175] used this resin to adsorb both metals, and then eluted the palladium with a 1 M solution of sodium hydroxide, and the platinum with 2·5 N nitric acid. Platinum(IV) chloride can also be separated from iridium(III) chloride, in which instance the iridium is eluted with a 1 M sodium hydroxide solution. The authors were able to apply their method to the quantitative removal of iron, copper and nickel, but they failed to elute platinum and iridium from the anion-exchanger, and recommended ignition of the latter to recover these metals.

Dowex-2 was used by MacNevin and Crummett[176, 177] to adsorb the complex chlorides of palladium, platinum, rhodium and iridium, followed by selective elution with an ammoniacal solution of ammonium chloride. The elution of palladium was satisfactory, but the remaining separations were ineffective. Better results were obtained with an ammoniacal solution of the four metals, and a column of the cation-exchanger Amberlite IR-100. It is suggested that platinum should be first isolated by hydrolysis, then palladium should be adsorbed selectively by cation-exchange, followed by the separation of rhodium from iridium by an electrolytic process. One may separate palladium as its ammonia complex from the complex iridium anion by using Amberlite IR-100.

Procedures for the above separations are described in Section II of this chapter.

The Chromatographic Separations of the Noble Metals

A second major advance in the analytical chemistry of the platinum metals has been the development of chromatographic methods of separation. The integration of these techniques with cation- and anion-exchange and fire assay separations will provide a whole new series of relatively simple and accurate methods of extraction and of determination of the six metals. By far the most difficult aspect of the analysis of these metals lies in determining the amounts present in ore deposits, and it is precisely in this area that chromatographic methods serve their most useful purpose.

One of the first chromatographic methods for the separation of the platinum metals involved the use of a column of carbon. The application of this adsorbing medium has, during the past decade, received only desultory attention, but in the present author's opinion carbon has considerable separatory potentialities. One must expect difficulties in achieving selectivity when the direct adsorption of platinum metals on carbon sites is expected. Adsorption through the intermediate action of platinum metal reagents, however, may yet prove profitable both on an analytical scale and perhaps with larger samples.

Dubrisay[178] stated that when a dilute solution of a noble metal species was passed through a column of finely divided carbon, the metals collected in the upper part of the tube, and could subsequently be extracted with suitable solvents. The method was proposed only for the approximate evaluation of precious metals in dilute solutions. The single result given was applied to silver, and indicated a moderately good recovery. The use of carbon as a selective adsorbent for group separations has received little attention. Bauer and Nagel[179] acquired a patent for thus removing gold, silver and platinum from ocean water. The ash of the resulting mixture was treated by conventional methods of isolation. Venturello and Saini[180] used alumina for the adsorption, and subsequently applied various reagents to reveal the presence of platinum, rhodium and iridium. The procedure was applied with good results to dilute solutions of the metals and their alloys.

Alumina was also used by Schwab and Ghosh[181] for the separation of the complex chlorides of iridium, platinum, palladium and rhodium, in this order. Both X-ray measurements and the colours of the various fractions confirmed the separation. Ashizawa[182] used a paper chromatographic method for the separation of palladium, nickel, cobalt and copper. The bluish-green adsorption band for palladium developed by dithizone occurred between those for nickel and cobalt, and one could detect 0·0005 μg. Interfering elements were eliminated by preliminary chemical treatments.

The most significant reports of the early researches with the platinum metals were introduced by a note by Lederer,[183] who used paper chromatography for the separation of silver, copper, palladium, platinum and gold. He correctly predicted the successful application of the method to the analysis of a silver assay bead, making the claim that chromatographic methods would supersede other methods of separation for this purpose. He used a paper cylinder which, after the addition of the solution of the precious metals, was placed in a dish of butanol saturated with 1 M hydrochloric acid, and the whole was placed for 20–24 hr in a crock in which the atmosphere was saturated with hydrochloric acid and butanol. The detailed method (Procedure 48) is included below.

In a later paper, Anderson and Lederer[184] recorded their use of an electrochromatographic method for the isolation of as much as 20 mg of copper from gold, platinum and palladium. The method required the use of paper-pulp strips, the ends of which were immersed in a hydrochloric acid solution of potassium chloride. Twelve volts were maintained between the carbon electrodes, and a current of 0·2 amp was used. The sample was added to the paper, and the spot was placed in the anode compartment. The paper was moistened with 1 M hydrochloric acid, and the whole was set aside overnight. The copper moved to the cathode as a blue band. The method will find restricted applications to the separation of associated base metals from the platinum metals. In a third paper, Lederer[185] reported a study of rhodium(III) complexes by paper electrophoresis and ion-exchange chromatography. Rhodium hydroxide, with hydrochloric, hydrobromic or nitric acids, produced unstable intermediate cations of low mobility. By using these complexes, rhodium could be separated chromatographically from platinum(IV) and palladium(II).

Majumdar and Chakrabartty[186] have indicated the possibility of limited group separations of the platinum metals by electrochromatography. At 150 volts for 5 hr, μg amounts of at least four ions could be isolated. The sequence of separation for different electrolytes was included, but unfortunately no analytical results were provided.

An interesting and potentially useful continuous separation of platinum metals by paper electrochromatography was described by MacNevin and Dunton.[187] The success of the method depended upon the fact that the rate of diffusion of the four metals in descending chromatography and in horizontal electrochromatography varied appreciably with each metal. Up to 100 mg of mixtures of two or three metals could thus be separated, but the fact that the conditions for separating rhodium required a slightly acid medium, under which conditions platinum was diffusely distributed, prevented its application to mixtures containing rhodium, platinum, palladium and iridium. The procedure involved the use of ethylenedinitrilotetra-acetic acid at pH 9 to complex iridium and palladium, under which conditions precipitation would otherwise occur. The equipment included suitable paper, 11 × 13 in. held vertically, and notched at top and bottom, with platinum electrodes interwoven at the two sides.

One must regret the lack of quantitative results, only a few of which are included to prove the separation by horizontal electrochromatography of rhodium(III), palladium(II), platinum(IV) and iridium(IV). The medium was 0·1 M in EDTA, and was adjusted to pH 9, at which acidity the rhodium remained stationary.

Burstall *et al.*[188] recorded the results of an extensive application of inorganic chromatography on cellulose to a variety of metals which included the six platinum metals. This work formed the basis for the later advances described below, but no quantitative results were included.

Fournier[189] separated platinum, palladium and rhodium chromatographically by applying butanol with nitric and hydrochloric acids as the solvent.

Kember, Wells and their associates have contributed the most useful advances in the paper chromatographic separations of platinum metals so far reported. In an informative article,[190] they described the separation of μg amounts of platinum, palladium, rhodium and iridium, and to a limited degree discussed separations from associated base metals present in mg amounts. The detailed procedure is included in Section II (Procedure 49).

Rees-Evans, Ryan and Wells[191] have recently described a cellulose column for the chromatographic separation of the four "non-volatile" platinum metals, each present in 100-mg amounts, and in the presence of limited amounts of associated base metals. The procedure involved 15–30 cm cellulose columns pretreated with solvents; one of the latter consisted of hexone with 3 per cent of concentrated hydrochloric acid, and the other, to be used for the collection of iridium, a solvent similar to the first but containing chlorine dioxide as an oxidant. The preparation of the metal sample involved evaporations in the presence of zinc chloride to prevent the formation of insoluble compounds; sodium chloride proved to have a deleterious influence during the chromatographic separations. The results indicated that the addition of 20 mg of each of copper, nickel and iron, 100 mg of zinc, and small amounts of mercuric chloride did not interfere in the subsequent determinations. Details were provided for the separation of various two component systems, the most useful of which was that of rhodium from iridium. The separation of platinum, palladium, rhodium and iridium required the removal of nitric acid by evaporation with hydrochloric acid, with an intermediate addition of chlorine, and the addition of hexone as a solvent. Platinum and iridium were collected as a single fraction, and were later separated by column extraction under reducing conditions, in order to decrease the mobility of the iridium. The palladium fraction followed that of the platinum–iridium mixture, leaving behind the immobile rhodium and nickel, which were subsequently removed by hydrochloric acid. Iron(III), copper and zinc were found with the platinum fraction, and mercury(II) chloride with the iridium fraction when that metal was separated from the rhodium.

The above authors inferred that their method was superior to that of the wet separations of base metals from the platinum metals by hydrolysis in the presence of nitrite. They stated that " the nitrite procedure for the separation of base metals has been found to be satisfactory when the total weight of platinum metals exceeds that of the base metals, but the accuracy of the separation is lowered when the reverse circumstances apply ". Apart from the fact that the accuracy of the nitrite separation is not necessarily lowered by the presence of higher proportions of base metals, the proposed column procedure, as described, involves equally low proportions of base metals, excluding the zinc, which is added as part of the procedure. While the question of their general relative value must await the results of continued application in the laboratory, the present author does not anticipate the abandonment of the existing methods of separations: rather, he believes that the essential improvements provided by chromatographic techniques will ultimately become integrated with the classical wet methods of fire-assay and the ion-exchange methods to provide simple and accurate methods of isolating and separating the platinum metals. The detailed procedure recommended by Rees-Evans *et al.*[191] is described in Section II (Procedure 51).

SECTION II

The Determination of Osmium in Meteoric Iron

The following procedure is applicable to siderite meteorites of the Cañon Diablo type.

Procedure 26[101]

Place a 1-g sample of the meteorite in an Erlenmeyer flask, and add 10 ml of 6 N sulphuric acid. Heat until the reaction has ceased. Transfer the supernatant liquid to a suitable beaker, and add 10 ml of hot 6 M hydrochloric acid to the residue in the flask. Add 10 ml of 6 N sulphuric acid, and evaporate to fumes of sulphuric acid. Add water to dissolve the crystallized salt, and repeat the fuming. Add 10 ml of water, and heat to dissolve all but the small residue. Transfer the retained sulphuric acid extract contained in the beaker and the solution in the flask to a suitable distillation flask (for this apparatus see Chapter 7, Equipment No. 8). Dilute to 1 N in acid. Add a solution of potassium permanganate until 1 drop excess is present as indicated by the colour; avoid getting the permanganate on the neck of the flask. Add about 50 mg of ammonium ferrous sulphate hexahydrate to destroy the permanganate and the higher oxides of manganese. The volume of the solution at this point should be 35–40 ml. Add a few small grains of pumice, connect the flask to the condenser, and heat the solution slowly to near its boiling point to make certain that higher manganese oxides have been completely dissolved. Dip the end of the condenser into 10 ml of 1 : 1 hydrochloric acid freshly saturated with sulphur dioxide, and contained in a 100-ml graduated cylinder, the upper half of which has been cut off; a large vial or test tube marked to indicate 20 ml is also suitable. Add 15 ml of concentrated nitric acid through the inlet tube of the flask, and distil so that 10 ml of distillate are collected in 10–15 min. Transfer the distillate to a 25-ml volumetric flask, rinsing the condenser and receiver with a few ml of water. Add 0·50 ml of a 10 per cent aqueous thiourea solution, and make up to the mark with water. Determine the transmittance of the solution after 5 min (longer standing does no harm), using a green filter.

In constructing the standard curve add 0, 25 and 50 μg of osmium(VIII) oxide to distillates obtained from an osmium-free nitric acid mixture comparable in composition to that obtained from meteoric iron. If the amount of osmium is likely to be less than 10 μg, use 5 ml of the hydrochloric acid–sulphur dioxide solution contained in a 25-ml graduated cylinder for collecting 10 ml of the distillate. Add 0·3 ml of the thiourea solution, read the volume of the solution in the graduated cylinder (which has been checked for accuracy), and determine the transmittance as described above.

Notes—1. The volume of the distillate in which the colour is to be developed can be kept as small as 15–25 ml. With a photoelectric photometer the limit of detectability of osmium is then 1 or 2 μg when a layer of solution 1 cm thick is examined in the green light. (A solution 1 cm thick containing 1 ppm of osmium gives an absorbance of about 0·015 with the green filter.)

2. The use of a visual colorimetric method is less satisfactory than a photometric method because thiourea gives a yellow colour with sulphur dioxide solution.

3. Because osmium(VIII) oxide is readily formed by the oxidation of osmium with nitric acid, and because meteoric iron is readily attacked by nitric acid, it may seem that a direct distillation from a nitric acid solution would be a simple procedure. Sandell[105] found that the use of 5 M nitric acid gave low osmium values. The explanation for this anomaly is not known.

The Determination of Osmium and Ruthenium in Siderite Meteorites (and in Iron–Copper–Nickel Assay Buttons)

The following method is applicable both to assay buttons which usually weigh about 25 g and to meteorite samples from mg amounts to more than 100 g. The upper limit is determined by the mechanics of the distillation, e.g. the size of the sample and flask, and the volume of the receiving flasks, etc. With small samples the amount of perchloric acid is reduced to an amount appropriate for dissolution. This distillation has been examined only for determinations of mg and μg amounts of osmium and ruthenium. One may expect that large amounts of these metals may alter the properties of the iron alloys to the extent that perchloric acid may not completely dissolve the osmium and ruthenium. In these instances the size of the alloy sample should be reduced. In its present state of development the collection of osmium and ruthenium by the base metal alloys is recommended only for analytical purposes, and the method is best applied to samples containing from about 25 μg to 20 mg of osmium or ruthenium.

A perchloric oxidation serves to remove both osmium and ruthenium and, as indicated in Section I, a proper choice of receiving liquids will facilitate the subsequent separation of the two metals.

Procedure 27[105]

Use the distillation equipment as in Chapter 7, Equipment No. 9.

Add 100 ml of water to the trap, 30 ml of a 3 per cent hydrogen peroxide solution to the first receiver and 10 ml to each of the remaining two receivers. Immerse the receivers in an ice bath. Pass a stream of cold water through the condenser, and apply a gentle suction through the whole system from the exit tube of the last receiver. Add 100 ml of 72 per cent perchloric acid to the sample of meteorite in the distillation flask, and boil gently over a low flame. If the reaction becomes too vigorous, discontinue the heating to regain control. Boil the solution for a total period of 2 hr. To ensure the complete distillation of the osmium and ruthenium, add 50 ml more of the perchloric acid to the distillation flask, and heat for another 30 min. Then add 15 ml of the perchloric acid to the trap, and boil the solution for 30 min. Transfer the receiving solutions containing the osmium and ruthenium to a previously chilled second distillation flask as quickly as possible to prevent a loss of osmium by volatilization, and wash the receivers and the delivery tubes thoroughly with cold 3 per cent sulphuric acid. Wash the tubes and receivers thoroughly with water to remove the sulphuric acid.

Add 100 ml of water to the trap and 30 ml of twice distilled 48 per cent hydrobromic acid to the first receiver and 10 ml of the same acid to each of the other receivers. Chill the receivers in an ice bath. Add 40 ml of a 30 per cent hydrogen peroxide solution and 5 ml of concentrated sulphuric acid to the chilled distillation flask containing the osmium and ruthenium distillates. Boil gently for 30 min. Add 15 ml of perchloric acid to the trap, and boil for 25 min. Draw a stream of air slowly through the system (about 3–5 bubbles per sec). Transfer the contents of the receivers to a 150-ml beaker, and rinse both receivers and tubes with 10 per cent hydrobromic acid. Evaporate the solution on a steam bath to 5 ml, transfer to a 30-ml beaker, and evaporate again to 0·5–1·0 ml. Transfer the solution to a 20-ml test tube by washing with water, and determine the osmium with anthranilic acid as directed in Procedure 152.

For mg amounts of osmium, adjust the evaporated osmium distillate to the required acidity for precipitation by thionalide, as directed in Procedure 78.

To recover the ruthenium in the pot liquid, add 100 ml of water to the trap, 30 ml of a 3 per cent hydrogen peroxide solution and 1 ml of 48 per cent hydrobromic acid to the first receiver, and 10 ml of a 3 per cent hydrogen peroxide solution to each of the other two receivers. Cool the receivers in an ice bath. Add 10 ml of concentrated sulphuric acid to the distillation flask and then add cautiously an excess of a 10 per cent sodium bromate solution (about 20 ml). Apply a gentle suction, and distil cautiously over a low flame for 1 hr. Then add 15 ml of the perchloric acid to the trap, and boil for 25 min. Disconnect the receivers from the water condenser, maintaining the connection between the two receivers. Add 8 ml of 48 per cent hydrobromic acid to the first receiver and 4 ml of the acid to the second receiver. Boil the liquid for 10 min. Transfer the contents of the receivers to a 150-ml beaker, rinse the tubes and the receivers with 10 per cent hydrobromic acid, and evaporate the combined solution to 5 ml. If a spectrophotometric method is to be used transfer the 5 ml of solution to a 30-ml beaker and evaporate again to 0·5–1·0 ml. Transfer to a 20-ml test tube, and apply the anthranilic acid method as described in Procedure 148. Other appropriate methods may be used.

For mg amounts treat the evaporated ruthenium solution (0·5–10 ml) to prepare for a thionalide precipitation (Procedure 72).

The Determination of Osmium and Ruthenium in Lead Alloys

Despite the facts that the physical and chemical properties of lead are little related to the noble metals and that lead is seldom associated with these metals in natural deposits, this metal is a suitable medium for a high temperature extraction of noble metals from a fused mixture of ore and flux. However, whereas the extraction can be made complete, the subsequent wet analysis of the lead button or regulus is complicated by partial reactions of the noble metals with the parting acid; the latter is usually nitric acid. The pertinent methods of analysis and the specific difficulties associated with the partial corrosion of each metal are discussed in relation to Procedure 28. It may be stated here that whereas the lead button is readily parted by nitric acid and that this acid may simultaneously volatilize octavalent osmium, the complete removal of osmium may not be accomplished. Furthermore, when ruthenium is to be determined consecutively the residual nitric acid must be destroyed. This is usually done by fuming with sulphuric acid, but obviously this is not practical in the presence of large amounts of lead. Because of these difficulties the determinations of osmium and ruthenium in lead buttons are more advantageously carried out by parting with perchloric acid, with the simultaneous distillation of both osmium and ruthenium in the presence of excess of perchloric acid. Here, as with the iron–copper–nickel alloys discussed above, the choice of receiving liquids should be appropriate to the required separation of osmium and ruthenium. For this purpose a cold hydrogen peroxide solution may be used to collect both metals, with a subsequent treatment with sulphuric acid and additional hydrogen peroxide to remove osmium selectively.

Alternatively the receiving liquid may be sulphur dioxide–hydrochloric acid in which instance an evaporation to remove sulphur dioxide is required prior to a second distillation with nitric acid, etc., to remove osmium. By this treatment the nitric acid in the distillation flask can be removed by an evaporation with hydrochloric acid. Finally, in preparation for the distillation of ruthenium, sulphuric acid is added, and evaporation to fumes is carried out to remove the hydrochloric acid.

Receiving solutions of sodium hydroxide may also be used, followed by a second distillation with nitric acid and, as stated above, treatments of the pot liquid to secure a sulphuric acid solution of ruthenium.

Other combinations of recovery liquids and oxidizing reagents will suggest themselves. The author recommends the use of a cold hydrogen peroxide solution for the collection of the combined tetroxides from a perchloric acid distillation.

Procedure 28[102, 21]

Equipment. The distillation equipment is described in Chapter 7, Equipment No. 10.

Procedure. Transfer the lead alloy (20–50 g) to the distillation flask, and add 100 ml of water to the trap, 25 ml of a 3 per cent hydrogen peroxide solution to the first receiver and 5 ml of this hydrogen peroxide solution to each of the other two receivers. Chill the receivers in an ice bath, pass water through the condenser, and apply suction to produce 2 or 3 bubbles per sec. Add 75 ml of 72 per cent perchloric acid, and heat very gently until the lead is completely dissolved and effervescence of hydrogen has ceased. Continue the heating until the white fumes of perchloric acid have disappeared and a colourless liquid is refluxing on the still wall (Note 1).

Cool to about 60°C, and add 8 ml of 36 per cent perchloric acid. Heat again to the removal of brown fumes. Repeat the addition of 8 ml of 36 per cent perchloric acid, intermittent heating twice to ensure the complete removal of the tetroxides. A complete distillation requires 0·5–1 hr. Add 15 ml of 72 per cent perchloric acid to the trap, and boil the solution for 30 min. Transfer the chilled receiving solution to a second chilled distillation flask as quickly as possible to prevent any loss of osmium, and wash the receivers and the delivery tubes with cold 3 per cent sulphuric acid. Remove the sulphuric acid thoroughly from the tubes and receivers by washing with water. Proceed with the separation of osmium and ruthenium as discussed for the iron–osmium–ruthenium alloy (Procedure 27).

Note 1—With amounts of ruthenium of the order of 10 mg, the brown ruthenium tetroxide can be seen condensing in the trap and on the still wall.

The previous methods describe satisfactory procedures for the isolation of osmium and ruthenium from base metals. By these methods both osmium and ruthenium are collected in one liquid. The details of the various suitable methods for separating osmium from ruthenium are described in Chapter 2, Section I.

The Determination of Noble Metals in Decorative Alloys

The decorative alloys of the noble metals do not usually contain osmium and ruthenium. In these instances, therefore, the processes of dissolution do not require a collection of gases.

Hard alloys, however, may contain appreciable proportions of iridium, ruthenium and osmium. These and alloys with rhodium require an exceptionally severe treatment. The preferred methods are chlorination in the presence of salts or wet chlorination in a closed system. Appropriate techniques are discussed in Chapter 1. In specific instances the dissolution methods involving prior alloying with tin or zinc are useful. These procedures are also described in Chapter 1.

The alloys amenable to direct acid attack contain high proportions of platinum, palladium and gold, and frequently such associated metals as nickel, copper, iron and silver.

In those instances where the composition of the alloy is unknown the subsequent analytical treatment is promoted by a qualitative examination. For this purpose there is no better method than a carefully prepared spectrographic examination, by which, with a little experience, the analytical chemist should be able to make a reasonable guess as to proportions of constituents. With significant amounts of iron or nickel the spectrogram should be obtained from an instrument with an appropriate dispersion. Descriptions of pertinent methods are recorded in Chapter 6.

The following method is suitable for the analyses of metals in amounts of the order of 50–200 mg each. It is not recommended for amounts of the order of a few mg.

Procedure 29[143] *(modified)*

Treat 0·2–0·4 g of the alloy with *aqua regia* until it is completely dissolved, or chlorinate the alloy by an appropriate method. If the former treatment accomplishes only partial dissolution, filter, burn, and chlorinate the residue. Add the resulting acid solution and 0·1 g of sodium chloride to a 400-ml beaker, and evaporate to dryness on a steam bath. Add a few ml of concentrated hydrochloric acid, and evaporate to dryness. Repeat this procedure to completely remove the nitric acid. Add 50 ml of water and a few drops of concentrated hydrochloric acid, and warm to dissolve the residue. Filter through a 7-cm Whatman filter paper, and wash well with water. Transfer the paper to a suitable crucible, and ignite to an ash. Add a few ml of *aqua regia*, and evaporate in the presence of a few mg of sodium chloride. Add a few drops of hydrochloric acid, and evaporate carefully to dryness. Repeat once or twice, then add a few ml of water and a drop of hydrochloric acid, filter into the original solution, and wash to make up to about 100 ml.

The precipitation of gold and base metals. Heat the slightly acid filtrate to 60°C, and add dropwise a saturated solution of sodium nitrite until the evolution of gas ceases and the solution becomes a light yellow-green; insufficient nitrite will result in a subsequent precipitation of rhodium. Boil the mixture for 15–30 min to ensure the coagulation of the gold. At this stage precipitated copper may stain the beaker wall. Cool the mixture to 60°C, add a few drops of phenolphthalein, and neutralize to a permanent pink by adding a 10 per cent sodium carbonate solution. Continue heating on a water bath at 60°C for 15 min, then filter through a Whatman No. 42 filter paper previously washed with a 1 per cent solution of sodium nitrite made neutral to the blue end-point of thymol blue.[144] Wash the precipitate with 50 ml of the 1 per cent nitrite solution. Then wash thoroughly with warm water, in order to ensure the absence of nitrite, which may dissolve some gold in the presence of acid. Retain the filtrate and washings for the determination of the platinum metals. Add to the mixed precipitate of gold and base metal hydrated oxides a solution of 0·1 N nitric acid, and allow to drain. Wash again with hot water and repeat the selective dissolution with nitric acid until the base metals are removed. The leaching acid can be treated to determine base metals by any conventional method.

Ignite the gold residue and weigh as the metal.

Note—If it is desired, the filtration of the mixed gold and base metals can be accomplished by using porous filtering crucibles with a suitable arrangement to collect the filtrate. It should be noted that the procedure described here is based on the assumption that the nitrite precipitation effectively removes gold and separates the palladium. Gilchrist[144] stated that the partial instability of the palladium–nitrite complex at a pH of 8–9 results in the retention of some palladium by the hydrated oxides of the base metals. Furthermore it is stated that the selective dissolution of the base metals to isolate the gold from the mixed precipitate may result in some dissolution of the gold if the nitrite is not removed completely from the mixed precipitate.

In order to recover co-precipitated platinum, rhodium and palladium and the gold in the acid extract of base metal oxides the latter are re-precipitated after an evaporation of the acid extract, dilution, adjustment of the acidity to pH 1·5 (red-orange end-point of thymol blue), addition of sodium nitrite, and neutralization of the boiling solution by sodium hydroxide to the blue end-point of thymol blue (pH 8). The second nitrite filtrate and washings are combined with the first nitrite filtrate, and will contain the platinum metals. The second acid dissolution of the hydrated oxides of the base metals allows the recovery of the traces of gold. This recovered gold is added to the first gold precipitate. This second acid extract is treated with dimethylglyoxime to recover palladium prior to the determination of such base metals as iron, copper, zinc and nickel.

At this stage one may use a choice of procedures for the separation and determination of palladium, platinum, rhodium and iridium.

Holzer and Zaussinger[143] precipitated palladium with dimethylglyoxime, followed by the division of the filtrate into two parts; one part was treated with bromate, and a subsequent hydrolysis was made to produce a separation from platinum. The mixed precipitates of the hydrated oxides of rhodium and iridium were subsequently reduced and weighed as mixed metals. The filtrate from this hydrolysis was used to determine the platinum, in which instance the bromate was destroyed, and the platinum was determined by reduction to metal.

This second part of the divided palladium filtrate was hydrolysed as described for the first part except that the oxides and paper were transferred to a flask, and the paper contents were treated with sulphuric and nitric acids to effect dissolution. The rhodium was then separated by precipitation with titanium(III) chloride and finally precipitated by hydrogen sulphide.

The above procedures, slightly modified, are described below together with the present author's comments concerning certain deficiencies. These comments are interjected after the appropriate sections of the procedure.

After the description of the Holzer and Zaussinger[143] method the present author's preferred procedure is described. This procedure is based on the method used by Gilchrist,[192] but with several modifications.

The determination of palladium. To the filtrate from the nitrite–gold–base metals precipitation add 0·2 M hydrochloric acid to decompose the nitrite, as indicated by the gas evolution. Boil carefully under a cover glass. Add a few drops of a 10 per cent hydrogen peroxide solution to ensure the oxidation of platinum(II) which would otherwise react with dimethylglyoxime to produce a blue complex giving a green tinge to the mixture (Note 1).

Add to the oxidized solution, heated to 60°C, a saturated, boiling, freshly prepared, aqueous solution of dimethylglyoxime. Cool under flowing water, and allow the precipitate to settle for 30 min. Filter through an ashless paper, transfer to a porcelain crucible, and ignite carefully. Reduce the residue in hydrogen, cool in carbon dioxide, and weigh (Note 2). Retain the filtrate and washings for the determination of the remaining platinum metals.

Notes—1. It is claimed that the appearance of the platinum(II) complex is avoided by the use of an aqueous dimethylglyoxime solution rather than an alcoholic solution because the latter may contain a reducing aldehyde. One may doubt this explanation of the contamination, and anyway sodium dimethylglyoximate can be used. With the aqueous solution, however, there is the advantage that on cooling the mixture the excess of reagent remains with the palladium precipitate, but there is the disadvantage that direct weighing is practically eliminated owing to the difficulty in removing the precipitant.

2. This ignition procedure almost invariably yields low results, and the preferred ignition is discussed in Procedure 40.

3. Holzer and Zaussinger recommended a re-precipitation in instances where the palladium dimethylglyoximate is obviously contaminated. The difficulties incidental to this procedure are discussed in Procedure 94.

The precipitation of rhodium and iridium. Boil the filtrate from the palladium dimethylglyoximate precipitation with hydrogen peroxide to decompose the organic constituents, and then divide into measured halves. To the first half add sodium carbonate, neutralizing to pH 7, dilute to 200–400 ml, and add 20 ml of a 10 per cent sodium bromate solution. Heat to 70°C, and add dropwise 10–20 ml of a 10 per cent sodium bromide solution. Heat to boiling for about 30 min, and again add the bromate and bromide (Note 1). Place the mixture on a water bath for about 30 min (Note 2).

Filter the resulting mixed oxides through a suitable paper, and wash thoroughly with a hot 1 per cent ammonium nitrate solution. Transfer to a porcelain crucible, and dry at 110°C. Place the crucible inside a second crucible covered by a mica plate that allows the passage of a hydrogen current. (A rose crucible and tube would also be satisfactory.) Heat in hydrogen at 160–180°C (Note 3). Ignite finally in air, reduce in hydrogen, and cool in carbon dioxide. Leach several times with a dilute solution of hydrochloric or nitric acid, rinse into a small filter, wash well, ignite, reduce, cool in carbon dioxide, and weigh as combined rhodium and iridium metals.

Notes—1. In the absence of bromine the required pH is attained, and boiling is continued for 1 hr to obtain a coagulated precipitate, which settles rapidly.

2. The hydrated iridium oxide forms and coagulates rapidly; the olive-green hydrated rhodium oxide forms more slowly. Its formation is hastened by the addition of a few drops of a 10 per cent carbonate solution following the disappearance of bromine fumes, then neutralizing again with a few drops of dilute hydrochloric acid, and again boiling. Holzer and Zaussinger[143] prefer this method of achieving the required oxidation state and acidity to that of Gilchrist.[192] The present author prefers the Gilchrist method, which is described in Procedure 30.

3. Careful ignition in the presence of ammonium salt, a technique used by Gilchrist, should be equally satisfactory. However, the ignition in hydrogen does encourage accuracy.

The separation of rhodium from iridium. This may be accomplished using the second half of the above palladium filtrate. Repeat the hydrolytic separation of rhodium and iridium as described above for the first half of the palladium filtrate, retaining the filtrate and washings for the determination of platinum. Transfer the filter and the washed precipitate of metal oxides to a 500-ml Erlenmeyer flask. Add 15 ml of concentrated sulphuric acid and a few drops of concentrated nitric acid. Heat to fumes, cool, dilute with a few ml of water, and fume again. Repeat to the complete removal of organic matter. Dilute to 200–300 ml, boil, and add 20–30 ml of titanium(III) chloride, prepared by adding 100 ml of 25 per cent hydrochloric acid to 50 ml of a 20 per cent titanium(III) chloride solution, iron free, boiling for 1 min, and then adding 1·5 l. of boiled water, the solution being stored over carbon dioxide, and allowed to stand for 24 hr before use. Continue boiling to coagulate the precipitated rhodium, and add a few drops of methylene blue to indicate, by its decolourization, the presence of an excess of the titanium salt. Add more of the latter, and boil if required. Expel air from the flask by adding a small amount of sodium carbonate. Place the flask on a steam bath, and allow the rhodium to settle. Filter through a suitable paper, wash with hot water, and transfer the paper and precipitate to a beaker.

Destroy the organic matter and dissolve the residue by using sulphuric and nitric acids as described above, and re-precipitate with titanium(III) chloride. Treat this second rhodium residue and paper with sulphuric and nitric acids to effect dissolution. Then add to the fumed solution 20 ml of 1 : 1 hydrochloric acid, and boil to the appearance of a rose pink (Note 1). Dilute the solution to 200 ml, and add 2–3 g of sulphosalicylic acid to mask the titanium salt. Add a few drops of a bromocresol purple solution, neutralize carefully with sodium carbonate and then with a sodium carbonate solution to obtain a distinct colour change. Filter the solution, and wash the paper thoroughly, the volume being 500–600 ml.

Cover the beaker with a cover glass perforated to allow the passage of hydrogen sulphide. Heat the solution to boiling, and pass a gentle current of hydrogen sulphide through the solution for 30 min. Allow the mixture to stand on a steam bath for a further 30 min. Filter through an 11-cm Whatman No. 42 paper or its equivalent, and wash thoroughly with hot 0·05 N sulphuric acid. Transfer the paper and the rhodium sulphide to a rose crucible, and ignite in a stream of hydrogen. Cool in carbon dioxide, transfer the contents to a 5-cm ashless filter paper, and leach with hot 0·05 M hydrochloric acid. Transfer the paper and residue to a second crucible, ignite in hydrogen, cool in carbon dioxide and weigh as rhodium metal. Subtract this weight from the combined weight of rhodium and iridium, obtained as described above to give the weight of iridium (Note 2).

Notes—1. Attention is directed to the improved method of treating a rhodium sulphate solution, as described in Procedure 87.

2. It should be noted that a method such as this may involve a high error when the proportion of rhodium to iridium is small. In general any of the separations of rhodium and iridium described in Chapter 2 will produce greater accuracy. Holzer and Zaussinger state that if iridium is to be determined directly, the removal of titanium with cupferron as described by Gilchrist[192] is applicable.

The determination of platinum. Platinum may be determined in either of the two filtrates obtained from the hydrolytic separation of rhodium and iridium, or if desired the filtrates may be combined.

Boil the filtrates, and add hydrochloric acid to remove the bromine. Neutralize with sodium carbonate, and add hydrazine hydrochloride to precipitate metallic platinum. Filter through an ashless 11-cm paper, wash well with hot water, and ignite in a current of hydrogen. Cool in carbon dioxide, and leach with hot 0·05 M hydrochloric acid. Again ignite in hydrogen, cool in carbon dioxide, and weigh as the metal.

Note—The platinum in the initial filtrate, after the removal of bromine, may be precipitated by any of the methods described in Chapter 3. Hydrogen sulphide or thiophenol are recommended.

Alternative Procedures

Alternative methods for the determination of gold, palladium, platinum, rhodium and iridium in mixtures of base metals are available. One useful procedure involves a variation of the above method in the techniques of precipitation, and is designed to provide for the determination in dental alloys of silver, tin, gold, indium, copper, zinc, nickel, platinum, palladium, rhodium and iridium, in this order of separation.[144] The procedure described below is a modification of this method and may be used for a variety of materials containing no osmium and ruthenium.

The method is not recommended when the proportions of base metals predominate greatly. For obvious reasons the limits of proportions cannot be stated with assurance. The amounts of platinum metals, however, should be 25–300 mg, with approximately the same amounts of base metals.

This method can be adapted to the liquid remaining after a sulphuric acid–bromate or a perchlorate distillation of osmium and ruthenium. In the latter instance the perchlorate in the solution should be removed by adding a little nitric acid and evaporating to dryness. The residue is treated with *aqua regia*, and the nitric acid destroyed by repeated evaporations with hydrochloric acid. This process should be repeated until the removal of perchloric acid is complete. It is recommended that the evaporation of perchloric acid be carried out in stainless steel chambers designed for this purpose.

With the sulphuric acid–bromate mixture the residual pot liquid must be treated with hydrochloric acid to decompose the bromate. The solution is then fumed with sulphuric acid to remove the chloride, and is diluted with water (see Procedures 30 and 31).

Procedure 30[144]

The separation of gold. Add to the hydrochloric acid solution of the metals (about 100 ml) sufficient 0·1 M sodium hydroxide solution to reach the red end-point of thymol blue (pH 1·2–2·8). Heat to boiling, and add 10 ml of a 10 per cent sodium nitrite solution. Boil the solution to coagulate the gold, and restore the red end-point of thymol blue by adding a sodium hydroxide solution. Add 20 ml of the 10 per cent sodium nitrite solution, and neutralize the hot liquid with the sodium hydroxide solution to reach the blue end-point of thymol blue (pH 8–9·6). Boil the mixture, and if necessary restore the blue end-point with the sodium hydroxide solution. Allow the precipitate of gold and base metals to settle by heating on a steam bath, and filter through an 11-cm Whatman No. 42 paper previously washed with a 1 per cent sodium nitrite solution. Filter the supernatant liquid, wash the residue with the sodium nitrite wash solution, and set aside the filtrate and wash the solution for the separation of platinum from palladium, rhodium and iridium.

Wash the gold–base metal precipitate with hot water to ensure the complete removal of sodium nitrite. Add to the mixture sufficient hot 0·1 M hydrochloric acid to dissolve the base metals, continue this leaching to the complete removal of base metals, and then wash with hot water. Place the filter and the gold precipitate in a porcelain crucible.

Re-precipitate the base metals from the filtrate by the procedure described above. Combine this second nitrite filtrate with the first filtrate for the removal of platinum as described below. Treat the re-precipitated base metals with hydrochloric acid as described previously, and add any small gold residue together with the paper to the first gold precipitate. Ignite to metallic gold, and weigh.

To recover traces of palladium that were associated with the base metal oxides, evaporate the hydrochloric acid extract, dilute, acidify and precipitate with dimethylglyoxime as described below. Add this palladium precipitate to the palladium removed after the separation of platinum.

The separation of platinum. To the platinum metals–sodium nitrite filtrate in a covered beaker cautiously add 6 M hydrochloric acid to destroy the nitrite. Evaporate to dryness on a steam bath. Treat the residue with a few ml of concentrated hydrochloric acid, and evaporate. Repeat this treatment to the complete destruction of nitrogen oxides. Add 1 or 2 ml of concentrated hydrochloric acid, and dilute to 200 ml with water. Heat to boiling, and add 20 ml of a 10 per cent sodium bromate solution. Add slowly a 10 per cent sodium hydrogen carbonate solution, and at the first appearance of a precipitate in the hot solution add the sodium hydrogen carbonate solution by means of a capillary. During this stage observe the pH change by means of a bromocresol purple solution (0·04 per cent), a drop of which is added intermittently to the stirring rod that is so constructed as to provide a glass globule at the end of the rod. With a little practice the required change from yellow to blue is readily detected (Note 1). Add a further 5 ml of sodium bromate solution, boil for a few min, and readjust the pH. Repeat this until the blue of the indicator is permanent.

Filter through a porcelain crucible with a porous filtering medium, A2 grade, and wash well with a hot, neutral, 1 per cent sodium chloride solution. Set the platinum filtrate aside to be combined later with the filtrates from the re-precipitated hydrated oxides. The hydrated oxides need not be removed quantitatively from the beaker although the residue and the wall of the beaker must be washed thoroughly to remove the platinum. Place the filtering crucible in the original beaker. Add to the crucible 1 : 1 hydrochloric acid almost sufficient to fill the crucible. Allow this to drain through the crucible. Add a few ml of water to the crucible, and allow this to drain into the beaker. While holding the crucible with platinum-tipped tongs wash the outside of the crucible with water, and transfer it to a suitable adapter fitted to a small clean suction flask. Add hot 1 : 1 hydrochloric acid, and allow it to drain. Wash again with water, and repeat to the complete removal of platinum metals solution. Transfer the liquid in the suction flask to the main solution of the hydrated oxides contained in the original beaker, and wash the flask thoroughly with small amounts of water (Note 2). Re-precipitate the hydrated oxides of the platinum metals as described above, and filter through the filtering crucible (Note 3).

Combine the platinum filtrates, unless the total volumes are excessively great in which instance evaporate singly to appropriate volumes prior to the additions. Add to the combined solutions 10 ml of concentrated hydrochloric acid, and evaporate to dryness on a steam bath. Repeat the additions of hydrochloric acid and the evaporations until the bromate is completely destroyed. Add a few ml of hydrochloric acid to the evaporated residue, dilute to about 100 ml, and filter. Wash the paper with 200 ml of 0·1 M hydrochloric acid.

Now prepare the platinum solution for a precipitation by one of the methods described in Chapter 3. The reagents hydrogen sulphide (Procedure 100) or thiophenol (Procedure 101) are recommended.

Notes—1. It will be noted that the progress of the hydrolysis is associated with a tendency of the solution to become acidic. The success of the platinum metals separation is significantly dependent upon the rate of neutralization so that when the addition of the basic solution is made with sufficient care the precipitation is a very satisfactory one.

2. The filtration of the oxides through filter paper usually involves difficulties with the subsequent dissolution of iridium by the hydrochloric acid leaching solution. The explanation for this persistent retention of iridium by paper is not known.

3. The number of re-precipitations of the hydrated oxides required to remove the platinum will depend upon the relative proportions and the amounts of platinum and palladium, rhodium and iridium. As would be expected, large proportions of the latter three oxides introduce difficulties.

THE DETERMINATION OF PALLADIUM

The solution of the chlorides of palladium, rhodium and iridium is prepared from the mixed hydroxides in the porous filtering crucible. The technique of dissolution is described above.

The selective precipitation of the palladium may be accomplished by one of many reagents and procedures described in Chapter 3. The present author prefers precipitation by dimethylglyoxime. The precipitate may be ignited or directly weighed. If ignition is used, the modified procedure in which the combustion is carried out rapidly with a Meker burner will produce the most accurate results. This method is described in detail in Procedure 94.

In general the palladium dimethylglyoximate is weighed directly. For this purpose the asbestos filtering medium in a Gooch crucible may be used, but the porous porcelain medium is preferable.

THE SEPARATION AND DETERMINATION OF RHODIUM AND IRIDIUM

Appropriate methods for the separation of rhodium from iridium are described in Chapter 2, Section I, and suitable methods for their determination are recorded in the appropriate chapters. Among the suitable methods for mg amounts the present author prefers the separation of rhodium from iridium by a selective precipitation of the former using copper metal, with the subsequent removal of copper from the iridium filtrate by cation-exchange. The details of the method are described in Procedure 8. In principle the procedure involves the addition of powdered copper metal, freshly prepared from copper oxide, to a 1 M hydrochloric acid solution of the mixed metal chlorides. The rhodium is freed from copper by dissolving the metallic precipitate in *aqua regia*, with a chlorination if required, and adding the solution to a cation-exchange column to remove copper. The rhodium effluent is treated to prepare for either a gravimetric or spectrophotometric finish. In the former instance thiobarbituric acid (Procedure 82) is recommended, and in the latter tin(II) (Procedure 158) is recommended.

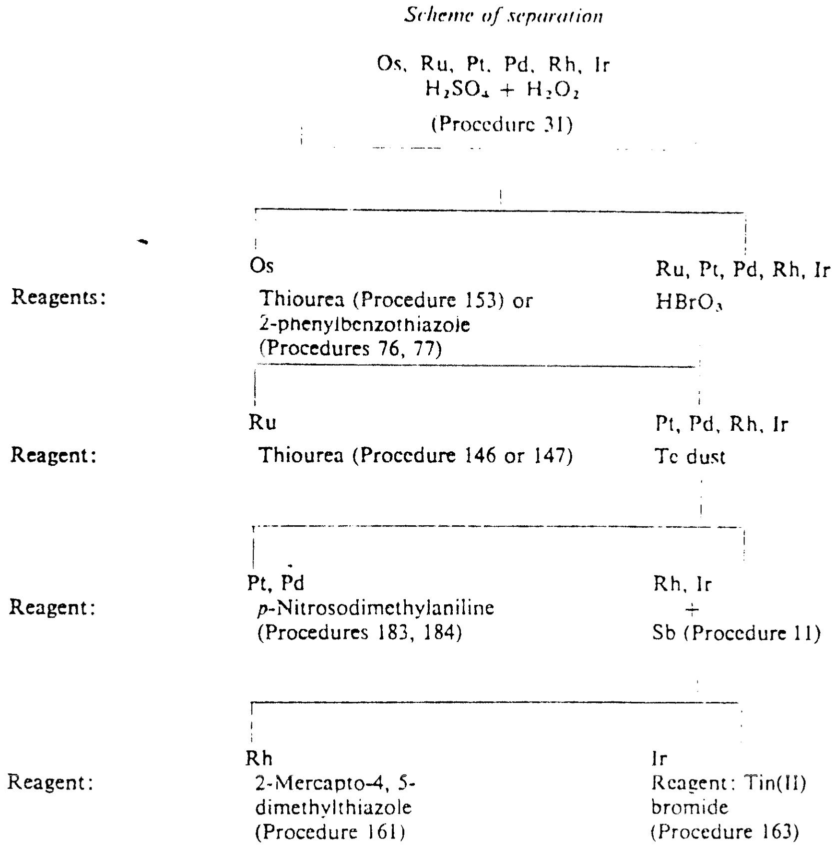

FIG. 2. Scheme of separation of the platinum metals.[53]

The filtrate of iridium and copper chloride is also passed through a cation-exchanger to eliminate copper, and the iridium in the effluent is determined gravimetrically using 2-mercaptobenzothiazole (Procedure 89 or 90) or spectrophotometrically using tin(II) chloride in hydrobromic acid (Procedure 163).

The above method for the separation of rhodium and iridium will allow a determination of the metals on both the macro and micro scales. Some variation in technique would be required for the analysis of μg amounts.

In this instance, for 10–100 μg, the solvent extraction method (Procedure 14) is the most rapid and involves the simplest techniques of all the recorded methods. By this method rhodium is complexed by a tin(II) bromide and is selectively extracted with isoamyl alcohol. Iridium is readily determined in the aqueous extract.

The Determination of
Osmium, Ruthenium, Palladium, Platinum, Rhodium and Iridium

The following procedure was developed specifically for work on the μg scale. The method has been tested for both mg and μg amounts of osmium and ruthenium, but has been proven only for μg amounts of palladium, platinum, rhodium and iridium.

A summary of the method is given in Fig. 2.

Procedure 31[53]

Apparatus. The distillation equipment is described in Chapter 7, Equipment No. 9.

Reagents

Bromic acid. Prepared by adding a stoichiometric quantity of sulphuric acid to a hot, nearly saturated solution of barium bromate. The latter is made[193] by dissolving 345·7 g of potassium bromate in 700 ml of hot water. To this is added a hot solution of 253 g of barium chloride dihydrate in 400 ml of water. Cool, and decant from the crystals. Wash the latter several times with 100-ml portions of cold water. The yield should be about 410 g.

Tellurium powder. Chips of tellurium ground to a fine powder in an agate mortar. The particles should be fine enough to form a suspension in the boiling sample.

Procedure

The separation of osmium. Transfer the mixture of soluble platinum metals salts or the solution of these salts to the distillation flask. If the amount of osmium is sufficiently large to allow a gravimetric finish add to the three receivers respectively 15, 5 and 5 ml of 40 per cent hydrobromic acid. If spectrophotometric determinations of the osmium are to be made, add 15, 5 and 5 ml of a 5 per cent thiourea solution in 1 : 1 ethanol–hydrochloric acid to these receivers (these liquids must be chilled in ice). Add 5 ml of 70 per cent C.P. perchloric acid to the trap and then 30 ml of 18 N sulphuric acid to the distillation flask. Heat the flask, and add dropwise a 10 per cent hydrogen peroxide solution. When the temperature has reached 115°C continue the boiling and the dropwise addition of hydrogen peroxide solution for a further 15 min. A total of about 30 ml of the hydrogen peroxide solution is recommended. During the final 15 min reflux the perchloric acid trap solution in order to transfer the osmium to the receivers. Allow the distillation flask to cool to 30 or 40°C, add 25 ml of water and 5 ml of a 30 per cent hydrogen peroxide solution in this order. Boil the flask and trap solutions for 15 min.

To determine osmium gravimetrically rinse the chilled receivers, containing hydrobromic acid, with 1 : 4 hydrobromic acid into a 250-ml beaker. Add 0·2 g of hydroxylammonium chloride, and place the beaker on a steam bath for 30 min. Precipitate the osmium with sufficient 2-phenylbenzothiazole to provide a supernatant liquid containing at least 0·8 mg of reagent per ml. After at least 24 hr filter the precipitate, reduce, and weigh (Procedure 76).

For a spectrophotometric finish, transfer the chilled thiourea receiving solutions to a 50-ml volumetric flask, rinsing with 1 : 1 ethanol–hydrochloric acid. Make up to volume with the same solution, and filter through an 11-cm. filter paper into the transmittance cell. Use the 1 : 1 ethanol–hydrochloric acid as a blank. Distil and prepare the osmium standards in a manner identical with the sample. The spectrophotometric method is described in Procedure 153.

The determination of ruthenium. After the distillation of osmium, allow the solution in the trap to cool, and dilute to 3 times its volume with water. Add to the trap 10 ml of 1 : 1 sulphuric acid, and to the three receivers 15, 5, and 5 ml of 1 : 1 ethanol–hydrochloric acid. Chill the receiving liquids in ice. Boil the liquid in the distillation flask to destroy the hydrogen peroxide. Add 5 ml of 5 per cent bromic acid, boil for 15 min, then add another 5 ml of the bromic acid to the distilling liquid and also to the trap. Boil both the flask and the trap liquids for 15 min. Boil the solutions in the three receivers for a few sec with the air stream passing through. Add 8 ml of a 5 per cent solution of thiourea in 1 : 1 ethanol–hydrochloric acid to the first receiver and 2 ml to the second and to the third receiver to reduce the bromine and to develop the colour of the ruthenium complex. Place a 600-ml beaker of water at 85°C around each receiver, and continue to warm the solutions for 15 min. Transfer the receiving solution to a 50-ml flask, and make up to volume with 1 : 1 ethanol–hydrochloric acid. Filter into a 2-cm cell, and determine the ruthenium as described in Procedure 146 or 147.

For gravimetric determinations, evaporate the receiving solutions to a few ml, filter, and adjust the acidity and volume for a precipitation by thionalide (Procedure 72).

The separation of platinum and palladium. Transfer the liquid in the distillation flask after the removal of osmium and ruthenium to a suitable beaker, and evaporate and fume to 1 ml. Do not heat excessively at this stage, otherwise the platinum will be complexed to a degree that appreciable proportions will pass into the filtrate from the tellurium precipitation. Cool the solution, and dilute with 1 ml of water. Add 5 ml of concentrated hydrochloric acid, cover with a glass, and boil for 30 min, adding hydrochloric acid to maintain the original volume. Remove the cover glass, and again evaporate carefully to just faint fumes of sulphuric acid. Dilute to 10 ml, cool, add approximately 50 mg of tellurium powder, and boil vigorously for 10 min. Continue heating to reduce the volume to 8 ml, add 3 ml of concentrated hydrochloric acid, a few crystals of sodium metabisulphite ($Na_2S_2O_5$) and 1 drop of 1 per cent hydriodic acid to precipitate tellurium, platinum and palladium (Note 1).

Stir the mixture of platinum, palladium and tellurium for 15 min, and add a few more crystals of sodium metabisulphite. Filter the metals by decantation through a 4-cm paper, and wash well with a 0·2 per cent solution of sodium metabisulphite in 3 M hydrochloric acid, so as to prevent peptizing the tellurium precipitate.

Reserve the filtrate for the rhodium and iridium determinations.

Transfer the filter and residue to a 5-ml silica crucible, and char over a low flame. Then place the crucible and its contents in a suitable Vycor combustion tube, and heat over a Meker flame for 15 min in a stream of hydrogen (Note 2). Continue heating the mixed precipitate in air. Transfer the cold crucible and its contents to a beaker, and add to the crucible a few ml of *aqua regia*. Heat to dissolve and then remove the washed crucible from the beaker with a stirring rod, taking care not to remove any of the metal solution. Transfer the beaker containing the leached solution to a steam bath, add 40 mg of sodium chloride, and evaporate. Repeat the evaporation thrice in the presence of a few ml of hydrochloric acid. Dissolve the dry residue in a few ml of water.

Determine the platinum and palladium by the additive colorimetric method, using *p*-nitrosodimethylaniline as the colour reagent. In this method the solution is adjusted to pH 2·2 and diluted to 10 ml. The method is described in Procedure 185 (Note 3).

Notes—1. The latter two reagents are added to precipitate the tellurium in solution, and also the platinum and palladium, so as to avoid their interference in the subsequent determinations of rhodium and iridium. The reduction of the tellurium by the sulphite is catalysed by the iodide; this species will interfere with the later determination of rhodium, however, if more than a trace is present. The iodide in excess would also produce hydrogen sulphide by reducing the sulphuric acid in the solution.

2. The heating period should ensure the removal of mechanically admixed tellurium, which would otherwise interfere in the determination of palladium and platinum.

3. In order to increase the sensitivity one may use an aqueous solution of *p*-nitrosodimethylaniline rather than the ethanolic solution. The increase in sensitivity is attained at the expense

of colour stability. Because of the low solubility of the reagent its solution must be prepared hot, with the resulting later deposition of a solid. Consequently one must prepare standards for each lot of reagent. For this modification see Procedure 184.

The aqueous solution is prepared by adding 165 mg of the *p*-nitrosodimethylaniline to 100 ml of boiling water, stirring for 30 min, and filtering.

4. The tellurium separation of platinum and palladium from rhodium and iridium may be adversely affected by high proportions of palladium. Under these conditions the palladium seems to catalyse the precipitation of iridium. The present method has been proved for amounts of palladium of the order of 20 μg. With larger amounts the separation of the palladium dimethylglyoximate can be made by extraction with chloroform, as described in Procedure 40, or by the usual precipitation, as described in Procedure 94. In these instances it would be necessary to evaporate the filtrate containing the platinum, rhodium and iridium, and to destroy the organic matter. This can be accomplished by the conventional method with nitric acid and 30 per cent hydrogen peroxide solution or with sulphuric acid and a few drops of nitric acid. If the latter mixture is used care must be exercised to avoid excessive fuming. Furthermore, the final sulphuric acid solution should be boiled with a few ml of concentrated hydrochloric acid. Note that the prior history of a platinum metals solution is of significant influence on subsequent determinations, particularly that of rhodium.

The determination of rhodium (see also Procedure 11). Evaporate the filtrate from the tellurium precipitation of platinum and palladium. Continue the heating to slight fumes only, avoiding temperatures above 200°C. Cool the solution, and dilute to about 8 ml. Add 75 mg of antimony dust of such a fineness as to provide a homogeneous mixture on boiling. Boil vigorously for 30 min, adding water to maintain the volume. Filter through a 4-cm paper, and wash with 5 ml of water. Set the filtrate aside for the determination of iridium. Transfer the paper and precipitate to the beaker used for the separation from iridium, and place it in a muffle furnace. Heat to 400–450°C for 10 hr, which period should produce complete combustion. Cool, and break up the residue with a glass rod. Add 0·5 ml of concentrated sulphuric acid, 1 ml of a 30 per cent hydrogen peroxide solution and 2 ml of concentrated hydrochloric acid. Cover with a ribbed cover glass, and evaporate to 1 ml (Notes 1 and 2).

Add to this rhodium solution 10 ml of concentrated hydrochloric acid, and treat as described in Procedure 161 except add twice the recommended amount of reagent, and boil the solution for 2 hr. Filter the coloured solution before making the absorbance measurements (Note 3).

Notes—1. The spectrophotometric reagent 2-mercapto-4, 5-dimethylthiazole (Procedure 161) is used for the determination of rhodium in preference to tin(II) chloride because with the latter there is a slight darkening due to the small amount of tellurium in the separated rhodium. If the mixture is allowed to stand the tellurium coagulates so that it can be removed by a fine texture filter paper.

2. The tin(II) chloride method (Procedure 157) can be applied providing a standard curve is prepared from samples containing the same amount of dissolved antimony as is used to effect the rhodium separation. This is necessary because the absorbance characteristics of the rhodium complex with stannous chloride are changed in the presence of antimony. If tin(II) chloride is to be used the 1 ml of evaporated solution must be treated with 1 ml of hydrochloric acid, and the solution must then be diluted to 5 ml. The dense precipitate of antimony oxychloride re-dissolves on heating.

3. It should be emphasized that the blank error is high if the solutions are not filtered prior to making absorbance measurements. This error should not exceed 0·4 μg.

The determination of iridium. Transfer the filtrate from the rhodium–antimony precipitation to a 250-ml flask fitted with a dropping tube and a thermometer well. Pass a current of nitrogen through the flask, and heat the contents to fuming. When the temperature reaches 160–200°C add dropwise 75 ml of concentrated hydrochloric acid, the antimony chloride then being readily volatilized (Note 1). Fume to about 1 ml and add a few ml of concentrated hydrochloric acid containing a few drops of hydrogen peroxide solution. For the determination of iridium the tin(II) bromide method is recommended (Procedure 163).

Notes— . Temperatures over 200°C will give low iridium recoveries.

2. An intense red colour may appear during the colour development with the bromide. This colour constituent should disappear when the samples are diluted to the recommended 50 ml. This dilution encourages the dissociation of the bromo complexes.

3. When the quantity of iridium to be determined is large, and therefore a relatively small aliquot is required, the antimony interference is correspondingly reduced, and the distillation can be omitted.

It is emphasized that certain variations in the above procedure may be advisable depending upon the absence of some of the platinum metals. Some of these modifications will be obvious in the absence of such constituents as iridium. Furthermore, the analytical chemist may prefer the introduction of different methods at the stage of the rhodium and iridium separation. Here, particularly, the copper separation (Procedure 8) or the tin(II) bromide extraction method (Procedure 14) may be preferable.

Anyway, the complete determination of the six or seven noble metals is a lengthy procedure; its satisfactory accomplishment requires more than a casual acquaintance with the recommended analytical methods.

The Determination of Noble Metals in Silver Assay Beads

The methods described below are recommended only for silver–noble metal alloys which contain at least 15 parts of silver to 1 of total platinum metals. With much smaller proportions of silver the selective dissolution of silver by nitric or sulphuric acids may be ineffective.

PARTING THE ALLOY

Both sulphuric and nitric acids have been recommended as parting acids for the silver beads which contain platinum metals and gold. The efficient use of nitric acid as a parting acid requires some prior knowledge of the composition of the bead. If the amount of gold present exceeds that of palladium, then most if not all of the palladium can be dissolved, together with the silver, in nitric acid parting media of various strengths. The presence of gold seems to assist the dissolution of palladium and platinum in nitric acid.

Iridium, rhodium and ruthenium may interfere with the dissolution of platinum and palladium in the nitric acid parting solution. With beads containing appreciable proportions of the more insoluble platinum metals and a ratio of 15 parts total platinum metals to 1 of silver, three successive cupellations and partings will not always dissolve the platinum. Beads containing only silver and palladium in a ratio of 15 to 1 require only one parting with nitric acid to dissolve the palladium completely. The presence of platinum in the bead decreases the effectiveness of the first nitric acid treatment on palladium.

The limited action of nitric acid on platinum in silver beads results in the formation of a colloidal suspension and not in a true solution. This can be made evident by allowing the nitric acid parting solution containing platinum to stand for some time: a brown solid will settle out.

In general the residue from the acid treatment must be re-treated two or three times with silver to form the 15 to 1 alloy bead, and subsequently parted, if the complete removal of platinum and palladium is to be effected. Even under these conditions, rhodium and iridium may prevent the complete removal of platinum and palladium. In general gold, rhodium and iridium are not attacked by nitric acid. This should not be interpreted to mean that μg amounts of rhodium will not be corroded. In the absence of appreciable amounts of rhodium and iridium, *aqua regia* will extract gold, platinum and palladium from the nitric acid parting residue.

Parting with nitric acid is one of the most widely used techniques for the analytical treatment of silver–noble metal assay beads. In the present author's opinion, however, it is relatively cumbersome and inaccurate compared to either the high temperature sulphuric acid parting or the modified sulphuric acid method. A procedure for the latter method is described below. Usually, nitric acid is used in the hope of a complete dissolution of silver, platinum and palladium. Toward this end the recommended procedures generally involve multiple partings, with intermediate inquarting* with silver. Tables 11, 12 and 13 indicate the resistance of both palladium and platinum to a nitric acid parting of silver beads containing various noble metals.

Important

TABLE 11. THE PLATINUM AND PALLADIUM IN THE FIRST NITRIC ACID SOLUTION[194]

Sample	Silver added (mg)	Other precious metal added (mg)	Silver recovered (mg)	Loss of silver (mg)	Precious metals in parting acid (mg)
1	675·0	30·0 Au	633·9	41·1	13·9 Pt
2	255·0	2·0 Ru	242·7	12·3	6·3 Pt
3	255·0	2·0 Rh	245·4	9·6	7·9 Pt
4	255·0	2·0 Ir	246·8	8·2	8·6 Pt
5	255·0	2·0 Pd	240·6	14·4	9·5 Pt, 1·5 Pd
6	255·0	—	241·8	13·2	7·0 Pt
7	450·0	15·0 Pd	436·9	13·1	10·7 Pt, 13·9 Pd
8	675·0	30·0 Pd	656·0	19·0	7·1 Pt, 28·6 Pd
9	450·0	15·0 Au	437·2	12·8	12·2 Pt
10	255·0	2·0 Au	241·5	13·5	9·4 Pt
11	225·0	—	213·0	12·0	6·8 Pt
12	675·0	30·0 Au	651·2	23·8	12·2 Pt
13	450·0	15·0 Ir	425·5	24·5	5·6 Pt
14	450·0	15·0 Rh	433·6	16·4	3·8 Pt
15	450·0	15·0 Ru	430·0	20·0	5·1 Pt
16	275·0	15·0 Au	263·1	11·9	12·8 Pt

15·0 mg platinum added in each instance.

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* The term *inquarting* really refers to the process of forming an alloy of 3 parts of silver to 1 of gold. It is used throughout the following discussion, however, to indicate the process of alloying silver and noble metals irrespective of their proportions.

TABLE 12. THE PLATINUM AND PALLADIUM IN THE SECOND NITRIC ACID SOLUTION[194]

Sample	Precious metals left after first parting (mg)	Silver added (mg)	Silver recovered (mg)	Loss of silver (mg)	Precious metals in parting acid (mg)
1	31·1	455·0	451·5	3·5	1·0 Pt
2	10·7	170·0	164·4	5·6	5·4 Pt
3	9·1	140·0	129·1	10·9	4·3 Pt
4	8·4	140·0	132·6	7·4	4·0 Pt
5	6·0	95·0	88·4	6·6	3·2 Pt, 0·5 Pd
6	8·0	120·0	107·7	12·3	4·5 Pt
7	5·4	95·0	91·8	3·2	3·6 Pt, 1·0 Pd
8	9·3	155·0	137·5	17·5	4·7 Pt, 1·2 Pd
9	17·8	270·0	258·0	12·0	2·6 Pt
10	7·6	130·0	123·8	6·2	3·7 Pt
11	8·2	125·0	118·7	6·3	5·6 Pt
12	32·8	495·0	483·9	11·1	2·8 Pt
16	17·2	85·0	82·2	2·8	2·1 Pt

TABLE 13. THE PLATINUM AND PALLADIUM IN THE THIRD NITRIC ACID SOLUTION[194]

Sample	Precious metals left after second parting (mg)	Silver added (mg)	Silver recovered (mg)	Loss of silver (mg)	Precious metals in parting acid (mg)	Total Pt and Pd recovered after 3 partings (mg)
2	5·3	85·0	82·8	2·2	3·4 Pt	15·1 Pt
3	4·8	72·0	65·7	6·3	0·1 Pt	12·3 Pt
4	4·4	66·0	65·0	1·0	nil	12·6 Pt
5	2·3	71·0	70·0	1·0	2·2 Pt 0·0 Pd	14·9 Pt 2·0 Pd
6	3·4	55·0	50·8	4·2	3·4 Pt	14·9 Pt
7	0·8	12·0	9·6	2·4	0·7 Pt 0·0 Pd	15·0 Pt 14·9 Pd
8	3·4	80·0	76·6	3·4	1·8 Pt 0·0 Pd	13·6 Pt 29·8 Pd
10	3·9	25·0	24·2	0·8	1·0 Pt	14·1 Pt
11	2·6	40·0	38·2	1·8	2·0 Pt	14·4 Pt

THE NITRIC ACID PARTING OF SILVER–NOBLE METAL BEADS

Procedure 32[194]

Do this

The silver bead should contain at least 15 parts of silver to 1 of total noble metals.

Holding it with forceps, dip the bead into 6 N acetic acid, and then into water. Repeat until the bead's surface is free of non-metallic impurities. Transfer the clean bead to a small beaker or to a large porcelain crucible. Add 25 ml of 1 : 4 nitric acid, and allow the reaction to proceed to completion, as indicated by the evolution of gas. Allow the residue to settle, and transfer the supernatant liquid to a 200-ml beaker. Add to the residue 25 ml of 1 : 1 nitric acid, warm slightly for 15 or 20 min, and again transfer the supernatant liquid to the 200-ml beaker. Repeat this leaching with 25 ml of 2 : 1 nitric acid. Evaporate the combined three parting acids on a steam bath to about 10 ml. Filter the residue, which will contain all of the gold and for practical purposes all of the rhodium and iridium, together with small amounts of platinum and palladium.

Inquart this residue with 15 parts of silver per 1 part of residue, and repeat the whole of the above parting procedure. Repeat the inquarting, cupellation and parting a second time for maximum accuracy. Retain the filtrates.

Note—These procedures will result in a residue of gold, rhodium and iridium effectively free of platinum and palladium, and also give two nitric acid filtrates of silver, platinum and palladium that together with the initial nitric acid parting solutions provide a total of three filtrates. The treatment of these filtrates to isolate silver is described immediately below. For the maximum accuracy, each of the three resulting silver chloride precipitates should be dissolved and re-precipitated to ensure freedom from platinum and particularly from palladium. The analytical chemist may then combine all six filtrates from the silver chloride precipitations and evaporate them, or evaporate singly and mix the solutions at a suitably reduced volume. The residue of gold, rhodium and iridium is treated as described later.

⊛ *The separation of silver.* To the parting acid filtrate add sufficient dilute hydrochloric acid to precipitate the silver chloride. Allow to stand, filter the coagulated silver chloride through a 7-cm filter paper, and wash with a little hot water. Set this filtrate (No. 1) aside. Transfer the filter paper and silver chloride to a 100-ml beaker, add 10 ml of concentrated sulphuric acid, and heat carefully to char the paper. Cool slightly, and add a few drops of fuming nitric acid. Heat carefully to char, cool, and again add a few drops of the nitric acid. Repeat this procedure to obtain a clear and colourless solution. Continue to fume to a moist residue, avoiding excessive temperatures, which will interfere with the subsequent separation of platinum. Add to the moist residue of silver sulphate, etc. 100 ml of hot water, and re-precipitate the silver chloride. Filter, and add this filtrate to filtrate No. 1. Dry the silver chloride at 140 C, and weigh, if this is desired. Evaporate the combined filtrates almost to dryness, and if necessary fume to a few ml at as low a temperature as possible. Add 3 ml of concentrated hydrochloric acid and evaporate. Repeat this 3 times. Add 50 ml of water and, drop by drop, a filtered 10 per cent sodium hydrogen carbonate solution, using bromophenol blue as the indicator. The technique is described in Procedure 30. Add 2 ml of a filtered 10 per cent sodium bromate solution, and boil for 15 min. Add the solution of sodium hydrogen carbonate to reach pH 6, as indicated by bromocresol purple.

Boil for about 15 min and filter the hydrated oxides of palladium and the traces of lead, iron, etc. through a 7-cm filter paper. Dissolve the precipitate with 4 ml of hot 1 : 1 hydrochloric acid, and wash the paper free of solution. Repeat the acid treatment and washings if necessary. Repeat the precipitation of the hydrated oxides of palladium, and combine this second filtrate with the first filtrate from the hydrated oxides for the determination of platinum.

The determination of palladium. Dissolve the brown palladium oxide in 4 ml of hot, 1 : 1 hydrochloric acid, wash well, and dilute the filtrate to 100 ml with water. Precipitate with dimethylglyoxime as described in Procedure 94.

The determination of platinum. Evaporate the two filtrates from the palladium hydrated oxides on a steam bath, and add concentrated hydrochloric acid to destroy the bromate. Continue this treatment to remove bromine, and finally add 150 ml of water. Filter the

solution, and adjust the acidity to that required for a precipitation by thiophenol or hydrogen sulphide as described in Procedures 101 and 100 respectively.

The determination of gold. Add about 5 ml of *aqua regia* to the insoluble from the several parting acid treatments. Warm to dissolve the gold. Repeat the extraction once or twice, and combine the *aqua regia* solutions. Evaporate to remove nitrogen oxides, and prepare the gold solutions for a precipitation by hydroquinone as described in Procedure 105.

The Separation and Determination of Rhodium and Iridium

In principle the separation of rhodium from iridium may appear to be a relatively simple procedure. It is a fact that rhodium metal in various forms, e.g. finely divided, is rather readily soluble in hot concentrated sulphuric acid. However, the rhodium that has been collected by fire assay with lead and subsequently cupelled may resist a quantitative attack by either boiling concentrated sulphuric acid or by fused sodium hydrogen sulphate.

Under rather exceptional circumstances *aqua regia* will attack iridium. This mixed acid has no appreciable effect on cupelled iridium admixed with rhodium. Also, notwithstanding the many published recipes, strong *aqua regia* will not dissolve iridium. None of these methods even approaches a selective separation.

The various effective methods for the dissolution of rhodium and iridium are described in Chapter 2. The available methods for the quantitative corrosion of this final " silver bead insoluble " are

(1) a wet chlorination in a closed system,

(2) an open system chlorination in the presence of sodium chloride, and

(3) a fusion with sodium peroxide in a silver crucible.

The fusion method has been used successfully by the author. The details are included in the description of the sulphuric acid parting method (Procedure 34), but in principle the procedure involves the use of a special thick walled silver crucible, a fusion at dull red heat with sodium peroxide, an extraction by nitric acid of the blue, iridium constituent, and the treatment of the filter paper and the brown rhodium compound with sulphuric and nitric acids. The combined solutions are evaporated, and the rhodium and iridium are precipitated as the hydrated oxides at pH 6, this treatment leaving the silver in solution.

The separation of 100–200 mg of rhodium and iridium may be accomplished by Procedures 8, 12 and 29. For micro amounts the separations by copper (Procedure 8), by antimony powder (Procedure 11) and by solvent extraction (Procedure 14) are recommended.

Rhodium can be determined gravimetrically using hydrogen sulphide (Procedure 87) or thiobarbituric acid (Procedure 82). Iridium can be determined gravimetrically using 2-mercaptobenzothiazole (Procedures 89 and 90).

The recommended colorimetric reagent for rhodium is tin(II) chloride and that for iridium is tin(II) chloride in hydrobromic acid. These methods are described in Procedures 157 and 163 respectively.

THE NITRIC ACID PARTING METHOD NO. 2

A nitric acid parting method followed by chromatographic separations and spectrophotometric determinations was applied by James[195] to silver assay beads containing platinum and palladium. The method requires a standard fire assay, and can be used for a few μg of platinum or palladium. Thus it is applicable to beads obtained from an assay ton of an ore that contains 1·5552 g (1 dwt.*) of platinum per ton of ore.

Procedure 33[195]

Reagents

Concentrated nitric acid.

Hydrochloric acid. C.P. acid passed through an Amberlite IRA-410 column to remove iron, and diluted as required.

Sodium chlorate. A.R., 2 per cent aqueous solution.

Stannous chloride reagent. Dissolve 11·25 g of A.R. stannous chloride in 100 ml of 3·5 M hydrochloric acid.

Thioglycollic acid. A 2·5 per cent aqueous solution.

Chromatography solvent. Pentanol 10 per cent v/v, hydrochloric acid (*d.* 1·18) 30 per cent v/v, Hexone 60 per cent v/v.

Paper. 2·5 cm strips of Whatman No. 1 filter paper.

Apparatus. As in Chapter 7, Equipment No. 26.

Procedure. Transfer the bead to a polished block of hard steel, and flatten it by hammering it carefully with a clean-faced hammer. Place the flake into the bulb of the vessel M described in Chapter 7, Equipment No. 26.

Add 0·5 ml of concentrated nitric acid to the bulb, and place the bulb on a heated sand bath, avoiding heating to the stems of the bulb. When the bead has been parted remove the bulb temporarily from the sand bath, and add 1 ml of concentrated hydrochloric acid to the edge of the bulb. Rotate the bulb to mix the solutions and to dissolve the platinum metals. Return the bulb to the sand bath, and evaporate the solution to < 0·5 ml as determined by up-ending the bulb and allowing the solution to enter the marked tube. Remove the bulb, and while it is still warm add 0·5 ml of the 2 per cent sodium chlorate solution, and mix by carefully rotating and tilting the contents. Then transfer the solution, free from residue, to the graduated stem of the bulb. Place the vessel upright in a suitable rack, and dry the bulb with an infrared lamp. Add 2–5 M hydrochloric acid to the stem to reach the 1·0 ml mark. Rotate and tilt the bulb to dissolve all soluble material.

The chromatographic separation. For routine work it is expedient to prepare a large sheet of graph paper with lines drawn across to indicate the end of the paper strips, the spotting position and the position at which the fold to support the paper when hanging will later be made. The principal graduation marks on the graph paper should be clearly numbered, starting from zero at the spotting position. This facilitates the subsequent reading of such data as is related to solvent front and band travel. The sheet of paper is then tacked to a clean working bench and completely covered with a sheet of polyethylene film.

Place in position a pair of strips of Whatman No. 1 filter paper 1 in. × 18 in. (2·5 cm × 45 cm), for each sample to be separated. Identify the strips by marking them with a pencil at the end remote from that to be spotted. Add 0·05 ml of the solution in the bulb to the strip, distributing it as evenly as possible across the full width of each strip at the spotting position, the solution penetrating to the polyethylene film, but being reabsorbed completely by the paper. Fold appropriately the ends of the paper, and dry by suspending the papers from a line by clothes pegs. In wet weather it may be necessary to dry them in a desiccator.

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* dwt. = pennyweight.

After drying, place each strip into its individual holder (figure N, Equipment No. 26, Chapter 7).

Insert the unit into a tall cylinder, which may be a tall gas jar (figure P, Equipment No. 26). Place in the bottom of the jar about 0·5 in. (1·3 cm) of the solvent mixture. Cover the jar with a lid, and seal by means of a rubber band which may be cut from a bicycle inner tube. Place the jar in a thermostatically controlled temperature compartment maintained at 25°C.

Allow the chromatograms to run overnight. Remove the holder and strips, and lightly mark the solvent front with a pencil. Suspend the strips to dry, and spray one pair with the tin(II) chloride reagent to indicate the position of the platinum band (yellow) and the palladium band (purple).

Place the paired strips in position on the covered graph paper to obtain the necessary information regarding the solvent front and band travel and band width obtained. Cut off the pertinent band positions from the untreated papers and transfer to 5-ml beakers. The sprayed platinum band may also be used for a determination.

To the platinum section add 2 ml of 2–5 M hydrochloric acid. To the palladium papers add 2 ml of 0·5 M hydrochloric acid. Cover the beakers, and place on a steam bath for 15 min. Filter the macerated sections by suction through No. 4 porosity filter funnels into 5-ml standard flasks. Complete the extraction as follows:

For platinum. Rinse the beaker consecutively with 1 ml of the stannous chloride reagent and 1 ml of water, transfer each rinse through the well-packed filter cake, and make up to the mark with water.

For palladium. Rinse the beaker consecutively with 1 ml of the thioglycollic acid solution and 1 ml of water, transfer each rinse through the funnel, and make up to the mark with water.

Transfer each extracted solution to a clean spectrophotometric cell, and read its absorbance as compared to a reagent blank. Use 1-cm cells. Measure the absorbance for platinum at 403 mμ and for palladium at 325mμ. Then read the metal content of each solution from a standard curve in terms of μg per 5 ml of solution.

Note—If one assay ton of sample is used, the assay in dwt. per ton may be obtained by multiplying the figure obtained from the standard curve by 0·4.

THE SULPHURIC ACID PARTING OF SILVER–NOBLE METAL BEADS

A treatment of the silver bead with hot concentrated sulphuric acid has the advantage of dissolving most of the silver, some of the palladium but none of the other metals under consideration if the proper conditions are used. Two procedures are recorded in the literature for the separation and determination of palladium and silver. The more classical method involves an initial removal of silver chloride. The problem here is one of adsorption of palladium. With large proportions of the latter it is strongly adsorbed on the silver chloride precipitate. Whereas it may appear that the reprecipitation of the silver chloride following dissolution with ammonia is an effective method, the practical application of this is associated with an accumulation of salts and with the usual difficulties associated with the presence of ammonia with the platinum metals. The procedure described below incorporates a sulphuric acid parting and an initial removal of palladium from the parting acid as the hydrated oxide.

The Sulphuric Acid Parting Method No. 1

Two methods of applying the sulphuric acid parting have been proposed. In one the parting acid is boiled, and retreatments are used in an attempt to dissolve both silver and palladium completely. The difficulty here is associated with the simultaneous dissolution of some rhodium, platinum and iridium, and with the occasional failure to remove either silver or palladium completely from the main portion of rhodium, iridium and platinum. Thus one must provide for the removal of small amounts of the four platinum metals from both parting acid and insoluble residue. In the presence of ruthenium the separations are further complicated. Osmium is seldom found in the silver bead except in very small traces alloyed perhaps with iridium, etc. In large proportions osmium will cause a violent decomposition of the silver bead. The procedure recorded below provides for a dissolution of minimum quantities of palladium, most of the silver but generally insignificant amounts of rhodium, platinum and iridium.

Procedure 34[115, 142]

Add to the clean bead in a 250-ml beaker, 30–40 ml of 95 per cent sulphuric acid, and heat just sufficiently to ensure a uniform and rapid rate of parting. Heat only for 4–7 min because the complete removal of silver is not necessary. Cool, dilute to about 175 ml with hot water, filter through a quantitative paper and wash thoroughly with hot water (Note 1).

Evaporate the filtrate and fume to 4–5 ml, then dilute to 200 ml. Add 3 ml of a filtered 10 per cent sodium bromate solution, and boil for 25 min. Reduce the acidity to about pH 4 with sodium hydrogen carbonate. Add 5 ml of the sodium bromate solution. Boil for 10–15 min, and now add sodium hydrogen carbonate solution to attain an acidity of pH 6 with bromocresol purple indicator added on the stirring rod as described in Procedure 88. Boil to precipitate and coagulate the brown hydrated palladium dioxide. Filter, wash with freshly boiled distilled water at pH 6 and transfer the paper and precipitate to a 125-ml beaker fitted with a cover glass. Add 5 ml of concentrated sulphuric acid and a few ml of concentrated nitric acid, preferably fuming nitric acid, and heat to fumes of sulphur trioxide. Cool, and repeat both the addition of nitric acid and the fuming to destroy the organic matter, about 5 min being sufficient for this operation. Cool, dilute to 40 ml with water, and add a few drops of hydrochloric acid sufficient to precipitate the silver chloride. Filter and wash the precipitate. If much palladium is present in the bead, or if the parting temperature was excessive, the silver chloride may contain adsorbed palladium. If this is so, re-dissolve the precipitate in sulphuric and nitric acids, and re-precipitate as described in Procedure 32.

The filtrate from the silver chloride precipitation should now contain no more than 4 ml of sulphuric acid per 100 ml of solution. Precipitate the palladium as its dimethylglyoximate, and filter. Set this washed precipitate and paper aside to be added to the palladium dimethylglyoximate recovered from the dissolution of the parting insoluble (the details for this precipitation are described in Procedure 94). Wash thoroughly the residue from the sulphuric parting acid with ammonium acetate and water to remove lead sulphate, etc. Discard these leaching liquids.

Transfer the washed residue and the paper to a 125-ml beaker fitted with a cover glass. Add 30 ml of *aqua regia*, and place on a steam bath for 2 hr. Dilute the solution to 20 ml, filter, and wash with hot water. Set the residue aside for the determination of rhodium and iridium (Note 2).

Add to the *aqua regia* extract 100 mg of sodium chloride, and evaporate to near dryness on a steam bath. Add a few ml of strong hydrochloric acid, and evaporate to remove nitric acid. Repeat this several times, three treatments being possible in 5 min if an excess of hydrochloric acid is avoided. Add 25 ml of water, and filter to remove the silver chloride.

Inexperience with these evaporations sometimes causes small amounts of gold to be baked out. If this occurs, burn the paper and silver chloride precipitate, treat the residue with *aqua regia*, evaporate the solution with three additions of hydrochloric acid, dilute with water, and then add the filtered solution to the first filtrate from the silver chloride precipitation. Acidify the total filtrate of 50–60 ml, and prepare it for the precipitation of gold by hydroquinone, as described in Procedure 105.

Notes—1. The residue contains essentially all the platinum, rhodium, iridium, gold, most of the palladium if much of this metal is present and a small amount of silver. The filtrate contains palladium and silver.

2. The *aqua regia* filtrate should contain practically all of the gold and platinum, and also the palladium unattacked by the sulphuric parting acid.

The determination of palladium. The hydroquinone filtrate from the gold precipitation can usually be treated directly to precipitate palladium dimethylglyoximate. This is filtered through the paper used to collect the palladium complex from the sulphuric acid parting solution. The details of the method are described in Procedure 94.

Note—3. It should be recalled here that where the amount of palladium is of the order of µg, the direct addition of dimethylglyoxime to the gold filtrate may produce no palladium precipitate. This eventuality is dealt with after the dissolution of platinum described below.

A further difficulty with the palladium separation is sometimes caused by the co-precipitation of platinum with the palladium. The oxidation of the mixed complexes by *aqua regia* and the re-precipitation of palladium is ineffective when high accuracy is required. The paper and precipitate should be treated in the usual manner with sulphuric and nitric acids. If much platinum has been carried with the precipitate it sometimes appears as metal after the treatment to destroy organic matter. In this instance the residue is filtered, the paper is ignited, and the residue is treated with *aqua regia*. The nitric acid is then removed with one or two additions of hydrochloric acid, and water is added. This is then filtered into the palladium solution and the latter is diluted to 175 ml. Palladium dimethylglyoximate is then re-precipitated.

The determination of platinum. Evaporate the filtrate and wash liquid from the palladium precipitation to dryness, and fume off all the sulphuric acid. Ignite the residue to an ash by holding the beaker over a Meker burner for 1 min. Add a few ml of *aqua regia* to the cooled beaker, and warm to dissolve the platinum. Evaporate to dryness, and add a few drops of concentrated hydrochloric acid. Evaporate, and repeat to remove the nitric acid. Add about 25 ml of water, filter, and wash to a volume of 100 ml. If there is any evidence of undissolved platinum in the above filtration, burn the paper and its contents, treat the ash with *aqua regia*, remove nitric acid, and filter the aqueous solution into the original platinum solution.

If the gold filtrate obtained from the hydroquinone precipitation showed no evidence of palladium dimethylglyoximate, test for palladium in the platinum solution as follows:

Extract a capillary drop of the platinum solution, and remove the organic matter and nitric acid in the usual manner. Transfer to a spot plate, and add a few drops of a saturated ethanolic solution of 5-*p*-dimethylaminobenzylidenerhodanine. If a definite purple colour is produced the platinum solution should be treated with dimethylglyoxime to remove the small amount of palladium whose presence was indicated.

Determine the platinum gravimetrically with hydrogen sulphide (Procedure 100) or with thiophenol (Procedure 101).

The separation and determination of rhodium and iridium. Place the final residue from the *aqua regia* treatment in a silver crucible, and carefully burn to an ash.

Silver crucibles. The silver crucibles available commercially frequently contain copper; they are prepared from spun silver and will allow about 12 fusions with sodium peroxide. The amount of silver corroded during a 5 min fusion with 1·5 g of sodium peroxide is 0·5 g or more. Thick-walled crucibles can be made by melting pure silver in a nickel crucible of an appropriate size. The metal is then cooled slowly, and cut and drilled to a size suitable for the fusion. Properly made crucibles may allow more than 50 fusions. The dimensions recommended for general work are: height 2 cm, top diam. 2·4 cm, bottom diam. 2·1 cm, wall thickness 0·4 cm.

Add to the black ignited residue in the silver crucible 3 g of sodium peroxide, and maintain at a dull red heat for 10 min (if thin-walled crucibles are used, less time is required to dissolve the residue). Allow the crucible to cool, and transfer it to a 250-ml beaker fitted with a cover. Add water to the crucible. Following dissolution, wash the crucible with water, and carefully transfer it to a small casserole; add sufficient 6 N nitric acid to clean the crucible, and wash it well with water. Transfer the casserole liquid to the original solution of the fusion, and add just sufficient nitric acid to dissolve the silver oxide.

If the heavy brown residue of rhodium oxide persists, filter this, and transfer the paper and residue to a beaker. Treat this with 6–7 ml of sulphuric acid and a few drops of fuming nitric acid to destroy the paper, and transfer the solution to the original beaker.

If only a little rhodium is present, add 6–7 ml of concentrated sulphuric acid directly to the original beaker, and evaporate and fume to 4 ml. Add 175 ml of hot water, and precipitate the hydrated dioxides of rhodium and iridium as directed above for the separation of palladium from the sulphuric acid parting solution. Take care to avoid acidities much above pH 6, otherwise hydrated silver oxide may precipitate (Note 5).

Dissolve the oxides with hydrochloric acid as directed for the dissolution of the palladium dioxide (Note 4).

Notes—4. Here one may encounter the usual difficulty of removing iridium from the filter paper. Careful washing with small portions of hot dilute hydrochloric acid should be satisfactory. If desired, however, the filtration of the oxide may be made with a porous filtering crucible, A2 grade.

5. Avoid the introduction of the sulphuric acid solution to the indicator bottle by means of the capillary used to transfer the indicator to the stirring rod; otherwise the separation of silver salts will result.

The determination of rhodium. Here the analytical chemist may choose one of several methods for the separation and determination of rhodium and iridium. In general the separation of rhodium by the selective precipitation of rhodium by copper, and the subsequent separation of the copper by cation-exchange is recommended. The above two procedures for the analysis of silver assay beads are recommended only for total amounts of platinum metals of the order of 10–200 mg, however, so that the precipitation of rhodium by titanium(III) chloride and the indirect determination of iridium described below is also applicable. The procedure, here described and used by the author with success, is essentially the method proposed by Gilchrist.[119]

Dilute the hydrochloric acid solution of rhodium and iridium to 100·0 ml. Transfer 50·0 ml of this solution to a beaker, dilute to 100 ml, and boil. Add dropwise a 20 per cent solution of titanium(III) chloride until the supernatant liquid appears purple. Continue boiling for 2 min, and filter. Wash the filter and the precipitate with cold 1 N sulphuric acid. Transfer the paper and metal to a 50-ml beaker, and add 2·5 ml of concentrated sulphuric acid and a few drops of fuming nitric acid. Char the paper in the usual manner, and take to heavy fumes. Repeat the additions of nitric acid and fuming until a clear solution is obtained. Wash the walls of the beaker with a small amount of water, and fume again. Dilute to 100 ml, and repeat the precipitation by titanium(III) chloride. Filter, wash, and redissolve the rhodium and paper as before with 2·5 ml of concentrated sulphuric and fuming nitric acids. Carefully wash the walls of the beaker with a few ml of water, and fume again. Add 20 ml of water, 2 ml of concentrated hydrochloric acid, boil for 15 min, and filter. If the residue in the paper suggests the presence of rhodium, treat again with sulphuric and nitric acids, etc. (Note 6). Determine the rhodium gravimetrically with hydrogen sulphide or thiobarbituric acid (Procedures 87 or 82 respectively).

Note—6. When very small amounts of rhodium are present, not an unusual condition with ores, etc., the pink rhodium colour may not appear.

The determination of iridium. The following is an indirect method, and is of course not recommended for less than 2 or 3 mg of iridium if high accuracy is required.

Add to the second 50·0-ml portion of the rhodium–iridium solution 5 ml of a 10 per cent sodium bromate solution. Boil for 20 min (Note 7). Add a filtered 10 per cent solution of sodium hydrogen carbonate to bring the pH of the solution to 4, as indicated externally on the stirring rod by bromophenol blue. Add a few ml of the sodium bromate solution, and boil. Add the sodium hydrogen carbonate solution to obtain a pH of 6, using a 0·04 per cent solution of bromocresol purple as the indicator. Boil to coagulate the hydrated dioxides of rhodium and iridium, and filter through paper, or preferably through a porous porcelain crucible. Wash with a hot 1 per cent ammonium chloride solution. If a porcelain filter is used, add a saturated solution of ammonium chloride to the filtered and washed oxides. If paper is used, transfer the paper and the oxides to a porcelain crucible, and moisten it with the saturated ammonium chloride solution. Ignite very carefully, an indication of a suitable heating rate being the production of a thin line of ammonium chloride vapour during the initial heating process (Note 8). Finally, ignite in air, then in hydrogen. Leach the mixed metals with 2 M hydrochloric acid, transfer to a filter, and wash with hot water. Dry, ignite in air, then in hydrogen, cool in hydrogen, and weigh.

The weight of iridium is the difference between the weight of the combined metals and that of rhodium (Note 9).

Notes—7. If the original liquid was blue it will now turn amber. The identity of the blue constituent is not known.

8. The ammonium chloride is used to prevent deflagration of the hydrated dioxides.

9. As would be expected, high errors may result when the proportion of rhodium is large. The method is of acceptable value when the proportion of metals are roughly comparable.

The Sulphuric Acid Parting Method No. 2

A new procedure for the determination of platinum, palladium and gold in silver beads was proposed by Barefoot and Beamish.[196] The method requires standard methods of determination for each constituent but the order of separation of silver, gold and palladium is reversed. After the modified parting method of the bead using sulphuric acid (Procedure 34), palladium is removed from the acid parting solution as its dimethylglyoximate, followed by silver if the determination of the latter is required. The parting residue is dissolved in *aqua regia*, and then palladium is removed as its dimethylglyoximate, followed by gold by using hydroquinone, then platinum by using zinc. The *aqua regia* insoluble, containing rhodium and iridium, may be chlorinated according to Procedure 8, etc., and rhodium and iridium separated by Procedures 8 or 14. For good accuracy it is desirable to produce a blank silver bead by simultaneous fusion with lead. The full procedure should be applied to the blank bead, and the blanks subtracted at the appropriate places. This blank helps to account for

(1) the ash content of filter papers when these are burned,
(2) the presence of silica resulting from the corrosion of laboratory glassware by the chemicals used in the analysis, and
(3) the presence of small quantities of impurities in the chemicals.

The time required to complete an analysis can be reduced by arranging a series of weighings which result in the determination of one constituent by differences.

Procedure 35[196]

Clean the silver bead by brushing it with a fine brush, then dipping it in acetic acid, as described in Procedure 32. Transfer the bead to a 50-ml beaker, add 2 ml of concentrated sulphuric acid, and heat carefully on a hot plate until the rapid evolution of bubbles ceases and the solution begins to turn orange, thus indicating the presence of palladium. Avoid continued heating that may result in some dissolution of platinum. Remove the beaker from the hot plate, and cool to room temperature. Add 25 ml of cold water, and filter through a 7-cm Whatman No. 42 filter paper. Transfer the residue to the filter, and wash with 50 ml of hot water. Combine the wash water and the filtrate in a 150-ml beaker. Set this solution *A* aside for the determination of palladium. Wash the parting residue 5 times with a hot 20 per cent ammonium acetate solution, and then 3 times with hot water. Discard these washings.

Palladium. Dilute filtrate *A* to 100 ml with chloride-free distilled water. Add 3 ml of a 1 per cent aqueous solution of sodium dimethylglyoximate, cool immediately to about 10 C and stand for 30 min. Transfer immediately the palladium dimethylglyoximate to a 7-cm Whatman No. 42 filter paper, and wash with 75 ml of hot water. Dry the filter under a lamp, transfer to a porcelain microcrucible, and treat with 6 drops of mixed acids, prepared by mixing 3 volumes of concentrated sulphuric acid, 3 volumes of nitric acid and 2 volumes of water, this treatment allowing the subsequent ignition of the precipitate without any loss of palladium. Heat the crucible slowly in a muffle furnace to char the contents. Then raise the temperature to 800°C, and ignite for 30 min. Cool, then heat in hydrogen, cool in nitrogen, and weigh as palladium metal. Subtract a blank at this stage.

Notes—1. The palladium may contain μg amounts of silver which are accounted for by the blank. This contamination is the result of chloride ion in the distilled water.

2. If desired the silver in the parting acid may be determined after the removal of the palladium. The above reversed procedure is preferred to the usual initial precipitation of silver followed by that of palladium dimethylglyoximate, because silver chloride is particularly susceptible to contamination by palladium.

3. The amount of palladium that escapes precipitation by the above procedure should not exceed a few μg.

The treatment of the parting insoluble. Transfer the filter and parting residue, partially dried, to a tared porcelain microcrucible. Heat slowly in a muffle furnace at about 500°C for 1·5 hr. Cool, heat in hydrogen for 5 min, cool in nitrogen, and weigh (Note 4). Transfer this residue to a 50-ml beaker, add 5 ml of *aqua regia*, cover the beaker, and place it on a steam bath for 1 hr. Add 5 drops of *aqua regia* to the crucible, place the crucible in a covered beaker, and heat on a steam bath for 30 min. After this digestion period wash the contents of the crucible into the main *aqua regia* extract, and dilute to 15 ml. Filter through a 7-cm Whatman No. 42 filter paper, and retain the filtrate in a 50-ml beaker. Transfer the solids to the filter, and wash with 10–15 ml of hot water. Combine the washings and filtrate. Reserve the filter and residue *B* which is used as described below.

To the filtrate add 0·1 g of sodium chloride, and evaporate on a steam bath to a moist residue, avoiding any drying or baking. Treat the moist salts 4 times with 3 or 4 drops of concentrated hydrochloric acid, with careful evaporations between the additions. Dissolve the salts in 10 ml of 0·1 M hydrochloric acid and 10 ml of water, and heat on a steam bath to coagulate the small quantity of silver chloride. Filter this through the above filter containing residue *B*, and wash with 50 ml of water. Place the filter and residue *B* in the original crucible, and heat slowly to 600°C. Cool the crucible, heat in hydrogen, cool in nitrogen and weigh as before. Subtract the blank. The resulting weight represents the quantity of silver and *aqua regia* insolubles, including rhodium and iridium, in the original parting residue. Subtract this weight from the total weight of the sulphuric acid parting residue to obtain the combined weight of palladium, gold and platinum not dissolved in the sulphuric acid parting solution. Add the weight of palladium in the parting acid to obtain the combined weight of platinum, gold and palladium present in the bead (Note 5).

Notes—4. After the subtraction of the blank this weight is made up of platinum, gold, rhodium, iridium, undissolved palladium, silver and a small quantity of other insolubles.

5. This technique has proved to provide accurate results as indicated by salted samples.

The separation of palladium from gold and platinum. Add slowly and with stirring to the filtrate from the above silver chloride filtration 10 ml of 0·1 M hydrochloric acid, 1 drop of nitric acid and 2 ml of a 1 per cent aqueous solution of sodium dimethylglyoximate. Chill for 30 min at 10 C, then filter immediately through a 7-cm Whatman No. 42 filter paper. Retain the filtrate in a 250-ml beaker. Wash the palladium dimethylglyoximate with 80–90 ml of hot water, adding the washings to the filtrate. Determine the palladium as previously described. This palladium will show only insignificant contamination by gold and none by platinum.

The separation of gold and platinum. To the palladium filtrate add immediately 1 ml of concentrated hydrochloric acid per 100 ml of filtrate. The solution should be 0·1 M in hydrochloric acid. Heat to boiling, and add dropwise 3 ml of a freshly prepared 1 per cent aqueous solution of hydroquinone, stirring continuously. Boil for 15 min, place on a steam bath for 30 min to coagulate the gold precipitate, cool, and filter immediately through a double filter composed of a 5·5-cm Whatman No. 44 filter paper superimposed on a 7-cm No. 42 paper. Transfer the gold to the filter with the aid of small sections of filter paper. Wash the precipitate with 40 ml of hot water, setting aside the filtrate and washings for the determination of platinum. Partially dry the filter and residue, place in a tared microcrucible, and ignite in a muffle furnace. Cool, weigh, and subtract the blank. This gold should reveal no significant contamination by platinum.

The determination of platinum. Evaporate the filtrate from the gold precipitation to 80 ml, and adjust the pH to 1·3 by means of a 1 N sodium hydroxide solution. Determine platinum as described in Procedure 103.

Note—6. As stated above, it is possible to obtain the weight of platinum by difference; however, if there is any doubt as to the accuracy of the results for gold and palladium, the determination of platinum should be carried out. Table 14 indicates the accuracy which can be obtained by the above method. Expts. 12–15 record the results of the analysis of a solution of palladium, gold and platinum prepared by mixing known volumes of standard solutions.

The determination of rhodium and iridium. The published procedure does not include directions for the determination of rhodium and iridium. This analysis, however, is readily made by chlorination and the subsequent separations, as described in Procedure 8. Attention should be paid to the identity of the constituents which contaminate the *aqua regia* insoluble. Associated base metals such as copper, iron and nickel are readily removed as directed in Procedure 8, and the appropriate treatment of the chlorinated residue will remove silica.

THE SOLVENT EXTRACTION OF GOLD, PALLADIUM, PLATINUM AND SILVER BY DITHIZONE

For the consecutive determination of palladium, gold, platinum and silver in silver assay beads, Young[156] used a combination of extractive and volumetric techniques. The method involves a sulphuric acid or *aqua regia* parting of the bead and a selective extraction of palladium dimethylglyoximate by chloroform from the acid parting solution. The palladium is then determined by a titration with dithizone in carbon tetrachloride. The *aqua regia* solution of the parting acid residue is prepared for titration of the gold with the dithizone–carbon tetrachloride titrant, and subsequently divalent platinum is similarly determined.

The method is rapid and provides reasonable accuracy. It is applicable to beads containing μg amounts of gold, palladium and platinum. The method should not be used indiscriminately, however. Whereas it has been stated that the remaining platinum metals do not react with dithizone, their presence in significant amounts in the bead may introduce appreciable errors, because of the resistance toward dissolution by *aqua regia* of the platinum and palladium incorporated in the final insoluble. The most accurate methods for assay bead or lead button analysis require the complete dissolution of the bead constituents prior to any separation.

TABLE 14. THE ANALYSIS OF SILVER BEADS FOR PALLADIUM, GOLD AND PLATINUM[196]

Expt. No.	Metals taken†			Metals found					
	Palladium (mg)	Gold (mg)	Platinum (mg)	Palladium (mg)			Gold (mg)	Platinum (mg)	
				Parting acid	Residue	Total		By analysis	By difference
1	2·98	...	...	2·98		2·98			
2	2·71	...	...	2·70		2·70			
3	2·33	...	...	2·27		2·27			
4	...	2·13	3·86		Total wt. of Au + Pt — —			6·58	Error = +0·59
5	...	0·85	1·23		Total wt. of Au + Pt — —			2·28	Error = +0·20
6*	...	2·89	4·25				2·84		4·21
7*	...	1·41	1·24				1·41		1·17
8*	1·30	1·65	2·97	0·79	Total wt. Pt, Au — — Pd in residue			5·05	Error = −0·08
9*	1·07	1·48	3·01	0·65	Total wt. Pt, Au — — Pd in residue			4·89	Error = −0·02
10*	1·42	0·75	2·37	0·28	1·14	1·42	0·74	2·42	2·43
11*	0·74	1·07	1·64	0·22	0·54	0·76	1·10	1·64	1·62
12	0·71	0·98	1·99			0·75	1·01	2·04	
13	0·71	0·98	1·99			0·74	0·97	2·03	
14	0·71	0·98	1·99			0·72	1·00		
15	0·71	0·98	1·99			0·75	0·99		

* 0·1 mg Rh + Ir present in the silver bead.

† Expts. 1–11, weight of silver taken = 0·1 g.

The Determination of Gold, Palladium and Platinum in Silver Beads Using Dithizone

Procedure 36[156]

Reagents

Dithizone solutions. (*a*) Concentrated stock solution: Stir thoroughly 45 mg of dithizone (diphenylthiocarbazone) powder with 200 ml of carbon tetrachloride, and filter into a 250-ml separatory funnel. Cover with 30–40 ml of sulphurous acid solution.

(*b*) Dilute standard solution: Dilute the stock dithizone solution 10 times with carbon tetrachloride, and standardize against weighed quantities of gold, palladium and platinum by the procedures described below. The solutions may conveniently contain 0·01–0·02 mg of gold, palladium or platinum per ml, and the factors of the dilute standard dithizone solution will be approximately 1 ml ≅ 0·01 mg of gold or platinum and 0·05 mg of palladium.

The standard metal solutions can be made by dissolving the metals in *aqua regia*, evaporating to dryness, taking up in hydrochloric acid, and diluting to appropriate volumes so that the hydrochloric acid concentration is about 1 per cent.

Stannous chloride. Dissolve 80 g of $SnCl_2 \cdot 2H_2O$ in 180 ml of warm hydrochloric acid, and dilute with 300 ml of water. Place a stick of tin in the bottle to keep the solution in the reduced state.

Procedure. Weigh the silver bead if the weight of silver is required, in which instance it is determined by the difference between the combined weight of gold, platinum and palladium and the weight of the bead. Transfer the bead to a 50-ml beaker, add 5 ml of 1 : 1 sulphuric acid, and fume strongly on a hot plate. In favourable instances the palladium and silver will dissolve, and the gold and platinum will remain as a residue. In those instances where parting is incomplete, apply the alternative procedure described below.

Cool, carefully dilute with water, and separate the soluble silver and palladium from the remaining metals by decanting the solution into a 100-ml separatory funnel. Wash the insoluble residue with water by decantation. If the gold and insoluble platinum metals are so finely divided that it is impossible to separate and wash by decantation, filter through a small Whatman No. 40 paper containing pulp; wash, dry, and ignite the paper and residue in a small porcelain crucible.

To the solution containing the silver and palladium, in about 50 ml in the separatory funnel, add 2 ml of a 1 per cent aqueous solution of sodium dimethylglyoximate. Stand for 10 min, shaking the separatory funnel occasionally to hasten the reaction. Extract the palladium dimethylglyoximate by shaking twice with 4–5-ml portions of chloroform and drawing off the lower layer into a 50-ml beaker. Evaporate the chloroform by placing the beaker on the edge of a hot plate, add 3–4 ml of hydrochloric acid and 2–3 ml of nitric acid, and evaporate to dryness.

Dissolve the palladium in 5 ml of hydrochloric acid with gentle heating, cool, and transfer the solution to a 50-ml separatory funnel. Rinse the beaker with 15 ml of water so that the final concentration of hydrochloric acid is 25 per cent. Add 0·2 ml of stannous chloride solution, and run in the standard dithizone solution in small portions from a 10-ml burette, shaking vigorously between additions, and withdrawing the lower layer from the separatory funnel. When all the palladium has been extracted the carbon tetrachloride layer in the funnel changes from the dull olive-green of palladium dithizonate to the unmistakable brilliant emerald green of dithizone.

Notes—1. The volume of dithizone solution required to extract the palladium is the measure of the quantity of the latter present.

If the palladium titration shows a colour change from olive-green to *yellow* near the end point it is probable that the reducing action of the stannous chloride has been exhausted and the yellow oxidation product of dithizone is appearing. The addition of a drop or two of stannous chloride will restore the true green colour of unchanged dithizone or the grey-green of palladium dithizonate.

2. The dithizone is standardized against known quantities of palladium by the procedure used for the sample. The usual precautions regarding cleanliness of glassware and reagent blanks, which apply to all dithizone procedures, must be observed.

3. By a simple modification of the above procedure, palladium may be determined not only in the presence of silver, but also in the presence of gold and platinum. This is of importance, for instance, where the method used to decompose the sample, or to part the assay bead, leaves gold, platinum and most of the palladium unattacked.

Dissolve the mixed metals in dilute *aqua regia*, and to the resulting solution containing silver, gold, platinum, palladium, etc., and about 0·2 ml of hydrochloric acid and 0·1 ml of nitric acid in a volume of 10 ml, add 2 ml of dimethylglyoxime solution, and proceed as described above. The presence of the small quantity of nitric acid prevents the precipitation of gold and the co-precipitation of platinum with the palladium dimethylglyoximate. After the withdrawal of the two chloroform extractions, retain the upper layer in the separatory funnel for the determination of the gold and platinum as described below.

Gold. Dissolve in *aqua regia* the residue of gold and platinum obtained in parting the assay bead, evaporate the resulting solution to dryness, and take up the chlorides in the minimum quantity of hydrochloric acid. Dilute this solution, or the solution of gold and platinum from which palladium has been removed by extraction with dimethylglyoxime and chloroform as described above, to 10–15 ml in a 50-ml separatory funnel, add 0·2 ml of hydrochloric acid and 0·1 ml of a 10 per cent sodium bromide solution (Note 4), and titrate with a standard dithizone solution (Note 6) as in the palladium analysis, adding 0·2-ml portions at a time, shaking vigorously (Note 5) until the lower layer shows the yellow colour of gold dithizonate, and then withdrawing the layer as for palladium. Continue the additions, shaking and drawing off until the dithizone layer remains green. This indicates that all the gold has been extracted.

4. The addition of sodium bromide prevents the interference of silver, which if present, would also give a yellow dithizonate.

5. Excessively long shaking may cause a slight fading of the dithizone colour at the end-point in the gold titration; reducing agents must be absent in order to keep any platinum present in the platinic state.

6. The dithizone is standardized against a known gold solution under the same conditions.

Platinum. After removing gold, as described above, and drawing off any excess of dithizone from the separatory funnel, add sufficient hydrochloric acid to bring the acidity to 25 per cent that of concentrated acid, and then add 0·2–0·3 ml of stannous chloride solution, shake, and allow to stand for several min. Now titrate the platinum with standard dithizone solution as described above, until the carbon tetrachloride layer no longer acquires the light yellow colour of platinous dithizonate. Determine the titration value of the dithizone solution against a known platinum solution under the same conditions.

7. With materials like assay beads, silver is usually determined by the difference from the initial weight of the bead. The other platinum metals, viz. osmium, ruthenium, rhodium and iridium, do not react with dithizone under the conditions described above. They will, therefore, be counted as silver in any difference calculation unless the gold and platinum metal residues are weighed after the parting of the bead (see discussion of " insoluble " below).

The Determination of Iridium in the Presence of Lead

Each of the available methods for parting silver–noble metal assay beads results in the isolation of what is frequently termed the " insoluble ". Not infrequently, and always without evidence, iridosmine or osmiridium is said to be a constituent of this insoluble. When, if ever, this mineral is present one cannot assume the absence of each of the remaining platinum metals in the insoluble, for these are usually present in many of the large variety of iridosmines. Anyway, any accurate determination of the platinum metals in ores or concentrates should include the complete dissolution of the insoluble, preferably prior to the determination of specific platinum metals (see the discussion prior to Procedure 39).

In general this insoluble will contain rhodium and iridium and possibly traces of other platinum metals associated with one or both of these two metals. In addition to the platinum metals one may invariably expect traces of lead resulting from incomplete cupellations. The removal of lead has proved to be difficult because the usual methods of precipitation are ineffective. Gilchrist was able to isolate 100 mg of lead from approximately 100 mg each of platinum and palladium by adjusting to pH 8 with sodium hydrogen carbonate in the presence of nitrite a boiling solution of lead chloride. The evaporated filtrates showed no evidence of lead when tested with hydrogen sulphide. Barefoot *et al.*[197] were unable thus to separate 1 mg of lead from 10 mg of iridium. In this instance there was no evidence of lead precipitation. The following method is recommended for the separation of 2 mg of lead from at least 10 mg of iridium. The method can also be used to separate lead from platinum, palladium and rhodium. For amounts of each platinum metal of the order of 25 mg or less, however, the positive errors inherent in these hydrolytic precipitations can be appreciable.

Procedure 37[197]

Dissolve the impure iridium metal by any of the methods recommended in Chapter 1. The author recommends either the exposed dry chlorination or the wet chlorination in an enclosed system.

Dilute the hydrochloric acid solution of the impure iridium to 20 ml with water, the pH being about 1 or less. Heat to boiling, and add 5 ml of a 10 per cent sodium nitrite solution for each sample weight of 10 mg or less. Adjust the pH of the hot solution to 6 with a 10 per cent solution of sodium hydrogen carbonate, as indicated externally by a 0·01 per cent solution of bromocresol purple. Add 1 ml of a 0·1 per cent solution of disodium hydrogen phosphate per mg of lead present, and boil for 5 min. In order to coagulate the finely divided lead phosphate, cool the solution, and add 10 ml of 95 per cent ethanol and 1 drop of a 0·5 per cent calcium chloride solution. Place on a steam bath for 2–3 hr.

Filter through a 7-cm quantitative paper, and wash a few times with a 1 per cent sodium nitrite solution adjusted to pH 6. Set aside the filtrate and washings. Add to the filter containing the lead phosphate 2 ml of 6 M hydrochloric acid, allow to drain, and wash several times with water. Collect this extract in the original beaker, and re-precipitate the lead with 5 ml of the sodium nitrite solution but only one half the volume of hydrogen phosphate solution. Filter, and combine the two filtrates from the lead phosphate precipitation. Add 1 ml of 12 M hydrochloric acid, and evaporate the filtrates to near dryness on a steam bath. Add 6 ml of 6 M hydrochloric acid, and again evaporate to a moist residue. Add 2 g of A.R. sodium chloride and 6 ml of 6 M hydrochloric acid, and again evaporate to dryness. Do not overheat the residue, otherwise losses of iridium in its subsequent precipitation may occur.

Dissolve the residue in a few ml of water, add a few drops of 6 M hydrochloric acid, and digest on a steam bath to coagulate the silica. Filter through a small paper, and wash the beaker wall and the residue six times with 0·1 M hydrochloric acid. Precipitate the iridium as the hydrated dioxide as described for rhodium in Procedure 88.

The above procedure should eliminate all but spectrographic traces of lead from the iridium. Table 15 indicates the accuracy which can be expected for mg amounts of iridium precipitated as the hydrated dioxide and weighed as the metal.

An alternative procedure for the determination of iridium in the presence of lead involves precipitation with 2-mercaptobenzothiazole. The method is described in Procedures 89 and 90.

The Determination of Iridium in the Presence of Platinum

Alloys of iridium and platinum are not readily attacked by *aqua regia*. The procedure, utilizing chlorination or fusion, involves a chemical separation and determination of the two constituents. Whereas this may be accomplished readily by an oxidation to form quadrivalent salts of the two metals, in which condition the iridium may be selectively precipitated as the hydrated dioxide, the method is lengthy, and requires considerable experience.

One of the best known methods for the determination of iridium in the presence of platinum and other platinum metals has its origin in the classical procedures developed by Deville and Stas in the middle of the 19th century. In principle the early procedures involved the preparation of a lead alloy by the direct fusion at about 1000°C of the noble metals with lead in a graphite crucible. The alloy was then parted with nitric acid, the residue was treated with *aqua regia*, and the insoluble material was fused with potassium hydroxide and nitrate. From this fused mixture ruthenium was the first to be isolated—by distillation—followed by a treatment of the hot liquid to isolate iridium, iron, silica and gold by a basic hydrolysis. Conventional methods were then used to purify the iridium. This method was examined in detail at the National Bureau of Standards and modified by Gilchrist.[198] It was found that the treatment with *aqua regia* of the lead alloy containing iridium almost invariably produces some dissolution of iridium, whose amounts are unpredictable but sufficiently small to be ignored for most analytical purposes. For high accuracy the iridium must be separated from the *aqua regia* extract of the parting acid residue. The optimum ratio of nitric acid to water was not critical. Strong acid solutions produced a residue that was rather finely divided for effective filtering; a very weak acid (1 : 8) prolonged the parting time.

TABLE 15. THE SEPARATION OF LEAD FROM IRIDIUM USING HYDROGEN PHOSPHATE[197]

Set No.	Iridium taken (mg)	Lead taken (mg)	No. of detns.	Average iridium recovery (mg)	Average deviation from the mean (mg)	Error of average recovery (%)	Test on hydrolytic filtrates*
1	10·28	1	8	10·03	±0·11	−2	Strong colour
2	2·50		2	2·50		0	No colour
3	5·00	1	3	4·95	±0·02	−1	No colour
4	5·00	2	1	5·04		+1	No colour
5	5·00	3	1	4·68		−6	Strong colour
6	4·99	1	2	4·96		−1	Trace of colour
7	4·99	2	4	4·99	±0·02	0	Trace of colour

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*The lithium sulphate–perchloric acid test was used.

Because lead is the classical collector of noble metals in fire assay procedures, some scattered data are available which deal with the behaviour of the noble metals when the alloy containing very high proportions of lead is treated with nitric acid or *aqua regia*.

In these assay procedures it has been determined that reasonable variations in fusion time and minor variations in lead proportions have little effect upon the recovery of noble metals. An inadequate fusion time results in a relative non-homogeneity and very large buttons, e.g. 35–40 g, producing an increasingly finely divided parting residue. In the latter instance there is an increased susceptibility to corrosion of the insoluble by nitric acid or *aqua regia*. With properly prepared lead alloys the addition of *aqua regia* to the parting insoluble will, in general, remove platinum, palladium, gold and such base metals as copper, nickel, etc. With fire assay buttons the *aqua regia* treatment will, in general, remove little ruthenium, osmium or rhodium. Gilchrist[198] found that rhodium was removed from the iridium by *aqua regia*. This difference in finding results, perhaps, from a difference in the character of the rhodium constituents and the difference in the metallurgical history of the parting residue from the lead alloys collected by fusion of natural and artificially prepared materials. Anyway the analysis of alloys of lead and noble metals other than those containing only platinum and iridium, or palladium, platinum and iridium or osmium, is best accomplished following a cupellation to remove the lead.

The method described below is recommended for the determination of iridium only in platinum or palladium alloys; it is not recommended when the latter two noble metals are to be determined along with iridium. The removal of lead from platinum or palladium is not a simple analytical problem, and better methods of analysis are available. In general the author has successfully used the method described below with alloys containing 20 per cent or less of iridium.

It can be readily adapted to the massive forms of alloys such as sheet, wire, etc.

Procedure 38[198]

Crucibles. The graphite crucibles may be constructed from 2 × 2 in. rods cut to lengths of about 3 in., drilled to a depth of 1·5 in. and tapered toward the bottom.

Procedure. Add 0·2 to 1 g of the platinum–iridium alloy to the graphite crucible, and cover with assay lead, about 10 g of granulated or folded lead sheet being sufficient. Fuse for 1 hr at red heat, remove the crucible, and place it on a copper block to cool. Transfer the alloy, cleaned with a camel-hair brush, to a 200-ml beaker. Add 75 ml of 2 N nitric acid, and heat on a steam bath to the complete parting of the lead button. Add an equal volume of water, and allow to settle. Decant through an 11-cm Whatman No. 42 filter paper, and treat the insoluble with portions of hot water each decanted through the paper.

Examine the filtrate for small particles, and re-filter if these are present. Transfer the paper and residue to the beaker containing the bulk of the insoluble, and add 20 ml of water, 6 ml of hydrochloric acid and 2 ml of concentrated nitric acid. Heat the mixture on a steam bath for 2 hr, at which time the residue in the beaker should be distinctly grey. Add an equal volume of water, and filter through a 7-cm Whatman No. 42 filter paper. Wash well with hot water and then with hot 0·1 M hydrochloric acid, then again with hot water. Transfer the paper and metal to a porcelain crucible, ignite carefully in air, then in hydrogen; cool in hydrogen, and weigh as iridium metal.

Note—In the absence of iron the results tend to be a little low as determined by a caustic fusion of the alloy and a subsequent wet analysis. Iron, when present, will appear as an insoluble alloy with the iridium. For the maximum accuracy the iridium should be dissolved, and the iron determined by suitable wet methods. This may be accomplished readily by chlorination and subsequently determining the iridium as described in Procedure 8.

The Analysis of Iridosmines

Before proceeding to the analysis of iridosmines the analytical chemist should become familiar with what little information is recorded about the physical and chemical properties of these complex minerals. Even fewer data are available concerning the mineralogical relationships of the iridosmines.

From the point of view of analysis one should be prepared for the determination of all seven of the noble metals as well as such base metals as iron, copper, nickel, etc. Generally the predominant platinum metals are iridium, osmium and ruthenium. The following is a detailed description of a generally applicable procedure and, because the mineral in some of its forms, e.g. Tasmanian iridosmine, is exceptionally resistant to corrosion, the method of dissolution is recorded in detail.

The apparatus is described in Chapter 7, Equipment No. 11.

Procedure 39[51]

Transfer a few mg of sodium chloride to the positions in the reaction tube indicated in the diagram by *K*, Equipment Nos. 2 and 11. Melt the salt, and rotate the tube to form the coatings as indicated in the above figures. Place the sample in the indicated position *B* with a spatula, and cover with finely powdered sodium chloride.

Add 10 ml of water to the first receiver, and then to each of the remaining receivers add concentrated hydrochloric acid to a depth of 3 cm. Pass chlorine through the tube at *M*, initially at a rapid rate, and then reduce the flow to 1 to 3 bubbles per min. Allow the sulphur dioxide to flow through the aperture M^1, indicated on Equipment No. 11, rapidly at first to remove the chlorine in each receiver, an insufficient rate resulting in a reduction of pressure sufficient to suck the liquids from the second and third receiver into the first receiver. Reduce the flow of sulphur dioxide to about 5 bubbles per min or to a rate sufficient to ensure an excess at all times.

Heat the tube to 700–720°C, and maintain this temperature for several hr. Cool the system, and displace the gases with nitrogen.

Remove the rubber tube leading to the chlorine supply, and detach the second and third receivers. Tilt the reaction tube toward the first receiver, and rinse with diluted hydrochloric acid into the first receiver. Force this acid through the entry orifice *P* using slight pressure supplied by a rubber bulb, heat the tube partly filled with the wash liquid to either dissolve or disintegrate any difficultly soluble sublimate. Repeat the heating and rinsing to the complete removal of the solids. If necessary carry out additional washings with the ignition tube disconnected from the flask and inverted.

Transfer the liquids in the second and third receivers to a beaker, evaporate to a few ml, and then add the remainder to the contents of the first receiver. Pour the solution containing the noble metal salts into the distillation flask described in Equipment No. 9, and boil under reduced pressure to remove most of the sulphur dioxide. Separate the osmium by oxidation with hydrogen peroxide in a sulphuric acid medium, collecting the osmium(VIII) oxide in either hydrobromic acid or in a thiourea–ethanol–hydrochloric acid solution. Then distil the ruthenium from a bromic acid–sulphuric acid medium and collect its volatile oxide in ethanol–hydrochloric acid. These methods[53] are described in Procedure 31.

The resulting pot liquid will contain the remaining noble metals and associated base metals. The latter may include copper, nickel, lead, iron, tin, cobalt, silver, etc. A variety of methods are available for the analysis of this liquid in the distillation flask. For large samples the methods proposed by Holzer and Zaussinger[143] (Procedure 29) or by Gilchrist[142, 144] (Procedure 30) may be used. These procedures involve an isolation of gold and base metals by hydrolysis in the presence of nitrite, in which medium the four platinum metals are complexed. Procedure 30, proposed by Gilchrist, provides for the separation of silver and tin, the collective separation of gold, copper, zinc and nickel and subsequently the platinum metals. The method used by Holzer and Zaussinger is somewhat simpler, and the details are described in Procedure 29.

The analytical chemist should modify the procedure to allow for the type of iridosmine to be analysed.

The two above methods[143, 144] have not been proven for samples of a few mg or less.

The following modification has been used successfully for a few mg of iridosmines containing the platinum metals with iron, copper and nickel, following the distillation of osmium and ruthenium as previously described.

Transfer the sulphuric acid solution in the distillation flask to a 50-ml beaker, and evaporate on a steam bath or at medium heat on a hot plate to about 1 ml. Add 3 ml of water, 5 ml of concentrated hydrochloric acid, and boil for 30 min. Add hydrochloric acid to maintain the volume during the heating. Finally, boil down to 3 ml, add 1·5 g of sodium chloride, and dilute to 30 ml. Transfer the solution to a small Dowex 50 ion-exchange column, and proceed as described in the second exchange separation (Procedure 47).

Evaporate the effluent to about 20 ml, and determine platinum, palladium, rhodium and iridium as described in Procedure 31. Elute the column with 2 M hydrochloric acid, and if desired determine iron, copper and nickel by conventional methods.

Concerning the above chlorinations it has been found that osmium is the most easily attacked of the platinum metals. The reaction begins at a low temperature and proceeds rapidly. Milligram amounts of the metal can be attacked completely in a few min at 575–600°C. A sublimate of osmium forms at various distances from the furnace. That nearest the source of heat is often difficultly soluble in the wash solution, but when the reaction tube containing the wash solution is heated the deposit will come free. This blue-black sublimate of osmium is entirely soluble in the hot sulphuric acid distilling liquid. Concerning ruthenium, quantitative recovery depends upon avoiding any condensation of the chloride on the hotter, glass surface. This means that the sodium chloride coating should remain unbroken and of such an extent that no glass is exposed over the sublimation area. This condition is fulfilled if the dimensions shown in Equipment No. 2, Chapter 7, are fulfilled and the quantity of ruthenium is small.

Coating the inside of the tube avoids the formation of insoluble platinum dichloride. Large amounts of platinum than ruthenium may be quantitatively chlorinated and recovered. Whereas the method of chlorination described above is recommended only for small amounts of the platinum metals there seems to be a good possibility that by modification of the techniques, relatively large amounts of platinum metals can be used. This extension of the method would be assisted by a heating arrangement in which the temperature change along the tube is retarded; of course a heavier layer of sodium chloride would be of assistance.

The Separation of Palladium from Lead Alloys

It is a surprising fact that no proven wet procedure has been recorded for the determination of all of the platinum metals in a lead button, despite the advantage that osmium is thus collected quantitatively and that a greater accuracy can be attained for at least the more insoluble platinum metals, which do not alloy with the silver bead. The latter is a far from satisfactory collector for osmium. Even small amounts of osmium(VIII) oxide are emitted from a silver bead with explosive force, and large amounts will cause a complete and violent disintegration of the bead.

During the parting of the lead button with nitric acid most of the palladium is dissolved, as are traces of platinum. The extent of dissolution of these and other platinum metals has not been recorded, but one may expect that the proportions dissolved will vary with the parting technique, the strength of acid and the metallurgical history of each alloy. The lead-assay button will generally contain small amounts of iron, copper and nickel. Irrespective of the technique of parting, appreciable proportions of palladium are attacked by nitric acid, and the separation of palladium from large proportions of lead is always a necessity.

For amounts of palladium between 10^{-3} and 10^{-6} g one may use solvent extraction by chloroform, followed by a spectrophotometric determination. For larger amounts the selective precipitation by salicylaldoxime is applicable. With the solvent extraction method there is no interference from platinum, nickel and copper. As little as 3 mg of iron prevents the extraction of 60 per cent of the palladium from a sample containing 250 μg of palladium. The interference is masked by the addition of EDTA, 0·5 g of EDTA complexing 50 mg of iron.

Procedure 40[158]

Transfer the clean button to a 250-ml beaker, add 90 ml of 1 : 2 nitric acid, and place on a steam bath until parting is complete. Evaporate to dryness, and add 100 ml of water containing 3 or 4 drops of concentrated nitric acid. Transfer the solution to a 250-ml, pear-shaped separatory funnel, and add 0·5 g of EDTA, and 3 ml of a 1 per cent aqueous solution of sodium dimethylglyoximate. Shake well and allow to stand for 1 hr. Extract the parting solution with four portions of chloroform (50, 25, 15 and 10 ml respectively) (Note 1). Collect the chloroform extracts in a 125-ml conical flask, and evaporate on a steam bath.

Add 12 ml of a 1 : 1 solution of concentrated nitric and sulphuric acids, and evaporate on a hot plate to fumes of sulphur trioxide. Add a few ml of water, and evaporate; repeat this three times. Add 25 ml of water, cool, and filter into a 100-ml volumetric flask. Wash the filter paper well with water. Add the potassium iodide reagent (500 g of potassium iodide and 5 ml of concentrated ammonia per l.), 1 ml per 100 μg of palladium. Add 5 ml of a sodium sulphite solution (1·5 g of anhydrous sodium sulphite in 250 ml of water). Dilute to volume with water (Note 2). Measure the absorbance of the solution at 408 mμ, the optimum range of concentration being 1–10 ppm of palladium metal when the solution is contained in 1-cm cells (Note 3).

Prepare the standard curve from blank lead buttons or the equivalent lead nitrate solution.

Notes—1. Three extractions are usually sufficient but the fourth is included as a precautionary measure. With >0·25 mg of palladium a precipitate of palladium dimethylglyoximate may form, but this does not hinder the extraction.

2. The sulphite effectively prevents the usual development of iodine in acid iodide solutions. The stability of the iodide solution is thus extended to more than 18 hr.

3. In general the iodide method is not a recommended spectrophotometric procedure because a wide variety of constituents will liberate iodine. This method, however, is particularly suitable for the determination of traces of palladium in lead buttons. After solvent extraction the maximum colour develops immediately for amounts of palladium up to 1 mg.

A Gravimetric Determination of Palladium in Lead Alloys

This method is recommended only for lead alloys rich in palladium. In general lead buttons from ores or concentrates will contain μg amounts of palladium so that the spectrophotometric method only is recommended.

Procedure 41[158]

Transfer the lead alloy to a 250-ml beaker, add 90 ml of 1 : 2 nitric acid, and place on a steam bath until parting is complete. Add 50 ml of water, and filter while hot through an 11-cm filter paper. Wash well with hot water, and evaporate the filtrate and washings to dryness on a steam bath. Add 100 ml of water containing a few drops of concentrated nitric acid. Filter while hot to remove any silica, the presence of silica being almost certain if the lead alloy is an assay button.

Add 10 ml of a salicylaldoxime solution to the hot filtrate, the reagent being prepared by making a hot saturated aqueous solution, and filtering it before use. Allow the precipitate to stand on a steam bath for 1 hr. Cool for 30 min, and filter through a 7-cm paper. Clean the beaker well with a small piece of paper, and add the latter to the filter. Partially dry the paper and residue under a heat lamp, fold carefully, and wrap the folded paper in a 5·5-cm paper. Transfer to a Coors 00000 porcelain crucible, and place this crucible inside a larger crucible. Ignite over a Meker burner at full heat without allowing the usual preliminary charring. Reduce the residue in hydrogen over the Meker burner, flush with nitrogen, and cool in the same gas. Transfer the crucible and its contents to a 125-ml beaker, and add 50 ml of *aqua regia*. Wash the palladium salt from the crucible, and rinse well with water. Evaporate to dryness, add a few ml of *aqua regia*, and again evaporate. Repeat the evaporation. Remove the nitric acid by three evaporations with hydrochloric acid, and dissolve the final residue in 8 ml of 1 : 32 hydrochloric acid.

Dilute with 25 ml of water, filter while hot, and wash the residue well with hot water. Dilute the filtrate and washings to 100 ml, and re-precipitate as described above.

Filter the palladium salicylaldoximate on an A2 porosity porcelain filtering crucible, dry at 115°C, and weigh.

Ion-exchange Separations

New methods for the separation of the platinum metals are becoming available. In general these involve separations restricted to specific groups of the six metals. Procedures for the separation of rhodium from iridium by anion- and cation-exchanges are now relatively numerous; the few acceptable methods have been described above. A variety of exchange methods have been proposed for certain separations such as the cationic retention of rhodium in the presence of platinum, palladium and iridium.[127]

THE ION-EXCHANGE SEPARATION OF PLATINUM AND PALLADIUM FROM RHODIUM AND IRIDIUM

A method for the separation of rhodium, iridium, palladium and platinum by using Amberlite IRA-400 was recorded by Berman and McBryde.[128] The four metals were used as their chlorides, and were eluted selectively with various acids. Trivalent rhodium and iridium were successfully eluted with 2 M hydrochloric acid, followed by divalent palladium with 9 M hydrochloric acid. Attempts to elute platinum with 2·4 M perchloric acid resulted in low values. These losses are due to the presence of divalent platinum, produced by the necessary reduction of iridium, and are recoverable from the palladium eluate. Thus the method is applicable to mixtures of rhodium, iridium and platinum or palladium. The subsequent separation of rhodium from iridium is described above in Procedure 12.

The following procedure may be used to separate the platinum and palladium from rhodium with iridium. It is applicable to mg amounts of the four metals and involves the prior isolation of platinum by a modified hydrolytic separation. The method has been tested for amounts of the order of a few hundred μg of each of the four platinum metals but no data are recorded for the application to a few μg. The use of cerium(IV) as a carrier, however, should facilitate the collection of the oxides of rhodium, iridium and palladium.

Procedure 42[128]

Transfer to a 30-ml beaker the platinum metals solution containing μg amounts of each of the four metals. Add 6 mg of sodium chloride, and evaporate to dryness on a steam bath. Dissolve the residue in 1 ml of 2 M hydrochloric acid, and dilute to 5 ml with water. Heat to boiling, and add 5 mg of cerium(IV) sulphate, then 5 ml of a filtered 10 per cent solution of sodium bromate. Add a filtered 10 per cent solution of sodium hydrogen carbonate until the first trace of a permanent precipitate is formed, then add 5 ml more of the sodium bromate solution. Continue the addition of hydrogen carbonate to the completion of precipitation, add 5 ml of the bromate solution, and boil for 10 min. Cool, allow to settle, and filter though an A2 grade porcelain filter crucible. Wash the precipitate with a 0·1 M sodium chloride solution.

Boil the filtrate with a little hydrochloric acid to destroy the bromate, and determine the platinum spectrophotometrically. The methods are recorded in Chapter 4; the tin(II) procedure (No. 179) is recommended.

Transfer the porcelain filtering crucible to a 150-ml beaker, and add a few ml of concentrated hydrochloric acid. Allow the solution of palladium, rhodium and iridium to pass through the crucible, and repeat with another addition of hydrochloric acid. Then wash the crucible clean with hot distilled water containing a few drops of hydrochloric acid, taking care to clean the pores of the crucible with the wash water. Remove the crucible, and evaporate the platinum metals solution to dryness on a steam bath. Add 1 ml of water, and reduce the iridium with a few drops of a 1 per cent hydroxylammonium chloride solution. Transfer the solution to a 3-cm bed of Amberlite IRA-400 in a column of 5 mm internal diam., the 100-mesh resin being previously freed of small particles by shaking with 2 M hydrochloric acid and pouring off the fines (Note 1). Elute the bed with 80 ml of 2 M hydrochloric acid to recover the rhodium and iridium. Then evaporate this effluent to dryness. Redissolve in 2 ml of 0·8 M hydrochloric acid 0·001 M cerium(IV) sulphate. Feed this solution via a dropper on to small columns containing 3-cm beds of Amberlite IRA-400 (Note 1) previously washed with the above cerium(IV) solution. Elute the rhodium with the latter, then recover the iridium from the resin by soxhlet extraction. The details are described in Procedure 12.

After the elution of rhodium and iridium add 50 ml of 9 M hydrochloric acid to elute the palladium. Evaporate this effluent to dryness in the presence of sodium chloride, and determine the palladium by any of the many suitable spectrophotometric methods.

Note—Prepare the beds by washing with 2 M hydrochloric acid. Conversion to the chloride form is ensured by prior stirring for several hr with 2 M hydrochloric acid.

THE ION-EXCHANGE SEPARATION OF PALLADIUM FROM IRIDIUM

A variety of separations of palladium and rhodium from mixtures of the platinum metals has been proposed by MacNevin and co-workers. Whereas certain separations together with procedures are recommended, it should be noted that a combination of these exchange reactions and others recorded elsewhere can accomplish many useful separations.

Initially MacNevin and Crummet[176] treated the anionic chloro complex solutions of palladium, platinum, rhodium and iridium with concentrated ammonia, and passed these solutions through the cation-exchanger Amberlite IR-100. Palladium was quantitatively retained as $[Pd(NH_3)_4]^{2+}$ while rhodium, iridium and platinum passed through the column quantitatively. The addition of acid to the eluate and subsequent passage through the anion-exchanger Dowex 2 resulted in the retention of the three metal chlorides. However, a solution of ammonium chloride and ammonia (0·025 M in each) eluted a mixture of platinum and rhodium with the complete retention of iridium. Here it is not unlikely that the adaptation of Amberlite IRA-400 for the retention of rhodium, iridium and platinum, with the subsequent elution of rhodium and iridium by 2 M hydrochloric acid as described by McBryde (Procedure 42) would have been successful.

The following is a suitable procedure for the separation of mg amounts of palladium and iridium; with some modification the method may prove suitable for more extensive separations.

Procedure 43[177]

The sample should contain not more than 10 mg of each metal.

Evaporate the chloride solution to dryness several times with hydrochloric acid, avoiding overheating during the final evaporation. Add 20 ml of water and 5 ml of concentrated ammonia solution. Stir the mixture, and allow it to pass through the resin Amberlite IR-100 at 10 ml per min (Note 1).

Wash the column with the ammonia–ammonium chloride solution, 50 ml usually being sufficient to remove all the iridium (Note 2).

Evaporate the iridium solution, and prepare for precipitation by 2-mercaptobenzothiazole. The details are described in Procedure 89. Add 50 ml of 1 M hydrochloric acid to elute the palladium, then wash with 50 ml of water. Evaporate the palladium solution, and prepare for precipitation by a suitable reagent as described in Chapter 3.

Notes—1. The resin is prepared by allowing it to stand overnight in a 0·2 M solution of hydrochloric acid. The mixture is stirred and poured into the exchange column previously filled with distilled water. The resin bed is 1 cm^2 × 10 cm.

2. The colour of the eluate may be used as a general guide to indicate the complete removal of iridium. The use of double the volume of wash solution over that required for the disappearance of colour in the eluate provides a wide margin of safety.

The Separation of Rhodium from Platinum, Palladium and Iridium

A potentially useful separation of rhodium from palladium, platinum and iridium is based on the relative ease of formation of cationic rhodium species. The pink form of rhodium is considered to be anionic and the yellow form cationic. MacNevin and McKay[127] prepared the yellow chloride form by adding concentrated sodium hydroxide solution to the pink rhodium chloride solution and then readjusting with hydrochloric acid to pH 3·5.

Under these conditions platinum and iridium retained their anionic form and, while palladium in the basic medium initially became partly cationic, a period of ageing prior to acidification reformed the palladium-containing anion. Concerning each separation of rhodium from palladium, platinum and iridium, however, some leakage of rhodium occurred from the cation-exchanger, this being attributed to the persistence of a small proportion of the pink anionic rhodium species. The addition of hydroquinone to the acid solution of the hydrated dioxide produced a constituent which was retained quantitatively by the cation-exchanger Dowex 50X-8, 20–50 mesh. The proposed procedure for the separation of rhodium from platinum, palladium and iridium was tested for amounts of the order of 10 mg of each metal and does not include the details for the separation and determination of palladium, platinum and iridium in the eluate.

Procedure 44[127]

Transfer the hydrochloric acid solution of rhodium, palladium, platinum and iridium, previously evaporated in the presence of sodium chloride, to a 150-ml beaker. Add to the volume of about 100 ml a 1 per cent aqueous solution of hydroquinone until no further colour change is observed. Add 5 ml of a 1 per cent EDTA solution, boil, and make alkaline with a concentrated solution of sodium hydroxide. Cool the suspension to room temperature, and add 3 M hydrochloric acid to attain a pH of 2·8. Bubble chlorine gas through the solution for 10 min to oxidize the iridium to the quadrivalent state. Add the solution to a column 50 cm × 14 mm containing about 20 g of Dowex 50 X-8 cation-exchange resin in the hydrogen form. Wash the resin with 50 ml of 10 per cent chlorine water to remove the platinum, palladium and iridium. Elute the rhodium with 3 M hydrochloric acid, and prepare the eluate for precipitation by thiobarbituric acid (Procedure 82).

The above method of separating rhodium merits a more extensive investigation.

A method analogous to that described above for the separation of rhodium from platinum was developed by Coufalik and Svach.[199] After dissolving the rhodium–platinum alloy in acid, a 20 per cent sodium hydroxide solution was added until a permanent precipitate was formed and after 10 min the acidity was adjusted to pH 3·5 by adding dilute hydrochloric acid. The solution was then transferred to a column of the strongly basic anion-exchanger OHL. The latter was prepared by immersion in water for 24 hr, and then conversion to the chloride form by hydrochloric acid. The rate of addition to the exchanger was about 2 ml per min. Rhodium was then eluted with 0·2 M hydrochloric acid and finally determined with tin(II) chloride. Whereas this method allows an average recovery of only about 96 per cent of the rhodium, it has some value for routine purposes.

Ion-exchange Separations with Perchloric Acid

The analytical treatment of perchloric acid solutions of platinum, palladium, rhodium and iridium presents an important problem because perchloric acid is one of the most useful reagents for the simultaneous removal of osmium and ruthenium from solutions of the noble metals. Thus, no method has yet been proven for the treatment of the distillation liquid after the removal of osmium and ruthenium. Whereas the removal of perchloric acid is quite feasible and presumably is without danger of explosion in the presence of nitric acid, there remain the problems of disposal of the evaporated acid and the details of the ensuing separations and determinations.

One of the first attempts to use ion-exchange methods for the separation of platinum, palladium, rhodium and iridium involved the conversion of the chlorides of these metals to perchlorates to produce cations of all but platinum. Stevenson *et al.*[174] evaporated the nitric–perchloric acid solution to remove the halide ion and to attain a volume of 0·2–0·5 ml of fuming perchloric acid. This solution was diluted and passed through a Dowex 50 resin, and the resin washed to remove the platinum. Palladium was then stripped with 0·05–0·5 M hydrochloric acid, followed by the slow elution of rhodium by 2 M hydrochloric acid, then iridium with 4–6 M hydrochloric acid. Unfortunately no data were provided. One may hope, however, that this investigation will continue.

The Ion-exchange Separation of Platinum from Palladium, Rhodium, Iridium and Associated Base Metals

The hydroxide form of the basic exchanger Permutit ES has been used by Blasius and Wachtel[175] to separate mg amounts of platinum from each of palladium, rhodium and iridium and from iron, copper and nickel collectively. For amounts of metal of the order of 25–50 mg, 6–8 g of the hydroxide form of Permutit ES was sufficient.

In order to separate platinum from palladium 10–20 ml of the solution of the complex chlorides were added to the resin at 15–20 drops per min. The palladium was eluted with 250-300 ml of 1 N sodium hydroxide, followed by a rinse with 50 ml of distilled water. The platinum was then eluted by 300 ml of 2·5 N nitric acid, and the resin again rinsed with water. The determinations of platinum and palladium were made gravimetrically by conventional methods.

To separate iridium from platinum Blasius and Wachtel[175] treated the weak hydrochloric acid solutions with sodium oxalate to reduce the iridium to the trivalent state. The iridium was eluted by 250 ml of a 1 N sodium hydroxide solution and the platinum again by 2·5 N nitric acid. Iridium and platinum were determined gravimetrically. For iridium the present author recommends 2-mercaptobenzothiazole (Procedure 89). With this reagent the eluate should be evaporated in the presence of hydrochloric acid.

The relative ease of eluting iridium(III) and thus separating iridium from palladium and platinum was also discussed by Kraus *et al.*[200] These authors used the anion-exchange resin Dowex 1, 200–230 mesh. Iridium(IV) was found to be strongly adsorbed over the range of 0·1–11·5 M hydrochloric acid while iridium(III) showed negligible adsorption over the same range. A few data indicated the feasibility of separating platinum and palladium from iridium(III).

For the separation of platinum and rhodium,[175] the chloro complex of rhodium was largely converted by the hydroxide form of the resin to a hydrated oxide, which was eluted with a 1 N sodium hydroxide solution, and the platinum again extracted with nitric acid. Rhodium may be readily converted to the pink chloride form and precipitated by thiobarbituric acid (Procedure 82). The separation of rhodium from iridium was incomplete.

Blasius and Wachtel[175] were also able to use the same anion-exchanger to separate platinum from iron, copper and nickel. Data for the recovery of the base metals were recorded. This method of separation is capable of wider application, and this possibility ought to be explored.

As a result of later and more extensive researches Blasius and Rexin[201] recorded brief procedures for a series of limited separations of palladium, platinum, rhodium and iridium. It should be noted here that none of the descriptions of these separations included data to indicate the efficiency of recovery. The concentrations of the platinum metals were in each instance 2–4 mg of the respective metals in 1 ml of solution. In principle the methods were based on the possibility of adsorption on the exchanger, not only through electrostatic exchange, but also through the *in situ* formation of precipitates and conversions from anionic to neutral and cationic complexes on the exchanger.

With certain separations, e.g. the separation of palladium from rhodium and iridium or from platinum, Amberlite IRC-50, in its acid form, was pretreated with salicylaldoxime, and the resulting palladium complex was eluted with 7 M hydrochloric acid. The effluent of rhodium and iridium or platinum contained traces of palladium. The exchangers applied by the authors were:

(1) Amberlite IR-4B, a weakly basic anion-exchanger, which provided the strongest adsorption of anions;

(2) Permutit ES and Dowex 1, two strongly basic anion-exchangers. With these two exchangers the binding strength of the anions is only partially related to the charges on the anion. The fineness of the exchanger also influences the strength of the exchanger;

(3) Amberlite IRC-50, a weakly acid cation-exchanger, whose sodium or ammonium form will retain palladium and aged rhodium constituents as their hydrated oxides with some leakages of rhodium. The ammonium form will retain only palladium from solutions also containing rhodium, iridium and platinum, previously treated to form neutral ammine and nitrite ammine complexes. Furthermore this resin pretreated with salicylaldoxime will provide the same selective retention of palladium;

(4) Permutit RS; a cation-exchanger which, like Amberlite IRC-50, will retain palladium and rhodium as their hydrated oxides.

Table 16 contains a summary of the analytical applications of the various exchangers.

A number of the proposed methods are particularly worthy of further examination. Some of the proposed exchanger separations for a two platinum metals system would provide few if any advantages over precipitation methods. Furthermore, certain of the proposed procedures fail to provide a complete separation, e.g. the separation of platinum from either rhodium or iridium by Permutit ES.

The Separation of Rhodium from Iridium

Procedure 45[201]

Exchange columns. The counter current columns used are 10–15 cm long and 1–2 cm wide, with fritted disks.

The stock solutions of the chloro complexes are made up to be 0·1 M in hydrochloric acid.

The nitrite complexes are prepared by heating the stock solution with a 25 per cent sodium nitrite solution, and 2 ml being used for 10-20 mg of the respective metal. The chlorohydroxy complex solutions are prepared by the addition of a 1 N sodium hydroxide solution to the acid stock solution to form a 0·1 N basic solution. The quantitative analytical methods used by the authors are unacceptable, and more suitable reagents are recommended in Chapter 3.

TABLE 16. THE SEPARATION OF TWO COMPONENT SYSTEMS[201]

Separation	Applied compounds	Medium	Exchanger	Reaction on the exchanger	Eluant
Rh–Pd	Chloro complexes	0·1 N HCl	Amberlite IRC-50/Na$^+$/NH$_4^+$	Pd: pptd. as oxyhydrate Rh: filtrate	1 N HCl
			Amberlite IRC-50/H$^+$/ Salicylaldoxime	Pd: pptd. as org. complex Rh: filtrate	Conc. HCl
	Hydroxo complexes	0·1 N NaOH	Amberlite IR-4B/Cl$^-$	Pd: pptd. as oxyhydrate Rh: pptd. as oxyhydrate	Dimethylglyoxime + NH$_3$ 1 N CH$_3$COOH
	Nitrito complexes	Neutral	Amberlite IRC-50/NH$_4^+$	Pd: bound as ammine complex Rh: filtrate	1 N HCl
			Permutit ES/OH$^-$/ normally wetted	Pd: bound as nitrito complex Rh: bound as nitrito complex	Ammine complex 1 N HNO$_3$
Rh–Ir	Hydroxo complexes	0·1 N NaOH	Amberlite IR-4B/Cl$^-$	Rh: pptd. as oxyhydrate Ir: bound as hydroxy-chloro complex	1 N CH$_3$COOH 1 N NaOH
Rh–Pt	Chloro complexes	0·1 N HCl	Permutit ES/Cl$^-$/ normally resp. weakly wetted	Rh: bound as chloro complex Pt: bound as chloro complex	2 N HCl Na$_2$SO$_3$–7 N HCl
Pd–Ir	Chloro complexes	0·1 N HCl	Amberlite IRC-50/Na$^+$/NH$_4^+$	Pd: pptd. as oxyhydrate Ir: filtrate	1 N HCl
			Amberlite IRC-50/H$^+$/ Salicylaldoxime	Pd: pptd. as org. complex Ir: filtrate	7 N HCl
			Amberlite IR-4B/Cl$^-$	Pd: bound as chloro complex Ir: bound as chloro complex	Dimethylglyoxime + NH$_3$ 1 N NaOH
	Nitrito complexes	Neutral	Amberlite IRC-50/NH$_4^+$	Pd: bound as ammine complex Ir: filtrate	1 N HCl
			Permutit ES/OH$^-$/normally wetted	Pd: bound as nitrito complex Ir: bound as nitrito complex	NH$_3$ ammine complex 1 N HNO$_3$
Pd–Pt	Chloro complexes	0·1 N HCl	Amberlite IRC-50/Na$^+$/NH$_4^+$	Pd: pptd. as oxyhydrate Pt: filtrate	1 N HCl
			Amberlite IRC-50/H$^+$/ Salicylaldoxime	Pd: pptd. as org. complex Pt: filtrate	7 N HCl
			Permutit ES/Cl$^-$/normally wetted	Pd: bound as chloro complex Pt: bound as chloro complex	1 N NaOH Na$_2$SO$_3$–7 N HCl
	Nitrito complexes	Neutral	Amberlite IRC-50/NH$_4^+$	Pd: bound as ammine complex Pt: filtrate	1 N HCl
Ir–Pt	Chloro complexes	0·1 N HCl	Permutit ES/Cl$^-$/normally resp. weakly wetted	Ir: bound as chloro complex Pt: bound as chloro complex	FeSO$_4$ 7 N HCl Na$_2$SO$_3$ 7 N HCl

For the separation of rhodium from either palladium or iridium the exchanger recommended is Amberlite IR-4B, chloride form. The solutions are prepared as the chlorohydroxy complexes in 0·1 N sodium hydroxide.

Procedure. Transfer 15–20 ml of the sodium hydroxide solution of the two metals to a column of the chloride form of Amberlite IR-4B. Elute the rhodium with 100 ml of 1 N acetic acid. If iridium is the second metal, elute with 100 ml of a 1 N sodium hydroxide solution.

Note—The iridium will contain traces of rhodium.

The separation of palladium from rhodium, iridium or platinum may be accomplished by converting their chloride solution to nitrito complexes, as described above. The ammonium form of Amberlite IRC-50 is used to adsorb selectively the palladium, which is finally eluted with 100 ml of 1 M hydrochloric acid.

In a second method for the separation of palladium from rhodium and iridium but not from platinum the neutral solutions of the nitrito complexes are adsorbed by the hydroxy form of Permutit ES. In this procedure the palladium is eluted with ammonia solution, and either rhodium or iridium with nitric acid.

The same separation can be effected by the acid form of the cation-exchanger IRC-50 when the latter is pretreated with an ethanolic solution of salicylaldoxime. Only the palladium complex is retained; it is then eluted with 7 M hydrochloric acid. There is, however, some leakage of palladium.

Blasius and Rexin[201] included procedures for the separation of palladium, iridium and platinum with either Amberlite IRC-50 (sodium or ammonium form) or the weakly wetted chloride form of Permutit ES. By this method palladium is first removed by the cation-exchanger and eluted with 1 M hydrochloric acid. Rhodium and iridium in the effluent from the palladium adsorption are separated by the anion-exchanger Permutit ES. Iridium is eluted with iron(II) sulphate–7 M hydrochloric acid whereas platinum is eluted with sodium sulphate–7 M hydrochloric acid.

The above cation- and anion-exchangers were also used for the separation of rhodium, palladium and platinum.

For rhodium, iridium and palladium the above authors used the chloride form of the anion-exchanger Amberlite IR-4B. The chloro complexes in solution were converted to the hydroxychloro complexes in 0·1 N sodium hydroxide. Rhodium was first eluted with 1 N acetic acid, then iridium with 1 N sodium hydroxide and finally palladium with an ammoniacal dimethylglyoxime solution.

None of the varieties of exchange methods recorded by Blasius and coworkers can be recommended without some reservations. Notwithstanding the absence of confirmatory data, some of these procedures may find useful applications, perhaps with some modifications, in the preparation of "feeding" solutions or in the character of the eluting reagents.

The Separation of Platinum Metals from Associated Base Metals by Cation-Exchange

Cation-exchange methods for the separation of mg amounts of iron, copper, nickel and lead from the platinum metals have been proposed. Pshenitsyn and co-workers[202] used the exchange resin KU-1 in either the H^+ or Na^+ form for the chloride salts of the base metals and the corresponding chloro complexes of the noble metals. The exchange method was recommended especially for mixtures of base metals with rhodium and iridium. Generally gold, platinum and palladium were isolated by mercurous chloride, then ruthenium by distillation with bromate, then rhodium and iridium were separated from copper, iron, nickel and lead by the cation-exchange resin KU-1. Several procedures were recommended for the separation and determination of rhodium and iridium. This report contains much useful information; a description of one of the methods used for the determination of platinum metals in tailings is described below.

In general the analytical procedures are a peculiar admixture of new and effective, and antiquated and relatively ineffective procedures. The amounts of both platinum metals and base metals are of the order of mg, and the accuracy of recovery is not high. The above authors confirmed the tendency for fresh rhodium solution to assume the cationic condition and for aged solutions to assume the anionic form; they also confirmed the relative difficulty of retaining nickel in the cationic condition. In general the preparations of solutions for the exchange reaction involved an evaporation of the hydrochloric acid solution in the presence of sodium chloride at a pH adjustment between 1–2. The following procedure is designed for the determination of combined platinum, palladium and rhodium in tailings.

Procedure 46[202]

Transfer 1–2 g of the tailings to a 400-ml beaker. Add 50–70 ml of 1 : 1 hydrochloric acid, and heat to slight boiling. Decant through a quantitative filter paper, and retain the liquid. Ignite the paper at as low a temperature as possible, and treat the residue with a second portion of 1 : 1 hydrochloric acid. Transfer the decanted liquid to the first portion. Repeat this 4 times.

Add zinc (see Procedure 103) to the combined decanted liquids, and set the metal precipitate *A* aside to be combined with the residue *B*, insoluble in the later *aqua regia* treatment. To the insoluble residue add 10 ml of 3 : 1 *aqua regia*, heat on a steam bath, filter the residue through a small quantitative paper, and wash with hot 0·1 M hydrochloric acid. Set the *aqua regia* extract *M* aside. Ignite the paper, and roast the residue. Transfer the residue to a gold crucible, and treat with hydrochloric acid to remove silica. Transfer again with hot water to a filter paper, and combine this residue *B* with the zinc precipitate *A*, obtained from the zinc–hydrochloric acid leach. Dry the residue, ignite, transfer to an agate mortar, and grind with 5 times its weight of barium peroxide. Heat the mixture in a corundum crucible at 750–800 C for 2 hr. Cool, and add sufficient 1 : 1 hydrochloric acid to dissolve the melt. Repeat the fusion if necessary.

Combine the solution with the *aqua regia* extract *M*, and evaporate with concentrated hydrochloric acid to coagulate the silica. Repeat the evaporation with hydrochloric acid to remove the oxides of nitrogen. Filter the silica, wash, and add hydrochloric acid until it is 5 per cent by volume. Precipitate by boiling for 30–40 min whilst passing hydrogen sulphide. Filter the sulphide precipitate, wash with 0·1 M hydrochloric acid, and dissolve it in a minimum amount of *aqua regia*. Evaporate on a steam bath in the presence of 1 g of sodium chloride. Moisten the residue with 0·85 ml of concentrated hydrochloric acid, and dilute to 100 ml with water. Check the pH of the solution with methyl violet: it should lie between 1–2. Transfer the solution, at 4–5 ml per min, to a column 1 cm diam. and 35 cm long, containing the H$^+$ or Na$^+$ form of Cationite KU-1, particle diam. 0·5–1 mm.

After thus removing the base metals, again treat the eluate to precipitate the sulphides of platinum, palladium and rhodium, and finally weigh the combined metals after reduction with hydrogen.

Note—Two further adaptations of the above method are described. In one the effluent solution from the exchange column is treated with mercury(I) to remove platinum and palladium simultaneously, and rhodium is determined as its sulphide.

In another, for low-grade tailings, these are treated to remove silica as described above, and the solution is then taken to fumes of sulphur dioxide in the presence of sodium sulphate. The sulphides of platinum, palladium, rhodium and copper are precipitated by using thiourea (see Procedure 91). The sulphide precipitate is dissolved in *aqua regia* and prepared for the Cationite column to remove copper. The three platinum metals are then determined as described in the above adaptation.

THE CATION-EXCHANGE SEPARATION OF PLATINUM METALS FROM LARGE PROPORTIONS OF BASE METALS

The cation-exchanger KU-2 was used by Anisimov *et al.*[203] to separate copper, iron, nickel, lead and zinc from the platinum metals. The material to be analysed was treated with *aqua regia* and finally evaporated with hydrochloric acid. Sodium chloride was added, and the solution was passed through 2 g of the exchanger in a column of 15 mm diam. and 20 cm high, at 50–60 drops per min.

Ion-exchange techniques to provide a concentration of the noble metals sufficient for detection by spectrographic methods are discussed briefly by Brooks and Ahrens.[204] The rocks bearing the traces of platinum metals were treated initially with mineral acids and subsequently by adsorption on anion-exchange columns. The resin was ignited, and tested spectrographically. No quantitative data were included in the report, and whereas the work was incomplete there is importance in the attempt to determine the noble metal content without recourse to fire assay methods.

In a series of publications it has been shown that platinum, palladium, rhodium, iridium and ruthenium in the form of chloro complexes can be separated from large amounts of copper, iron and nickel by selective adsorption of the base metals on the cation-exchanger Dowex 50X-8 (acid form). Specifically, the method has been applied to the base metal collection of the platinum metals by a new fire assay procedure. This assay is described in detail in Procedure 60. The base metal alloys, weighing up to about 35 g, are parted with acids, and even μg amounts of the platinum metals may be accurately recovered from the effluent. The presence of osmium in the collecting button gives no difficulty because the parting procedure involves the use of hydrochloric acid and a final addition of nitric acid, during which process the osmium is removed as the tetroxide. Up to the present time it has been generally assumed that a resin separation of ruthenium or osmium is incomplete, and this has been attributed to such factors as the ease of reduction and particularly to the ease of hydrolysis of the metal salts. There seems little doubt that the latter tendency is the principal explanation for the failure of the exchange separation. Ruthenium and osmium salts form hydrated oxides quantitatively at pH 4. There is some evidence to indicate that ruthenium in a chloride solution at pH 1·5 may fail to pass quantitatively through the cation-exchanger Dowex 50. Many attempts, under these conditions, have yielded 95–98 per cent recovery of ruthenium. On the other hand the recent successful use of the above exchanger for the quantitative separation of ruthenium and osmium from base metals seems to be due to a shift in pH to about 1·0 and the use of freshly prepared solutions. Furthermore, success in achieving complete passage of ruthenium through the cation-exchanger seems also to be assisted by a prior evaporation in the presence of both sodium chloride and hydrochloric acid. This guess is in agreement with other data and with opinions expressed by various authors.[202] Furthermore, the fact that the dissolution of an iron–copper–nickel alloy of ruthenium will produce a solution from which the cation-exchanger fails to retain significant amounts of ruthenium is probably also due to the presence of large amounts of base metal chlorides. All of these data find an explanation in a reduction of the tendency for ruthenium to hydrolyse.

Fragmentary reports have indicated that both anion- and cation-exchange columns have been used to collect ruthenium from mixed constituents. Solutions of Bikini ashes collected on board ship have been subjected to exchange reactions in columns of the cation-exchange resin Dowex 50.[205] An anion-exchange resin Dowex 1 was also used to separate ruthenium from tellurium, caesium and rare earth elements.[206]

The procedure recommended below for the separation of the five platinum metals from base metals is an integration of the procedures used by: Coburn *et al.*[207] to isolate iron, copper and nickel; Marks and Beamish[208] for the separation of rhodium and iridium from base metals; Plummer and Beamish[107] for the separation of platinum and palladium; Zachariasen[209] for the separation of ruthenium.

If gold is present along with platinum, palladium, rhodium, iridium, ruthenium and large amounts of iron, some difficulty is experienced in the complete separation of gold by the cation resin. The cation-exchanger Dowex 50 will allow a quantitative passage of gold when in the form of pure gold chloride, but in the presence of iron there is retention of about 1 per cent of the gold content. This may be due to the reduction to metal in the presence of iron(II) if the latter is a constituent of any equilibrium in the complex solution. The explanation for the small loss is not yet clear.

The success of the procedure described below encourages the prediction that the cation-exchange method may be used for a variety of useful analytical processes such as the separation of noble metals from ores, concentrates, iron meteorites, minerals and other base metal products carrying large or small proportions of noble metals. The role played by osmium is not yet clear, but there is good evidence to suggest that it too may be quantitatively separated along with its noble metal associates. There are few data to support the commonly expressed opinion that the ease of reduction of osmium compounds vitiates against passage through an organic ion-exchanger. One need not use the salts in which osmium exhibits a high valence, and the lower valencies will provide a resistance to reduction comparable to that shown by ruthenium.

Procedure 47[209]

Transfer the alloy of noble metals–iron–copper–nickel to a 600-ml beaker. The weight of alloy should not exceed about 35 g. Add 200 ml of concentrated hydrochloric acid, cover with a clock glass, and place on a steam bath out of direct contact with the steam to avoid an excessive rate of reaction. Allow to stand overnight, and then place in direct contact with the steam for 24 hr. Add carefully 5 ml of concentrated nitric acid, dropwise if necessary, to avoid spattering. After the vigorous reaction has subsided add a further 5 ml of nitric acid. Following the violent reaction, place glass hooks on the beaker edge, and evaporate to dryness on a steam bath. Cool the residue, add 8 ml of concentrated hydrochloric acid, and then small portions of water, 10 ml at a time, in order to dissolve the residue. Adjust the volume to 250 ml with water, filter into a 2 l. flask, and adjust to 1·5 l. with water, the pH now being 1·2–1·5. Add this solution to the column of 20–50 mesh Dowex 50X cation-exchanger. The tower for the solution resulting from the dissolution of a 25 g button should be 70 cm long and 4 cm diam., filled with the exchanger, whose total wet weight should be about 700 g. Use a passage rate of 1·5 l. per hr. Wash the exchanger with water, collect the effluent and washings in a 4-l. beaker, adjust to pH 1·5 with hydrochloric acid, and evaporate on a steam bath to about 50 ml. Transfer the solution to a 150-ml beaker, and evaporate to dryness on a steam bath in the presence of 3–4 ml of a 2 per cent sodium chloride solution. Dissolve the residue in 30 ml of water. Adjust the pH to 1·5 with hydrochloric acid, and transfer the solution to a small tower of Dowex 50X, 4 cm long and 10 mm diam. Wash the column with water adjusted to pH 1·5. Collect the effluent and washings in a beaker of suitable size, and evaporate to dryness in the presence of a few g of sodium chloride. Add concentrated nitric acid and a 30 per cent hydrogen peroxide solution, and evaporate to dryness to remove organic matter. Repeat this oxidation 3 times. Add a few ml of concentrated hydrochloric acid, and evaporate to dryness. Repeat 3 times, then dilute to a suitable volume. The separation and determination of palladium, platinum, rhodium and iridium may be accomplished by a choice of methods. For μg amounts, and in the absence of ruthenium, the chromatographic method recorded in Procedure 50 is recommended. For mg amounts the method recorded in Procedure 51 is suitable. Here one may choose a combination of methods to suit the particular purpose of the analysis.

Chromatographic Separations

THE CHROMATOGRAPHIC SEPARATION OF GOLD, PLATINUM, PALLADIUM AND SILVER

Procedure 48[183]

One drop of the noble metal solution should contain approximately 0·1 mg of each metal.

Weigh the alloy, and transfer it to a 10-ml volumetric flask. Add a few ml of *aqua regia*, and following dissolution add an equal volume of water and make up to volume. Measure an appropriate volume of the solution with a calibrated pipette, and transfer to a small porcelain crucible; evaporate carefully under a lamp to about 1 drop.

Prepare a cylinder of Whatman No. 1 paper, 28 cm high and 26 cm wide. Transfer the drop of the evaporated solution to a position 2·5 cm from the bottom of the cylinder, previously marked with a pencil. Wash the crucible with water added by means of a dropper drawn to a capillary at one end and containing a small rubber bulb at the opposite end. With care the washing can be accomplished with a few drops of water. If necessary the drops on the paper can be evaporated intermittently by careful exposure to a lamp prior to the addition of further drops. Clean a 5-gallon (imperial) crock and place within it a glass dish containing sufficient n-butanol saturated with 1 M hydrochloric acid. Add the n-butanol solution to the bottom of the crock to ensure an atmosphere saturated with the gaseous mixture. Place the cylinder within the glass dish in a position to avoid any direct contact of the stain with the butanol solution. Allow to stand for 20–24 hr (Notes 1 and 2).

Following the 24-hr period, expose the cylinder to ammonia, then to hydrogen sulphide (Note 3).

To determine each constituent, cut out the areas of deposition, transfer each section to a 50-ml beaker, and keep the latter overnight at about 400°C. Add a few drops of *aqua regia* to dissolve the ash, evaporate in the presence of hydrochloric acid to remove nitric acid, and prepare for the desired spectrophotometric method. For silver, treat the ignited ash with nitric acid, the subsequent treatment depending on the method of determination.

Notes—1. On ascent two liquid fronts are observed, one being the front of the dehydrated butanol and the second being the front of the aqueous phase, about 5 cm below the upper front. The aqueous phase has a dark front which does not fade on drying, and is convenient to use as a reference for R_f values. Extracted substanses in the upper butanol layer will thus have an R_f value greater than unity.

2. Silver is deposited at the place where the drop is applied ($R_f = 0$). Copper moves slowly, ($R_f = 0·1$). Palladium has an R_f of 0·6, platinum an R_f of 0·72–0·80 and gold an R_f of 1·05–1·13.

3. Silver and copper produce black spots which fade in about 1 hr. The spots of gold and platinum are yellow-brown and that of palladium orange-brown. A very small amount of gold is reduced; it leaves a trail of purple colloidal gold. This small amount is usually insignificant. The spots of platinum, palladium and gold deepen on storage and can be kept as permanent records of the analyses.

The Chromatographic Separation of Rhodium, Iridium, Palladium and Platinum

The most complete chromatographic methods yet recorded for rhodium, iridium, palladium and platinum were developed by Kember and Wells,[190] and co-workers. These methods and their modifications will find increasing applications where μg amounts of the noble metals are to be determined, and particularly when traces of base metals are associated with noble metals. Despite this potential usefulness, however, one cannot use the methods indiscriminately. Methods of dissolution and the proportions of the metals present can be significant.

Some conception of the limitations imposed by the separational methods were discussed by Kember and Wells. They recorded the following data:

Platinum. Qualitative tests with the hexone solvent (see later) show that when more than 1·5 mg of platinum are present on the strip severe trailing of the metal occurs, particularly along the extreme edges. With the n-butanol solvents less platinum can be tolerated, owing to the closeness of the platinum and palladium bands. Excellent separations are obtained with the hexone solvent on a mixture of platinum (1·4 mg of platinum on the strip) containing about 0·1 per cent each of rhodium and palladium.

Palladium. The width of the palladium band when the hexone solvent is used increases if the quantity of palladium exceeds 200 μg, but unlike the other metals, both the leading and trailing edges of the band remain very sharp. A mixture containing palladium (3 mg of palladium on the strip) and about 0·1 per cent each of platinum and rhodium can be analysed successfully. With the n-butanol solvents, the same limitations apply as for platinum.

Rhodium. With all solvents the width of the rhodium band increases with an increase in loading by diffusion towards the palladium band. The upper limits are 3 mg for the hexone solvent and 5 mg for the n-butanol solvents. Mixtures of rhodium containing about 0·1 per cent of platinum, palladium and iridium can be successfully analysed.

Iridium. The upper limits for iridium are lower for both solvent mixtures. With the n-butanol solvent the limit is 0·5 mg, and above this backward trailing causes interference.

Base metals. Analyses have been carried out in the presence of large amounts of commonly occurring base metals which remain comparatively immobile in one or other of the solvents. Tests have shown that up to 5 mg of some of these metals can be tolerated before distortion of the palladium band occurs. Sodium is only slightly soluble in the solvents and is regarded as an immobile metal.

In the presence of large amounts of metals that move in the centre of the strip, distortion of the platinum metal bands occurs. This can be avoided by a change of solvent.

Metals that move in or near the solvent front impose a similar practical limitation. As their quantity increases the bands occupy more fully the space between the wet and dry solvent fronts, increasing this area above its normal limits. This reduces the space available for the platinum metal bands, so that not more than 5 mg of base metal can be present on the strip.

The procedure described below relies on the absence of osmium and ruthenium. The chromatograms are unacceptable when the hexone solvent is used and iridium is to be determined in the presence of more than 20 μg of ruthenium. With the n-butanol solvent, however, iridium and ruthenium are separated. Concerning rhodium, not more than 2 μg of ruthenium can be tolerated with either the hexone or butanol solvents. Osmium will interfere with platinum, both through its position on the strip and in the subsequent determination. It should be noted here that these interferences are usually disregarded with the claim that both osmium and ruthenium can be removed as their volatile oxides, but this removal from chloride solutions in which form the noble metals are separated chromatographically is not generally recommended The distillation of ruthenium(VIII) oxide is usually made from a sulphuric or perchloric acid solution, and chromatographic separations in these media have not been recorded. Recent researches have indicated, however, that the distillation of at least μg amounts of both osmium and ruthenium can be made successfully from a hydrochloric acid medium.

Procedure 49[190]

Solvents. The solvent used may be one of the following:

(1) 60 parts by volume of isobutyl methyl ketone (hexone), 10 parts of n-pentanol and 30 parts of hydrochloric acid, $d = 1{\cdot}18$. This solvent yields well-defined bands for rhodium, palladium, platinum and gold in this order of decreasing R_f values. Iridium in low concentrations is reduced to the trivalent state, and in this condition it remains with rhodium as a partially separated band. The solvent is therefore recommended for the separations of either rhodium or iridium from the remaining noble metals.

(2) n-Butanol saturated with 3 M hydrochloric acid and containing hydrogen peroxide. This solvent is used for the separation of rhodium from iridium previously isolated by the hexone solvent. The peroxide effectively moves the iridium away from the rhodium because the iridium is selectively oxidized to the more mobile iridium(IV).

(3) n-Butanol saturated with 3 M hydrochloric acid. This solvent is useful for separations involving base metals because the base metals are thus made relatively immobile.

Paper. Whatman No. 1 filter paper in 45-cm long, 3-cm wide strips is satisfactory. No. 4 paper is faster, No. 20 is slower, and Nos. 3 MM and 15 are thicker but offer no advantages.

Apparatus. A glass jar, 50 cm high and 7·5 cm internal diam. The jar is fitted with a stopper from which is suspended a 30-cm solvent container and two strip supports. Downward diffusion is generally used, but upward diffusion is equally satisfactory.

Procedure. To the test chloride solution, free from cyanide, potassium and ammonia, in 1–5 M hydrochloric acid, add a 1 per cent w/v solution of sodium chlorate, and make up to a suitable known volume (Note 1). Transfer accurately 0·05 ml aliquots of the solution to the required number of strips, drawing the tip of the pipette across the strip along a line 7 cm from one end of each strip of filter paper (Note 2). Set the strips aside to dry for 1 hr in air or for 30 min in a vacuum desiccator, desiccator drying being necessary if the atmosphere is humid or if deliquescent salts are present in high proportions in the mixture.

Fold each strip 4 cm from the sample end, and place it in the chromatographic jar containing the required solvent for development by downward diffusion. Place the jar in a protected position in which the temperature can be maintained between 22 and 26°C, and leave overnight (14–18 hr) (Note 3). Remove the strips from the jars, and set them aside to dry, preferably hanging in clips to avoid contamination (Note 4). Spray one strip with a stannous chloride solution (11·25 g of A.R. material in 100 ml of 3·5 M hydrochloric acid). Warm gently to indicate the position of the platinum metal bands, viz., rhodium, yellow-orange; palladium, brown; platinum, yellow; gold, yellow. Lay the other strip or strips on a glass plate and divide them into sections at points between the bands and 1 cm beyond the furthest detected position, using the control strip as a guide. The strip can be divided by placing a small piece of glass across it and lifting the free end with a pair of tweezers, breaking it cleanly along the line. Transfer each section to a 10-ml microbeaker, and carry out determinations on these sections as described below.

Notes—1. The chlorate serves to oxidize platinum(II) to platinum(IV). This avoids double bands.

2. The number of strips depends on the analysis required, e.g. if both iridium and rhodium are to be determined. In general two strips are prepared for each analysis, one as a control.

3. Much lower temperatures encourage diffuse bands and double platinum bands. Higher temperatures offer no advantages. By using strips of No. 4 paper the time of standing can be reduced to 6 or 7 hr. This gives slightly wider bands and is not advisable when the quantity of any component of the mixture approaches the upper limit.

4. The strips are very fragile at this stage if the hexone solvent has been used, and they become more brittle as the solvent evaporates.

The Removal of the Metals from the Paper

The aqueous extraction apparatus, Chapter 7, Equipment No. 12, is used to remove the metals from each portion of the strip. The same general instructions apply to all metals, the only variation being the type and order of extracting solutions; these are given in the following section. The volume of the calibrated flask *A* should be chosen to provide a concentration which will give a reasonable light transmission in the final colorimetric determination, 5- or 10-ml flasks normally being used. The extract for the determination of iridium is collected in a tall tube (made from a specimen tube 7·5 cm × 2·5 cm in diam.) provided with a lip.

Add the first extraction solution to the paper, cover the beaker with a watch-glass, and warm on a steam bath for 10 min unless otherwise stated. Break up the paper to a coarse pulp with a small glass rod, which is then left in the beaker. Do not allow prolonged heating, otherwise a fine pulp is formed that is difficult to filter. Allow the pulp to settle, and filter the mixture through the funnel of the extraction apparatus directly into a calibrated flask *A*, applying gentle suction. Then transfer the pulp to the funnel, pressing it into a wad with the glass rod. Release the vacuum *D*, and add the second extraction solution to the funnel, transferring it via the beaker. Leave to soak for 1 min, then filter into the flask. Repeat this stage with the other extraction solutions. Remove the flask, make up to the mark with water, and measure the transmittance using the spectrophotometer. For iridium analyses remove the tube, and wash the filtrate into the titration vessel with the minimum amount of water.

Extraction solutions. The volumes given are for a 5-ml flask; alter the volumes in proportion for other sizes of flask.

Rhodium (upper section).
(1) 1 ml of stannous chloride solution + 1 ml of 5 M hydrochloric acid. Heat for 30 min.
(2) 1 ml of 5 M hydrochloric acid.
(3) 1 ml of water.

Palladium (centre section), by thioglycollic acid method.
(1) 1 ml of M hydrochloric acid + 1 ml of water.
(2) 1 ml of thioglycollic acid solution.
(3) 1 ml of water.

Palladium (centre section), by *p*-nitrosodimethylaniline method.
(1) 1 ml of sodium acetate solution + 1 ml of water.
(2) 0·1 ml of *p*-nitrosodimethylaniline + 0·9 ml of water.
(3) 1 ml of water.

Platinum (lower section).
(1) 1 ml of 5 M hydrochloric acid + 1 ml of water.
(2) 1 ml of stannous chloride solution.
(3) 1 ml of water.

Iridium (upper or lower section according to solvent used).
(1) Add 0·2 ml of liquid bromine to the paper, leave to soak for 5 min with the beaker covered, then add 1·8 ml of water.
(2), (3) 1 ml of 1 M hydrochloric acid.

Determinations. Make all final measurements on a Unicam spectrophotometer or a similar instrument, using 1-cm cells (silica for palladium by thioglycollic acid and glass for the others), and making comparisons against reagent blanks. Prepare standard curves, using the same reagents as were used in the aqueous extraction method over the ranges given below. In preparing the standard curve for palladium by the *p*-nitrosodimethylaniline method, add 0·5 ml of 0·1 M hydrochloric acid to each 5 ml of solution to give the required pH. During the actual determinations the residual acid in the paper is sufficient.

The values of wavelength and range involved are as follows:

	Wavelength	Range in 5 ml of solution (μg)
Rhodium	480 mμ	0–100
Palladium (thioglycollic acid method)	325 mμ	0–50
Palladium (*p*-nitrosodimethylaniline method)	525 mμ	0–1·5
Platinum	403 mμ	0–100

The Determination of Iridium

With the procedure described above and with the hexone solvent, iridium and rhodium appear as two closely associated bands. No method of selectively separating these two bands has been developed. To determine both rhodium and iridium two chromatograms are necessary. By the volumetric method described below for iridium there is no appreciable interference from rhodium. Thus the combined bands from the hexone separation may be used for the iridium determination. A second chromatogram obtained as described above, but with the solvent No. 3 (n-butanol/peroxide), will move the iridium in the trivalent state, so that the rhodium band is isolated.

To the bromine water extract of iridium add 0·4 ml of a lithium sulphate solution (see Procedure 120), and heat to fumes of sulphur trioxide, preferably under infrared lamps, and in the titration vessel, although some charring will still probably occur, because of traces of solvent and decomposed cellulose present. Add 0·2 ml of perchloric acid, and heat to fumes, repeating this until a clear solution is obtained. Add 0·2 ml of perchloric acid, 1 drop of 3,3′-dichlorobenzidine solution as indicator, and heat to 300–320° C (Note 1). Leave for 10 sec at this stage, then remove and cool rapidly. Add 2 ml of water, and cool again. Transfer the vessel to the titration apparatus, and titrate with the hydroquinone solution (diluted 10 times from stock solution, i.e. 0·01 ml of hydroquinone solution ≡ 1 μg of iridium, see Procedure 120). Standardize the diluted hydroquinone solution by a series of titrations against known quantities of iridium, first to the discharge of the purple colour. Then add one drop of indicator to produce a yellow colour, and add further hydroquinone solution until this colour is just discharged.

The titration may be repeated after evaporating the solution again to fumes of sulphur trioxide and repeating all stages.

Note 1—The temperature is fairly critical. If a lower temperature is used, a longer time of heating is necessary; this must be determined by experiment. The solution first turns yellow then brown. This colour is discharged and the final solution is colourless or purple, according to the amount of iridium present.

A MODIFIED CHROMATOGRAPHIC DETERMINATION OF PLATINUM, PALLADIUM, RHODIUM AND IRIDIUM

This method was designed to provide improved procedures for the determination of platinum and palladium, and particularly improved methods of determining rhodium and iridium in order to avoid the necessity of two chromatograms.

To produce the chromatogram, sodium chlorate was replaced by sodium chloride with the result that iridium was quantitatively fixed in a band adjacent to the immobile rhodium band. It is not unlikely that this substitution is the cause of the appearance of a few μg of platinum with the palladium band. This contamination is of no significance because the two bands are combined, and may be analysed for platinum and palladium by a variety of methods. The additive absorbance method is described in Procedure 185, and the *p*-nitrosodimethylaniline–chloroform extraction method is described below. In the present author's opinion this approach provides for rapid and accurate determinations.

Procedure 50

After the removal of the chromatographic strips from the jar (Procedure 49) leave them suspended in air for at least 15 min. Spray the control strip with the tin(II) chloride solution, and gently heat the strip with a lamp maintained at an appropriate distance. Cut the sample strip with scissors to isolate rhodium together with iridium and platinum together with palladium. Place the platinum–palladium band in a 30-ml beaker, and ignite overnight in an oven at 400–450°C. Treat the ash with 8 ml of *aqua regia*, and, with a cover glass on, place on a steam bath and evaporate to near dryness. Repeat this treatment. Treat the residue 3 times with 5 ml of concentrated hydrochloric acid, with intermittent evaporations to dryness, then evaporate 3 times with 12 drops of concentrated hydrochloric acid. Cool the evaporated residue, and rinse the watch glass and the wall of the beaker with a few ml of water whose acidity has been adjusted to pH 3 with hydrochloric acid. Transfer the solution to a 75-ml, pear shaped separatory funnel, and wash with 8 ml of water at pH 3.

Add 0·5 ml of the *p*-nitrosodimethylaniline solution to the 10 ml of solution (see Procedure 168), followed by 5 ml of 95 per cent ethanol. Shake for 5 min, remove the red palladium complex by an extraction with 10 ml of chloroform, and return the extract to the original beaker. Add to the separatory funnel 0·5 ml of chloroform, extract as above, and add the extract to the original beaker.

For the determination of palladium, cover the beaker with a Speedvap cover glass, and evaporate to a wet residue. Remove the beaker, and allow the residue to dry at room temperature. Cover with a watch glass, and destroy the organic matter with fuming nitric acid and a 30 per cent hydrogen peroxide solution in the usual way. Convert to the chloride form, and determine palladium by the *p*-nitrosodimethylaniline method (Procedure 168).

For the determination of platinum, transfer the aqueous phase from the palladium separation to a 50-ml beaker, covered with a Speedvap cover glass. Wash the separatory funnel thoroughly with water, and add the washings to the platinum solution. Evaporate to dryness on a steam bath, and continue as with the chloroform–palladium extract, including the destruction of organic matter. Determine platinum by the tin(II) chloride method (Procedure 179).

The separation and determination of rhodium and iridium. After the removal of the platinum–palladium section of the chromatogram, place the remaining strip with the rhodium–iridium band over a Kleenex sheet of similar size, and fold carefully to protect the metal-containing bands. Place the folded paper in an A2 porosity porcelain filtering crucible, and set the latter inside a larger porcelain crucible. Place the crucibles in a furnace at 400–450°C as described above. Place the filtering crucible containing the ash in a Vycor tube, and heat for 30–45 min to about 600°C in a current of hydrogen. Remove the crucible, add about 10 mg of sodium chloride, transfer the crucible to a Vycor tube, and pass chlorine over the residue at about 650–700 C for 4 hr.

Raise the level of the tube to allow the crucible to slip into a 250-ml beaker. Rinse into this beaker the inner tube surface with 1 M hydrochloric acid. Evaporate on a steam bath to about 20 ml, and remove the crucible, washing thoroughly with 1 M hydrochloric acid. Filter the solution through the washed crucible, and wash with water to a volume of 75 ml. Evaporate the filtrate on a steam bath to a small volume, transfer to a 30-ml beaker, and evaporate to dryness. Add a few drops of 47–49 per cent re-distilled hydrobromic acid, and treat by solvent extraction with isoamyl alcohol as described in Procedure 14.

THE CHROMATOGRAPHIC SEPARATION OF RHODIUM, IRIDIUM, PALLADIUM AND PLATINUM ON THE MACRO SCALE

This method allows the separation of each of the four metals in quantities of the order of 75 mg. The solvent mixtures are acid–hexone and acid–oxidant–hexone. The columns contain cellulose powder, the volume of which varies with the separation required. Both oxidizing and reducing conditions are applied: under oxidizing conditions platinum and iridium move together. A separation requires a second column and reducing conditions. The reduction is accomplished by tin(II) chloride, which allows the collection of iridium as a first fraction, and subsequently platinum is eluted with the acid solvent. Palladium is collected as a second fraction. Rhodium is almost immobile with both oxidizing and reducing solvents, but is readily eluted with water. The method of separating the four metals is about comparable in speed and accuracy to the better chemical separations.

The authors of the method described below recommended a prior nitrite separation of small proportions of such base metals as copper, nickel, tin, etc. (Procedures 29 or 30). In the presence of large amounts of associated base metals the present author recommends a prior cation-exchange separation at pH 1·3–1·5 (Procedure 47).

Procedure 51[191]

Equipment

Cellulose. Fine grade Whatman ashless cellulose powder.

Columns. The adsorption tubes are 1·8 ± 0·1 cm internal diam. Columns 15 cm long are suitable for the separation of two-component systems. Thirty-cm columns are used to separate three- or four-component systems. The columns are treated by passing 5 ml of acid solvent per cm of cellulose-column height. When oxidizing conditions are required, a minimum of 50 ml of oxidizing solvents are used to treat the cellulose.

The glass tubes may be widened at the upper end to form a funnel. The lower end is narrowed and closed by a short length of polyvinyl chloride tubing fitted with a tap. The inside surface of the glass extraction tube is treated with dichlorodimethylsilane to encourage water repelling properties.[210]

Solvents. Acid solvent: Hexone containing 3 per cent v/v of concentrated hydrochloric acid.

Oxidizing solvent (generator solvent): 100 ml of hexone containing 4 per cent v/v of concentrated hydrochloric acid added to a mixture of 4 g of sodium chlorate and 12 g of cellulose powder to absorb the water formed by the reaction, the solvent then being decanted from the cellulose and mixed with an equal volume of hexone containing 4 per cent v/v of concentrated hydrochloric acid.

Procedure. Transfer the chloride solution of the four metals, preferably in their fully oxidized states, to a 400-ml beaker. Add zinc chloride in an amount at least equal to the combined weight of platinum and iridium. If nitric acid is present evaporate to dryness on a steam bath, add a few ml of strong hydrochloric acid, and again evaporate. Repeat this 3 times. Add 5 ml of concentrated hydrochloric acid. In the absence of nitric acid, evaporate to dryness on a steam bath in the presence of zinc chloride, and add about 5 ml of concentrated hydrochloric acid.

In either of the above instances saturate the solution with chlorine.

Evaporate again, avoiding any overheating of the residue, remove excess of acid and condensate from the wall of the beaker at as low a temperature as possible. Dissolve the residue in 1·0 ml of concentrated hydrochloric acid saturated with chlorine, add 10 ml of generator solvent and then 10 ml of hexone. Replace each withdrawal of solvent by the addition to the generator of the same volume of hexone containing 4 per cent v/v of concentrated hydrochloric acid, and stir the mixture (Notes 1, 2 and 3).

Allow the level of the sample solution to fall to the top of the cellulose column, and then rinse the beaker with successive 3–4 ml portions of oxidizing solvent, any aqueous phase being retained in the beaker. Keep the volume of washing solvent to a minimum. Elute the mixture by the addition of oxidizing solvent, care being taken to ensure that the level of the solvent does not fall below the top of the cellulose column.

A wide diffuse band of iridium moves rapidly down the column, its brown colour masking the presence of some platinum that moves with it, sometimes a little ahead of but not detached from the iridium band. The bulk of the platinum follows the iridium as an adjacent merging band. As elution proceeds, the deep yellow platinum band moves completely away from the fairly compact orange-brown palladium band. Palladium moves away from the immobile rhodium, but at a much slower rate than does the wide platinum-iridium band.

Collect the platinum and iridium as a single fraction of about 200–250 ml in a 500-ml round-bottomed flask fitted with a ground-glass socket to facilitate the subsequent distillation (Note 4).

To avoid any loss of iridium from the platinum-iridium fraction, let the palladium band approach the bottom of the column before collecting the palladium fraction. Maintain fully oxidizing conditions to prevent any retention of iridium in the palladium band.

Collect the palladium fraction, 100–150 ml, in a similar 500-ml round-bottomed flask, discontinuing the addition of solvent to the column as soon as all of the palladium has been eluted.

Transfer any rhodium remaining in the sample beaker to the column with a jet of distilled water, and acidify the aqueous solution with a few drops of dilute hydrochloric acid (Note 5). Collect the rhodium fraction, about 100 ml, in a 250-ml beaker, and evaporate the hexone layer with an infrared lamp.

Notes—1. The initial acidity of the sample solution is rather high, but it decreases as the elution proceeds.

2. It is important to limit the initial volume of the sample solution and the solvent washings of the sample beaker. If the total volume of sample solution is too great, chromatographic separation commences before the last of the platinum-bearing solution comes into contact with the cellulose.

3. If a few drops of aqueous phase separate from the hexone solution of the sample, this aqueous phase should be retained in the beaker by careful decantation of the hexone and the hexone washings. Some of the rhodium present in the sample will remain in the aqueous phase, and is indicated by a characteristic rose red colour. The remaining rhodium is immobile at the top of the column, and is indicated by a narrow red band.

4. Any zinc, iron or copper present will move with the platinum and iridium, but any nickel present will be retained at the top of the column with the rhodium.

5. Because both rhodium and nickel move rapidly down the column, the major proportion of the oxidizing solvent remaining in the column should be run either into the palladium fraction or to waste, otherwise the aqueous rhodium fraction will be accompanied by an inconveniently large volume of hexone.

The separation of platinum from iridium. Add water to the flask containing the first fraction, and fit a Claisen head and condenser. Pass a current of air through a fine capillary reaching almost to the bottom of the flask, and distil the hexone and a limited amount of water. Transfer the remaining aqueous solution to a 150-ml beaker, and remove any carbonaceous deposit (resulting from break-down of the hexone) from the wall of the flask with hot *aqua regia*. Add the acid solution to the beaker, and evaporate the mixture to dryness, finishing on a steam bath. Repeatedly treat the residue with small portions of concentrated hydrochloric acid, and evaporate to ensure the complete removal of nitrate under conditions that avoid overheating the residue. Dissolve the residue in 1·0 ml of concentrated hydrochloric acid, add 0·2 g of stannous chloride, and dissolve the solid by gentle agitation.

Add 20 ml of hexone to the solution, the latter becoming highly coloured (Note 1).

Equilibrate a 15-cm cellulose column with the acid-hexone, and decant the reduced

platinum-iridium mixture on to it, avoiding the transfer of any of the aqueous phase. Rinse the beaker repeatedly with 3–4-ml portions of acid-hexone and transfer the washings to the column, still retaining the aqueous phase. Collect the platinum fraction in a 500-ml round bottomed flask, and distil off the hexone as described above, transferring the aqueous solution and acid washings of the flask to a 400-ml beaker. Elute the reduced iridium from the top of the column by adding the faintly acidified water used to rinse the sample beaker in the same way as that described for the elution of rhodium. Collect the iridium solution in a 400-ml beaker, and evaporate the solvent.

At this stage, the four platinum metals are quantitatively separate, and the assay methods selected will depend on the identity and concentration of any base metals present.

Palladium is free of interference and can be precipitated by dimethylglyoxime or any other of the many suitable precipitants.

Platinum may be contaminated with copper, zinc and tin. Evaporate the solution to a few ml, and add concentrated hydrochloric acid. Boil off the tin chloride, with the intermittent addition of bromine to assist the process. Evaporate to dryness, and dissolve in water containing a few drops of hydrochloric acid. Remove the base metal impurities by hydrolysis, nitrite being present to complex the platinum (Procedures 29, 30, 52). Evaporate the nitrite filtrate, and determine platinum by using one of the gravimetric reagents, e.g. thiophenol (Procedure 101).

Iridium may be precipitated by 2-mercaptobenzothiazole (Procedure 89).

Rhodium may be precipitated by thiobarbituric acid (Procedure 82).

Note—The colour is that of an orange-red tin-platinum complex of unknown identity. This complex is unstable in hexone, and tends to break down in the cold to form the required yellow chloroplatinic acid. If this does not occur, heat the contents of the beaker to encourage this decomposition.

Some restricted separations

The separation of iridium from rhodium. Add 0·25 g of mercuric chloride to the hydrochloric acid solution of the metal chlorides contained in a 150-ml beaker, and evaporate to dryness on a steam bath. Add a few ml of dilute hydrochloric acid, saturate the solution with chlorine, and again evaporate to dryness. Dissolve the residue in 1·0 ml of concentrated hydrochloric acid saturated with chlorine, add 10 ml of generator solvent and then 10 ml of hexone. Use a 15-cm cellulose column equilibrated with solvent, and pass through a minimum of 50 ml of oxidizing solvent before decanting the sample solution on to the column. Retain any aqueous phase, and rinse the beaker with successive 3–4-ml portions of oxidizing solvent. Maintain oxidizing conditions throughout the separation to prevent any retention of trace amounts of iridium. Collect the iridium fraction in a 500-ml round-bottomed flask, and elute the rhodium with water.

The separation of rhodium from other platinum metals. Use the oxidizing solvent even in the absence of iridium, because it is desirable to repress the formation of any slower-moving reduction product of platinum. Use a 15-cm column for the separation of rhodium from platinum or palladium, but a 30-cm column for the separation of all three metals.

The separation of palladium from iridium. Use a 15-cm column, and maintain oxidizing conditions throughout to keep iridium moving away from the less mobile palladium.

Note—A separation based on the retention of reduced iridium will fail because of the marked effect of reduction on the chromatographic behaviour of palladium.

The separation of platinum from iridium. This separation has already been described above.

Note—It is noteworthy that, under the reducing conditions that apply in this instance, the chromatographic behaviour of platinum differs from its behaviour under fully oxidizing conditions. When the platinum-iridium mixture has been reduced by stannous chloride, and the solvent solution transferred to the column, the platinum invariably appears in two forms. A wide, mobile, yellow band accounts for most of it, and a slow-moving, dull pink band represents the remainder. The two bands may separate, but both should be collected in one fraction. Sufficient solvent should be used to remove all trace of the less mobile product before commencing to elute the iridium with water. Water elutes iridium very rapidly.

If a relatively large amount of platinum is being separated from a trace of iridium, it may be impossible to detect the presence of iridium at the top of the column by visual inspection. An operator unfamiliar with the characteristic colours of the various platinum metal complexes could mistake the slow-moving platinum band for iridium, and collect it as such in a separate fraction. Iridium would then be rejected with the column packing, and part of the platinum would be reported as iridium, so that the value found for platinum would be less than the true one. If sufficient iridium is present to be plainly seen at the top of the column, its colour is a dull greyish-green; it cannot be confused with the dull pink of the slow-moving platinum band.

The separation of platinum from palladium. Use a 30-cm column and oxidizing conditions throughout the separation.

OTHER CHROMATOGRAPHIC SEPARATIONS

Chromatographic methods for the detection of the seven noble metals were recorded by Blasius and Fischer.[211] The concentrations of the metals were of the order of 20 g per l. and nitrito- and nitroso-chloro complexes were used as well as the customary chloro complexes.

TABLE 17. PAPER CHROMATOGRAPHIC SEPARATIONS[211]

Separation	Metal solutions	Solvent solutions	R_f value
Ru Pd Pt Au Rh Pd Pt Au Ir Pt Os Ir Pt	Chloro complexes in 1 M HCl	n-Butanol: 3·5 N HCl = 7 : 3 25% $NaNO_2$ solution	Au > Pt > Pd > Ru Au > Pt > Pd > Rh Ir > Pt Ir > Pt > Os
Ru Rh Pd	Chloro complexes (Rh, Pd), nitroso-chloro complexes (Ru) in 1 N HCl	Methyl ethyl ketone–HCl (1·19) = 7 : 3	Ru > Pd > Rh
Ru Rh Ru Rh Pd Ru Rh Pt	Nitrito complex in 3·5 N $NaNO_2$ solution	Ethanol : isopropanol : 25% $NaNO_2$ solution = 6 : 1 : 3	Ru > Rh Ru > Pd > Rh Ru > Pt > Rh
Ru Rh Pd Os Ir Pt Au	Chloro complexes in 1 M HCl	n-Butanol : 3·5 N HCl = 7·3 (for Ru, Rh, Pd, Os, Pt, Au detection), 25% $NaNO_2$ solution for Ir detection	Au > Os = Pt Pd > Ru = Rh Ir ≈ Rh ≈ Ru > Pd > Pt > Os > Au

Three types of solvent solutions were used. One contained by volume 70 parts of n-butanol and 30 parts of 3·5 M hydrochloric acid. A second was a 25 per cent aqueous sodium nitrite solution, and a third, used only for small proportions of ruthenium in the presence of large proportions of rhodium, contained, in parts by volume, 60 of ethanol, 10 of isopropanol and 30 of the 25 per cent sodium nitrite solution. Ruthenium and osmium deposits were developed by thiourea, rhodium, palladium, platinum, and gold by a tin(II) chloride solution containing sodium iodide. Iridium collected by the nitrite solvent was treated with concentrated hydrochloric acid to produce a narrow brown zone. The use of these reagents precluded any subsequent quantitative applications. In order to detect each of the seven metals a variety of chromatograms, solvents and feed solutions were required. Table 17 indicates the various separations and the conditions required. These are included to indicate potential methods for quantitative separations.

The Wet Determination of the Six Platinum Metals in High Concentrates

The method recorded below is the first complete procedure for the direct quantitative determination of the six metals in concentrated natural deposits. Payne[212] also applied the procedure to synthetic samples containing amounts of the metals from a few mg to about 100 mg. The recovered values indicate very acceptable accuracy.

The method involves the fusion of the sample with sodium peroxide, acidification with hydrochloric acid, and oxidation to remove osmium and ruthenium simultaneously. The pot liquid is treated hydrolytically in the presence of nitrite to precipitate the base metals. The mixture is made up to a known volume. Half this volume is filtered and treated for the remaining four platinum metals. This 50 per cent aliquot is passed through a cation-exchanger, and the effluent is added to a cellulose column to separate each of the four platinum metals. The column and technique is similar to that described in Procedure 51 except that a single column is used.

For a few mg of metal the original procedure directs the use of spectrophotometric finishes.

The recommended gravimetric methods are a hydrolytic precipitation for osmium, rhodium and iridium, a magnesium reduction for platinum and a dimethylglyoximate precipitation for palladium. For ruthenium the evaporated distillate is treated directly by ignition in hydrogen.

The absorptiometric reagents recommended are thiourea for osmium and ruthenium and tin(II) chloride for platinum. Palladium and rhodium are determined as their chloro complexes.

The determination of iridium was accomplished by measuring the difference in absorbance between the oxidized and reduced forms of the chloro acid. The method involved the use of two aliquots of the iridium solution. 50 ml of 1 to 1 hydrochloric acid were added to each, the solutions were boiled for 5 min, cooled and each transferred to a 100-ml calibrated flask.

One solution was diluted to about 90 ml with 1 to 1 hydrochloric acid, and 4 ml of freshly prepared chlorine water were added. The flask was placed in a boiling water bath for 30 min, cooled, and adjusted to volume with the diluted hydrochloric acid.

The second solution was treated with 2 drops of a 5 per cent hydroquinone solution, and diluted to the mark with the 1 to 1 hydrochloric acid. This solution was used as the reference solution. The absorbance of the first or oxidized solution was measured at 4900 Å in 4-cm cells.

It should be noted that if the method described below is applied to materials with high proportions of iridium, the latter may contaminate the rhodium. It is then necessary to determine the iridium in the rhodium extract. This may be accomplished by the method described below, or that in Procedure 51.

Absorptiometric methods were used by Payne[212] for amounts of a few mg to about 10 mg. Over this range gravimetric methods remain applicable and these are recommended by the present author. The most suitable gravimetric method for each metal is indicated in the appropriate part of the procedure described below. Although the procedure is not a suitable one for μg amounts of the six platinum metals, a reference is included to indicate a suitable spectrophotometric method for each metal. In general the procedure follows the original, but appropriate variations are integrated and comments are interjected where they may clarify difficulties experienced by the analytical chemist.

It should be noted that the procedure has been found satisfactory for concentrates containing high proportions of platinum metals and presumably of low sulphur content. One may expect some difficulty with samples containing osmium and appreciable sulphur. In any case this problem requires further investigation.

Procedure 52[212]

Apparatus

Ruthenium distillation train. This consists of a 500-ml distillation flask with a dropping funnel, four 250-ml receivers and a Drechsel bottle. Connections are made via Quickfit & Quartz spherical joints. The complete train is shown in Chapter 7, Equipment No. 13A.

Ion-exchange column. The column is made by joining a length of Pyrex glass tubing (14 × 1¼ in., 35 × 3·1 cm) to the cut off top and bottom portions of a standard Quickfit & Quartz CR/32/20 chromatography column (see Equipment No. 13B). It is filled with Zeo-Karb 225, and prepared by acid washing, etc. in the usual manner.

Cellulose column. A standard Quickfit & Quartz CR/32/40 column equipped with a reservoir and tap adapter. The preparation of the column is described below.

Reagents

Hydrochloric acid. (1 + 1) solution.

Ethanolic sodium hydroxide solution. A 10 per cent solution of sodium hydroxide in 10 per cent industrial ethanol.

Hydroquinone. Pure, as a 5 per cent w/v solution.

Dimethylglyoxime solution. As its salt, 5 per cent w/v solution in water.

Acid solvent. Isobutyl methyl ketone containing 2 per cent v/v of hydrochloric acid.

Reducing solvent. Acid solvent plus 0·05 per cent of hydroquinone.

Oxidizing solvent. Freshly prepared (see below) cellulose powder. Whatman standard grade.

Procedure

The dissolution of the sample. Weigh the crushed sample (containing not more than 0·25 g of platinum metals) into a nickel crucible, and moisten with a few drops of water. Introduce about 5 ml of hydrofluoric acid, and evaporate the mixture to dryness. Heat the crucible gently, and raise the temperature slowly to a bright red heat (under cover of hydrogen if osmium is to be determined), taking care to avoid loss by spitting.

When cool, add 10 g of sodium peroxide, and mix the sample intimately with the aid of a glass rod. Heat the crucible slowly until the contents sinter, maintain in this state for 30 min, and then raise the temperature to bright red heat, swirling the melt to ensure complete attack. Avoid prolonged heating at this temperature, to minimize attack on the crucible, 1 or 2 min being usually sufficient.

Set the crucible aside to cool, then place it in a 400-ml beaker, and just cover the crucible with water. When the violent reaction has subsided, rinse the cover and sides of the beaker, remove the crucible with a pair of forceps, wash it inside and out, clean the surface with a rubber-tipped glass rod, and wash again.

Transfer the contents of the beaker, with washings, to the ruthenium distillation flask, and connect the flask to the train. Place 150 ml of (1 + 1) hydrochloric acid in each receiver and 150 ml of the ethanolic sodium hydroxide solution in the Drechsel bottle. Meanwhile, place 20 ml of the hydrochloric acid in the nickel crucible, and heat to dissolve any particles adhering to the surface. With a suction pump, draw a slow current of air through the distillation train, and transfer the acid to the distillation flask. Rinse the crucible with a further 15 ml of acid, and add the rinsings to the contents of the flask.

The distillation of osmium and ruthenium. Heat the flask slowly, and boil the contents gently for about 10 min, maintaining a steady flow of air through the train. Add 10 ml of a 20 per cent w/v sodium chlorate solution, a few drops at a time, and then 35 ml of a 10 per cent w/v sodium bromate solution in 5-ml portions at intervals of 2 min. Boil the solution continuously while the additions are made and then for a further 30 min to complete the volatilization of osmium and ruthenium.

Some 15 min before the end of the distillation, heat the contents of the first receiver to boiling to reduce most of the ruthenium to the tervalent state, any ruthenium still unreduced, together with osmium and oxides of chlorine, etc. passing into the second receiver. Heat the contents of this in turn, and so on until the osmium and other volatile products are finally absorbed in the ethanolic sodium hydroxide solution. Most of the ruthenium will be in the first receiver, a little in the second and only a trace in the third. The distillation is then complete.

Combine the distillates containing the ruthenium in a 1-l. beaker, evaporate to a small volume, transfer to a 150-ml beaker, and again evaporate to a small volume, but not to dryness. Set the solution aside for the subsequent determination of ruthenium as described below (p. 160).

Transfer the solution containing the osmium to a beaker, and set it aside for the determination as described below (pp. 160, 161).

The treatment of the pot liquid from the ruthenium distillation. Transfer the residual liquor from the distillation to a 600-ml beaker; rinse the dropping funnel and flask with 50 ml of hydrochloric acid, and cautiously add the rinsings to the main solution. Rinse the funnel and flask with hot water, cover the beaker, and boil the solution vigorously to reduce the volume to about 100 ml, taking care to remove the beaker before crystallization of the salts causes severe bumping. Transfer the beaker to a low-heat hot plate, and continue the evaporation until the contents are almost dry. On no account allow the salts to bake.

The nitrite separation. Dissolve the salts in about 150 ml of water, boil for 5 min, and then dilute to about 400 ml with hot water. To the boiling solution add sodium nitrite a little at a time until the pH changes to 7 (measured with test paper), and then, after another small addition of nitrite, boil for a further 5 min. When cool, transfer the solution and precipitate to a 500-ml calibrated flask, and make up to the mark with distilled water.

Mix the contents of the flask well, and filter through a Whatman No. 40 filter paper, rejecting the first few ml of filtrate. Collect 250 ml of the filtrate in a dry calibrated flask, and set aside; then continue the filtration, and allow the filter paper and precipitate to drain. Wash the precipitate once with cold water, and discard the remaining filtrate.

Transfer the filter paper and precipitate to a 400-ml beaker, add 2 ml of the hydrochloric acid and 20 ml of water, and bring to the boil. Boil for 5 min, dilute to about 100 ml, and repeat the nitrite treatment as before. When cool, transfer the solution, precipitate and filter-paper to a 200-ml calibrated flask, and filter as before, but this time collect 100 ml of filtrate. Discard the remaining filtrate and precipitate, any gold in the original sample being in this precipitate.

Transfer the two filtrates (which now represent one half of the original sample, Note 1) to a 600-ml beaker, and rinse the flask with distilled water. Add 4 ml of hydrochloric acid, and heat the solution to boiling. Boil for not more than 1 min to remove excess of nitrous fumes, then cool as rapidly as possible, and adjust the pH to about 3 with sodium hydroxide (Note 2).

Notes—1. It will be recognized that this method of providing an aliquot is in error by that amount of platinum metals contained in the volume of solution displaced by the precipitate of base metal hydroxides. This error can be calculated from the densities of the solution and the solid, and its significance will depend upon the proportions of the two mechanically mixed constituents. For very small amounts of precipitate, and where good accuracy is not required, this error can be ignored.

2. Excess of nitrate results in the disruption of the column owing to the liberation of free nitrous acid. On the other hand if insufficient nitrite is present some palladium may be lost in the cationic form.

The removal of base metals by ion-exchange. Regenerate the resin (Zeo-Karb 225) with the (1 + 1) hydrochloric acid, and then elute with water until the effluent is at pH 7. Place the reservoir in position, and fill with the solution of the nitrites of the platinum metals. Pass the solution through the column at about 1 drop per sec, refilling the reservoir as necessary. When all the solution has been transferred, rinse the beaker 2 or 3 times, and add the washings in the same manner. Immediately before the last few ml of solution become absorbed, rinse the reservoir with about 20 ml of water, and allow this to pass through. Repeat with several successive 20-ml portions, fill the reservoir with water, and continue the elution until the effluent is neutral.

The treatment of the ion-exchange effluent. Evaporate the effluent (now free from sodium, nickel, etc.) to a small volume, and then transfer to a 250-ml beaker; add 2 ml of a 10 per cent w/v lithium chloride solution, and continue the evaporation to dryness. Moisten the residue with a few drops of water, add 10 ml of 60 per cent perchloric acid, and evaporate until copious fumes are evolved. Continue heating until all the free perchloric acid has been expelled, and then set aside to cool. Rinse the wall of the beaker with the minimum amount of water, and evaporate again until the evolution of fumes ceases completely (Note 1).

Treat the cooled residue with 5 ml of (1 + 1) hydrochloric acid, and evaporate to dryness. Repeat this treatment at least 6 times (up to 10 times for materials very rich in iridium). Dissolve the residue in 20 ml of concentrated hydrochloric acid, and bring to the boil in a covered beaker. Continue boiling until the volume has been reduced to about 15 ml, remove the cover, and evaporate gently to 5–10 ml (Notes 2 and 3).

Notes—1. Perchloric acid is required for the necessary destruction of the nitroso complexes of the platinum metals. To remove the perchloric acid and thus allow the formation of chloro complexes an evaporation is necessary. Lithium chloride allows the evaporation under conditions that prevent the reduction of the chloro complexes of the platinum metals.

2. Evaporations to smaller volumes, e.g. 2 ml as stated in the published procedure, may result in the extraction of rhodium and its transfer to the column, especially when the rhodium value is as high as 100 mg. In a private communication the author recommends a 5 N acid concentration at this stage.

3. It is most important not to allow the contents of the beaker to solidify at this stage, otherwise the final treatment with 20 ml of hydrochloric acid will have to be repeated. If, however, the residual liquor tends to crystallize on cooling, add hydrochloric acid 1 drop at a time until the solid redissolves.

The chromatographic separation. The cellulose column should be freshly prepared as follows:

Prepare a quantity of acid solvent by adding 20 ml of hydrochloric acid to 1 l. of isobutyl methyl ketone. Take 200 ml of this acid solvent, and add Whatman standard grade cellulose powder until a thin slurry is formed. Pour the mixture into the column in the usual manner, adding sufficient to form a bed of cellulose about 35 cm deep. Allow to drain, leaving about 1 cm of solvent over the cellulose, and then set aside until required.

Add to the cold solution of platinum metals a small amount of solid hydroquinone and then 10 ml of reducing solvent. Stir vigorously until the iridium has been reduced, adding more solid hydroquinone if necessary.

Begin the column separation by opening the tap fully. Immediately the solvent has drained, introduce the first extract by careful decantation, avoiding the transfer of any of the aqueous phase. Repeat the extraction with a further 10 ml of reducing solvent, and, as soon as the first extract has been taken up, transfer in the same way. Continue the extractions in this manner, with 10 ml of reducing solvent at a time, and avoiding the transfer of the aqueous phase. Do not allow the column to drain at any time to such an extent that air is introduced between the column wall and the cellulose.

As the elution proceeds the platinum band will move ahead, with the palladium band following somewhat more slowly. Collect the platinum fraction, however, as soon as the extractions are begun, for an almost invisible platinum band moves ahead of the main one, and may otherwise be lost.

As soon as it is evident that all of the palladium has been extracted and transferred to the column, make a final extract from the beaker with the acid solvent not containing hydroquinone, then place the reservoir in position, fill with reducing solvent, and continue the elution. Meanwhile, set aside the beaker containing the iridium and rhodium.

When the main platinum band has reached the lower end of the column, a gap of some inches should have appeared between it and the following palladium band. Continue to collect the platinum fraction until just before the palladium starts to come through.

At this point, change the receiver, and collect the palladium fraction in the same way, replenishing the reservoir with reducing solvent as necessary. Immediately the last of the palladium comes through, remove the reservoir, and elute with two or three successive portions of the acid solvent (non-reducing) to remove the hydroquinone and render the ensuing oxidation treatment fully effective. The column is then ready for the second stage, and meanwhile elution is stopped.

Extract the iridium by elution with an oxidizing solvent. Freshly prepare this solvent as follows:

Take 100 ml of the acid solvent, add 2 ml of hydrochloric acid and then 4 g of sodium chlorate. Stir thoroughly until the solution becomes cloudy, add 10 g of cellulose powder, and macerate. Decant the clear liquid into another beaker, and dilute 50 ml of this to 250 ml with the acid solvent.

Add 10 ml of the above oxidizing solvent to the original beaker which contains an aqueous rhodium solution, and shake. Add to the column. Repeat the extraction with 10 ml of oxidizing solvent exactly as was done above for platinum and palladium. When all of the iridium has been extracted, and the dark brown band is well clear of the residual pink rhodium band (Note 1), place the reservoir in position, and continue eluting with the acid solvent containing a little of the oxidizing solvent. When it is certain that all of the iridium has been collected, dilute the residual rhodium-containing phase with a little water, remove the reservoir, and transfer the solution to the column. Rinse the beaker 2 or 3 times. When these washings have almost been absorbed, fill the reservoir with water, and continue eluting. When the pink band has almost reached the lower end of the cellulose, collect the rhodium fraction in a separate beaker.

Notes—1. Despite care in avoiding any transfer of the aqueous phase, a small amount of rhodium usually finds its way on to the column.

2. In a private communication Payne states that the use of an acid solvent containing 1 vol. of tri-n-butyl phosphate with 2 vol. of isobutyl methyl ketone containing 2 per cent of hydrochloric acid allows the use of a cellulose column about 10 cm long. Platinum and palladium, however, cannot then be separated: this is conveniently accomplished by conventional methods. The technique of reducing with hydroquinone followed by oxidizing with the appropriate solvent enables platinum and palladium to be eluted together, then the iridium, leaving rhodium on the column as before. Also the platinum metals can be back-extracted from the solvent with water, provided that petroleum spirit (b.p. 60–80°C) is added to the solvent in the proportions of 1 vol. of petroleum to 2 vol. of solvent. The aqueous extract is then cleaned by extracting twice with carbon tetrachloride.

The treatment of individual fractions. To the platinum and palladium fractions add 1 g of lithium carbonate per 100 ml of ketone. To the iridium and rhodium fractions add 5 ml of a 10 per cent w/v lithium chloride solution. Evaporate the respective fractions by gentle boiling on an electric hot plate in a well ventilated fume cupboard. Continue the evaporation to dryness, but avoid heating the residue beyond the point necessary just to remove the ketone.

When cool, add 10 ml of water to each and then 50 ml of nitric acid. Cover the beakers, and heat gently. When the first vigorous reaction has subsided, bring the solutions to the boil, and continue boiling until brown fumes are no longer evolved, adding more nitric acid if required. Then add 25 ml of 60 per cent perchloric acid, boil until most of the nitric acid has been expelled, remove the covers, and evaporate the solutions until fumes are evolved. Continue fuming until the volume has been reduced to 5 ml for iridium or until the salts have begun to crystallize for the other metals. Set aside the iridium fraction for subsequent determination. Add 50 ml of (1 + 1) hydrochloric acid to the others; heat the solutions to boiling to reconvert the metals to the chloro complexes, and treat the rhodium and the platinum and palladium fractions as described below.

Gravimetric methods. Gravimetric methods are recommended for 2 mg or more of each metal. Whereas the method described above is not specifically recommended for µg amounts of metals, a suggested list of spectrophotometric methods for each metal is included. These may be useful for quantities of metals of the order of 1 mg or less.

Ruthenium. Treat the evaporated ruthenium–hydrochloric acid distillates in the 150-ml beaker with thionalide (Procedure 72).

Osmium. Acidify the sodium hydroxide–ethanol solution of osmium with hydrochloric acid, and evaporate to a small volume. Transfer to a 150-ml beaker, and precipitate osmium by using thionalide, as directed in Procedure 78.

Rhodium. Transfer the rhodium solution to a 150-ml beaker, and precipitate with thiobarbituric acid, as described in Procedure 82. Alternatively the hydrolytic precipitation described below for iridium may be applied.

Iridium. Dilute the perchlorate solution containing the iridium to about 200 ml with hot water, and add a sodium hydrogen carbonate solution until the pH changes to about 4. Add 10 ml of a 10 per cent sodium bromate solution, and boil gently for about 30 min to coagulate the precipitate, adding more sodium bromate solution if necessary to keep the pH between 6·5–7·0. Allow the precipitate to settle, and then filter through a Whatman No. 40 filter paper, washing well with hot water. Then wash with a 5 per cent ammonium chloride solution to prevent deflagration during the subsequent ignition. Dry the paper and precipitate, ignite carefully, and treat the iridium dioxide with hydrofluoric and nitric acids in the usual manner. Collect the precipitate once again, ignite, reduce under hydrogen, and weigh as usual.

Platinum. Treat the chloro complexes to precipitate platinum by using zinc, as described in Procedure 103. Alternative procedures involve hydrogen sulphide (Procedure 100) and thiophenol (Procedure 101).

Palladium. Prepare the solution of the chloro complex for a hydrolytic precipitation, as described for rhodium in Procedure 88. Then dissolve with hydrochloric acid and precipitate with dimethylglyoxime, as described in Procedure 94.

Spectrophotometric methods

Ruthenium. Dilute the original solution to 100 ml in a calibrated flask, and extract an aliquot equivalent to about 1 mg of ruthenium. Transfer the aliquot to a 150-ml beaker, add 5 ml of (1 + 1) sulphuric acid, and evaporate until copious fumes are evolved. After fuming for 2 or 3 min, cool the solution, add 60 ml of (1 + 1) hydrochloric acid and boil for 5 min.

Cool the solution, and transfer to a 100-ml calibrated flask, rinsing the beaker with water to bring the volume to about 85 ml. Add 10 ml of a 10 per cent thiourea solution, mix well, and heat the flask in a water bath at 50 ± 2°C for 30 min. Cool, make up to the mark with water, and measure the absorbance at 6750 Å in a 4-cm cell. Calculate the amount of ruthenium by comparison with a standard.

The standard is prepared as follows: Add 1·00 ml of a standard ruthenium solution (1 per cent in hydrochloric acid and 1 per cent in ruthenium chloride standardized by thionalide) to a 150-ml beaker, then add 5 ml of (1 + 1) sulphuric acid. Evaporate to fumes for 2 or 3 min, cool and continue as above.

Note—In a private communication the author states that the thiourea method has been replaced by the sodium thiocyanate method (see Procedure 145).

Osmium. Boil the alkaline osmate solution from the distillation to expel most of the ethanol, cool, and make up to a suitable volume from which an aliquot containing 1 mg of osmium may be taken. Transfer the aliquot to a 100-ml calibrated flask, and neutralize with hydrochloric acid, keeping the solution as cool as possible. Add 30 ml of concentrated hydrochloric acid, then 10 ml of the 10 per cent thiourea solution, and dilute to the mark. Mix well, immerse the flask in a water bath at 75 ± 2°C for 30 min, cool, and measure the adsorbance of the solution at 4800 Å in a 4-cm cell. Calculate the amount of osmium present by comparison with the standard.

To prepare the standard add 1 ml of the standard osmium solution (a sodium hydroxide distillate standardized gravimetrically, and containing 1 mg of osmium per ml) to a 100-ml calibrated flask, add 60 ml of (1 + 1) hydrochloric acid and then 10 ml of the 10 per cent thiourea solution, and dilute to the mark with water.

Add the small amount of iridium found in the rhodium solution (below) to this result.

Rhodium. The rhodium solution may contain a trace of iridium if the original material contained a high percentage of this metal; it is necessary to determine it to correct the main iridium figure.

Transfer a small portion of the previously oxidized and diluted solution (see " The Treatment of Individual Fractions " above) to a dry beaker, and add a few crystals of hydroquinone. With this reduced solution in the reference or water cell, measure the absorbance of the oxidized solution at 4900 Å in a 4-cm cell. Calculate the amount of iridium present by reference to the iridium standard, and correct the main iridium figure as necessary. Then filter the reduced solution through a dry Whatman No. 540 filter paper into a dry beaker, and measure the absorbance of this filtrate against water at 5150 Å in a 4-cm cell. Calculate the amount of rhodium present by comparison with the standard.

Prepare the standard from rhodium chloride to contain about 1 mg of metal per ml, and standardize by thiobarbituric acid (Procedure 82).

Iridium. Adjust the perchlorate solution to a suitable volume from which an aliquot containing 1 mg of iridium may be taken. Transfer 2 aliquots to 150-ml beakers, add 50 ml of (1 + 1) hydrochloric acid to each, and boil for 5 min. When cool, transfer each solution to a 100-ml calibrated flask, make the first solution up to about 90 ml with (1 + 1) hydrochloric acid and add 4 ml of freshly prepared chlorine water. Place the flask in a boiling-water bath for 30 min, then cool, and adjust the volume with (1 + 1) hydrochloric acid. Meanwhile, treat the second solution with 2 drops of a 5 per cent hydroquinone solution, and dilute to the mark with (1 + 1) hydrochloric acid. With the reduced solution in the reference or water cell, measure the absorbance of the oxidized solution at 4900 Å in 4-cm cells. Calculate the amount of iridium by comparing the absorbance with that of the standard.

Prepare the standard by precipitating hydrolytically from an iridium–chlorine solution (see above) sufficient oxide to produce a hydrochloric acid solution containing about 1 mg of iridium per ml of solution.

Palladium. Measure an aliquot representing about 10 mg of palladium, and make up to 100 ml in a calibrated flask with (1 + 1) hydrochloric acid. Mix well, filter a portion through a dry Whatman No. 540 filter paper into a dry beaker, and measure the absorbance of the filtrate at 4700 Å in 4-cm cells. Calculate the amount of palladium present by comparison with the standard.

Prepare the standard from a palladium chloride solution standardized gravimetrically, potassium iodide being an acceptable precipitant (Procedure 96). Transfer 10 ml of this solution, which should contain about 1 mg of palladium per ml, to a 250-ml beaker. Add 5 ml of nitric acid and then 5 ml of perchloric acid, and evaporate to about 2 ml of acid. Cool, add 50 ml of (1 + 1) hydrochloric acid, and boil for 10 min. Cool, dilute to 100·0 ml with the (1 + 1) hydrochloric acid. Measure the absorbance at the same time as that of the unknown.

Platinum. Transfer an aliquot representing about 0·35 mg of platinum to a 150-ml beaker, add 5 ml of perchloric acid, and evaporate until fumes are evolved. While fumes are being evolved, add about 10 drops of hydrobromic acid, and continue heating until most of the excess of perchloric acid has been removed; then cool, add 50 ml of (1 + 1) hydrochloric acid, and boil to reconvert the platinum to the chloro complex. Cool again, transfer the solution to a 100-ml calibrated flask, and dilute to about 80 ml with (1 + 1) hydrochloric acid. Add 10 ml of a 20 per cent tin(II) chloride solution, and dilute to the mark. Mix well, set aside for 30 min, and then measure the absorbance at 4030 Å in a 4-cm cell; compare with a standard.

Prepare the standard from platinum sponge and *aqua regia*. Remove the nitric acid as usual, and dilute to provide 0·1 g of platinum per l.

Fire Assay for Noble Metals

EXTRACTION FROM ORES

The classical method of assay for noble metals involves the preparation of suitable fusion mixtures and a subsequent heating to provide a slag. In general the extraction of noble metals from this fused mixture is accomplished by providing for the production *in situ* of an alloying or collecting metal, of which the most frequently used is lead. This practice has grown out of an irrational assumption that the platinum metals are as noble as gold. All of these metals will form oxides when heated in air by a bunsen flame; platinum at higher temperatures suffers a loss of weight now known to be due to the formation of oxides. There is also the fact that the reduction of gold salts to the metal is accomplished with relative ease. It is surprising that the fire assay for even the more common platinum metals has been acceptably successful.

Deville and Debray[213] fused the ore with borax in the presence of wood charcoal and silver to produce an alloy said to contain all of the platinum metals. Perry[214] fused alloys of the metals with lead and silver, cupelled to remove the base metals, and then re-alloyed with silver. Deville *et al.*[215] applied fusion methods to larger samples of ores and alloys previously treated with *aqua regia*. The residues were fused with litharge, silica and carbon to produce a lead button. Partition with nitric acid then gave a residue from which a zinc alloy was prepared. This alloy on treatment with acid produced finely divided iridium, osmium, etc., which could then be satisfactorily corroded with fused nitrates. It is interesting to note that the authors concerned used a fusion with lead followed by acid treatments to produce fairly pure iridium crystals.

It is significant that in 1885 Wilm[216] criticized the contemporary methods of analysis for the platinum metals, and submitted that no satisfactory procedure had been recorded. In 1919, Duparc[217] stated that, prior to the development of his procedures, it was difficult or impossible to obtain concordant results from the same sample.

Hampton[218] drew attention to the ease with which vanadium, as NH_4VO_3, could be mistaken for $(NH_4)_2PtCl_6$, and suggested that some presumably dishonest assays may have arisen from this error. He charged the U.S. Bureau of Standards with failure to draw attention to the sources of error in the determination of platinum. Davis[219] reported that the results from various assayers for a concentrate containing 40–50 per cent of copper varied so much that the U.S. Bureau of Mines was requested to devise an analytical scheme.

As late as 1940 Lathe[220] stated that so far as he was aware " no simple and at the same time reliable methods for the determination of metals of the platinum group in ores and concentrates have yet been published. There is in the literature much that is uncertain, contradictory, or inapplicable to any particular case ". Perry[214] also criticized these " established " methods, and recommended an initial selective parting with sulphuric acid to remove silver, followed by re-alloying with silver, parting with nitric acid to remove platinum, and treating the residue with *aqua regia* to remove gold. The insoluble residue was called iridosmine.

The U.S. Bureau of Mines, in 1921, published an extensive pamphlet dealing with various aspects of platinum metals assaying. A significant part of the publication dealt with the claim that platinum metals may occur in natural deposits in forms which resist determination by the classical lead collection. An array of evidence was marshalled by Davis to refute this claim, and whereas the present author agrees with the conclusions in general, one does well to remember that negative evidence is not conclusive evidence.

One of the questionable aspects of the fire assay concerns the influence of the character of the platinum metals minerals. Because one cannot write with assurance the mechanically mixed composition, the claim is sometimes made that for certain ores the collection by molten lead is ineffective. To avoid this possibility, wet treatments of the ore with various mixed acids were sometimes applied before the fire assay in order to convert platinum metals to forms which were known to be amenable to fire assay procedures. The fact that all of the platinum metals except palladium and rhodium resisted attack by single mineral acids suggested to the early analytical chemist the use of selective dissolution or corrosion to separate associated base metals.

Wilm[221] and others recorded methods that involved collective precipitations from solutions of ores by zinc or iron, and the subsequent removal of base metals by nitric or hydrochloric acid. Seliverstov[222] decomposed the ores with concentrated sulphuric acid, and treated the mixture with sulphur to form sulphides that were filtered, roasted and then fire assayed to form a bisilicate slag. For high valued ores, an alternative procedure was provided by which the roasted residue was treated with formic acid, then with *aqua regia* to extract selectively the black residue: after filtration the platinum and palladium were precipitated by formic acid in an ammoniacal medium. The residues were treated to determine platinum, palladium, gold, rhodium and iridium. Karpov and Fedorova[223] used an *aqua regia* extract of the ore, and digested the residue with ammonium acetate to extract lead sulphate and silver chloride. The residue was fused with silver and borax. The resulting silver bead was treated with sulphuric acid, the insoluble was fused with sodium peroxide and sodium hydroxide, and the osmium and ruthenium were distilled from a chlorinated solution. The procedure involved the separation of platinum and iridium by using ammonium chloride, then roasting, followed by cupellation with silver, parting with nitric acid, and re-precipitation of the platinum with ammonium chloride. The iridium residue was purified by fusing it with bismuth, then treating it with nitric acid and *aqua regia*. Rhodium was separated from the acid by using zinc, this process being followed by fusion with silver and parting with acids.

Zhemchuzhnü *et al.*[224] described a somewhat similar modification for the treatment of the *aqua regia* residue, and included a procedure for the treatment of the *aqua regia* extract. The method involved an oxidation by chlorine and the precipitation of platinum and iridium with ammonium chloride, followed by the removal of palladium and gold with dimethylglyoxime from a portion of the filtrate, and by treatment of the palladium–gold filtrate with zinc to precipitate rhodium and the remaining iridium. Gold was also produced by a reduction with sodium nitrite of a second portion of the filtrate from the platinum–iridium precipitation, and subsequently palladium was precipitated by mercuric cyanide. The iridium precipitates were collected, and fused with soda to dissolve ruthenium selectively. Lovely[225] recommended a combination assay method which involved the conversion of ores or concentrates by fusion in a plumbago crucible with iron, sulphur and carbon to form a matte: this was subsequently ground, and treated with *aqua regia*, from which mixture osmium and ruthenium were said to be evolved. Methods of separating platinum thorium, iridium, polonium, actinium, palladium, gold and rhodium were included. A similar method of concentration was described by Griffith.[226] He fused nickel-copper ores of the Sudbury district, containing between 15 per cent and 50 per cent of sulphides; beyond these limits either sulphate blanks were added or the sulphide ore was partially roasted and silica added to the charge. The fused matte was removed from the broken pot, and treated with dilute sulphuric acid to produce a final residue of 20–30 g that was assayed in the usual manner. Griffith did not prove that the matte is a sufficiently effective collector, and the low palladium recovery was ascribed, without sufficient evidence, to the failure of sulphuric acid to extract all of this metal. A somewhat comparable method for the analysis of platinum concentrates was described by Schwitter.[227] A series of *aqua regia* extractions resulted in a residue that was then alloyed with lead; the latter was parted with nitric acid, and the ignited residue was erroneously termed osmium. From the *aqua regia* extract the author removed platinum with ammonium chloride, gold with ferrous sulphate and palladium with potassium iodide. In the final filtrate zinc was used to collect rhodium and iridium.

In the present author's opinion none of the above combination assays can be considered efficient; none has been proved accurate or precise. In many instances the methods of determining individual metals are outdated. In practically all instances large samples of ore or concentrate are required, because each determination involves a precipitation reaction. Adams[228] stated that preliminary acid treatment applied to South African flotation concentrates provided no advantage and proved extremely tedious.

The single recorded research which deals quantitatively with the merits of leaching is of Hoffman *et al.*[229] The authors used a technique involving a preliminary treatment of the oxidized ore or concentrate with hydrochloric acid, followed by a hydrogen sulphide precipitation from the acid extract or by a zinc precipitation. These authors' results indicated that " leaching processes do not, in general, provide values higher than those obtained by normal fire assay ".

An extraction of platinum from ores by an amalgamation process was described by Plaksin and Shtamova.[230] The 65-mesh ore was treated with dilute sulphuric acid, and then ground with zinc amalgam, mercury, copper sulphate and sulphuric acid. The ore was then washed with a caustic solution which, the authors claimed, resulted in removal of 90–97 per cent of the platinum. Unfortunately no further publications of this interesting extraction are known.

Aside from the classical lead collection, various procedures have been considered for the analytical concentration of the platinum metals. The separation of noble metals in copper–nickel slimes was accomplished by Pshenitsyn and Lazareva[231] through a fusion with borax. The platinum groups were selectively removed from copper, nickel, iron and lead by a fusion at 1200°C for 2 hr. The fused mixture was boiled with hydrochloric acid, and the residue weighed as noble metals. Obviously this method could not give good accuracy.

A method based on the fact that arsenic and antimony speisses are good collectors of osmium, iridium and ruthenium, but less effective for platinum and palladium, has been reported by Rusden and Henderson.[232] The fluxing mixture included arsenic as well as the conventional mixture, and the fusion was carried out in the presence of an iron rod. These authors found[232] that the fused mixture solidified in distinct layers—lead on the bottom, then speiss, then matte and finally slag. The addition of iron filings assayer, and sodium (1 : 2) borate, disodium tetraborate and sodium pyroborate, used by the chemist.

A further deficiency associated with all of the various nomenclatures is that none allows for the difference in basicity between the various oxides such as between K_2O and MgO, or the relative acidity of the acid oxides such as between B_2O_3 and SiO_2. Thus a bisilicate is $Na_2O\cdot SiO_2$ or $MgO\cdot SiO_2$. By analogy with the relative fluxing ability of KOH and $Mg(OH)_2$ on aluminium one cannot expect that the time and temperature required to produce a fluid flux with all basic oxides or with all acid oxides will be even comparable. On the assumption, however, that in the period of fire assay the reactions proceed to completion, the ultimate fluxing ability of the oxides may be comparable. The assayers' expressions for various compounds, together with the acceptable chemical nomenclature, are recorded in Table 18.

TABLE 18. THE CLASSIFICATION OF SILICATES AND BORATES

Chemical formula	Oxygen ratio acid to base	Nomenclature	
		Assayers	Chemical
$2Na_2O\cdot SiO_2$	1 : 1	monosilicate	sodium (2 : 1) silicate sodium orthosilicate
$Na_2O\cdot SiO_2$	2 : 1	bisilicate	sodium (1 : 1) silicate sodium metasilicate
$2Na_2O\cdot 3SiO_2$	3 : 1	trisilicate	sodium (2 : 3) silicate sodium mesosilicate
$3Na_2O\cdot B_2O_3$	1 : 1	monoborate	sodium (3 : 1) borate sodium orthoborate
$2Na_2O\cdot B_2O_3$	3 : 2	sesquiborate	sodium (2 : 1) borate sodium pyroborate
$Na_2O\cdot B_2O_3$	3 : 1	triborate	sodium (1 : 1) borate sodium metaborate
$Na_2O\cdot 2B_2O_3$	6 : 1	hexaborate	sodium (1 : 2) borate sodium tetra- or pyroborate

The assayers' expressions are used throughout the following discussions.

SLAGS

The above assayers' nomenclature can also be applied to slag constituents. Thus $2CuO\cdot SiO_2$ is a monosilicate slag and $5CuO\cdot SiO_2B_2O_3$ is also a monosilicate slag.

In general, for platinum fire assays the slags may be regarded as silicates and borates of the oxides of copper, iron and nickel, mutually dissolved with lead silicates and borates. The metals present in the slag may sometimes be indicated by its colour subsequent to cooling. In general slags from platinum assays should be clear. Assays of cupels and pots, however, are sometimes required, and the resulting slags are very often opaque.

White opaque slags are obtained with materials containing large proportions of calcium, magnesium, aluminium and zinc. The base metals associated with platinum, and appearing in the slag, are usually copper, iron, nickel with traces of tin, cobalt, manganese, chromium, selenium and tellurium. The traces have little influence on the colour of the slag. Lead, of course, is present as a necessary addition to the flux and, as a fused silicate with soda ash, it provides colourless glasses. In general shades of green indicate iron(II). The latter interferes with the normal colour of copper, which is the brick red of copper(I) silicate or borate. In the presence of iron, the slag becomes dark or black. Manganese, in large quantities, produces a similar effect, although in small amounts, when present alone, the slag is a light pink or purple.

After a fire assay one should examine the slag visually. If it is black, the homogeneity of the slag colour can be determined on a thin chip.

Concerning the properties of a satisfactory slag Bugbee[234] states the following:

(1) It should have a comparatively low formation temperature, readily attainable in assay furnaces.
(2) It should be pasty at and near its formation temperature, in order to hold up the particles of reduced lead until the precious metals are liberated from their mechanical or chemical bonds, and are free to alloy with the lead.
(3) It should be thin and fluid when heated to somewhat above its melting point, so that shots of lead may settle through it readily.
(4) It should have a low capacity for noble metals, and should allow a complete decomposition of the ore by the fluxes.
(5) It should not attack the material of the crucible to any great extent.
(6) Its specific gravity should be low, to allow a good separation of lead and slag.
(7) When cold, it should separate readily from the lead and be homogeneous, thus indicating complete decomposition of the ore.
(8) It should contain practically all the impurities of the ore.

Concerning the question of whether or not there is an optimum slag composition for each ore Bugbee[234] states "that no two assayers working on the same ore will agree exactly on the flux proportions to use, so it is safe to say that, for any given ore, there is a comparatively wide range within which the four common flux constituents may be varied, and still, in the hands of an able assayer, yield practically identical results ". Smith[235] stated that the best fluxes to be used in each particular instance must be left to the judgement and experience of the assayer. The present author agrees with these opinions.

FUSION TEMPERATURES

The initial temperature, the rate of heating, and the finishing temperature are important factors in a successful fire assay for the noble metals. Obviously the degree to which these variables may be controlled will depend somewhat upon the character of the heating equipment, e.g. furnaces which are heated by gas and air, by coke and air, or by electrical methods.

To the degree that heating can be controlled it is desirable to subject the pot contents to an initial sintering temperature. At about 600°C the litharge is reduced by carbon, and the resulting lead droplets are homogeneously mixed with the charge. Simultaneously, a relatively slow chemical action between the flux constituents and ore takes place. Carbon dioxide is evolved, and provides some mixing during the reaction between the base and acid constituents. This is an important phase of the assay, and may occupy some 15–20 min, varying beyond these limits with viscous slags.

After the sintering process the temperature is increased to a full red heat, usually about 1100–1200°C for platinum metals assays. During this period the mix continuously becomes less viscous, and the lead droplets with their noble metal content drop to the bottom of the pot to form the button.

Some assayers suggest a high finishing temperature, e.g. 1200°C. The hope is to allow the noble metals which do not alloy readily with lead to fall to the button area. This is, of course, a reasonable precaution because such metals as iridium and the alloy iridosmine do not react readily with lead. These noble metal constituents have a density comparable to that of gold, and should fall readily through the fluid flux. In those instances where assays for a high iridium content are required the assayer may wisely choose to finish at about 1200°C. It has been the present author's experience that in many instances the finishing temperature need not proceed much beyond about 1100°C. With the type of furnace used by the author (Chapter 7, Equipment No. 16) the sintering process described above is accomplished without any regulation of temperature. The pot charges are placed in the furnace at about 900°C. Presumably the rate of heating from the cold charge allows the simultaneous production of lead and a sufficient decomposition of the ore. Because the rate of temperature rise is normally slow the controls are immediately adjusted to allow an ultimate temperature of 1100–1200°C. Normally this period varies between about 50 and 60 min, but may be considerably extended as the heating bars become aged. The slag is quite fluid during the final period of about 20 min. In various industrial laboratories the charges are inserted at about 950°C, and are allowed to remain at this temperature for 45 min before pouring. Under these conditions the slags are usually reassayed. The problem of slag losses has been investigated for each of the six platinum metals, and the variations of these losses with the six metals and with slag compositions are discussed below.

LEAD BUTTONS

No data have been recorded to allow a prediction of the optimum button size for any particular ore or type of sample. It has been stated that the weight of lead button should be related to the amount of charge, increasing somewhat from certain lower unstated limits. On the other hand the data recorded for silver determinations by fire assay suggest that the collecting power of a given weight of lead bears no precise relationship to the amount of the charge.

Undoubtedly, the amounts of the noble metals in the ore sample will set limits to the lowest weight of lead required for a quantitative collection. This relationship has not been expressed numerically.

One may approach this problem from a reasonable point of view, however. It is traditional that a generally satisfactory button size varies between 25 and 35 g. Evidence is presented below to indicate that 10 g buttons may be ineffective for complete collection in some instances. One may guess that with high values of noble metals some advantages may accrue from amounts of lead in excess of 35 g, in that there may be some improvement in collection during the fall of the larger lead weight. Anyway, if larger amounts of lead are desired this should not be accomplished at the expense of the litharge added as a flux.

Concerning the identity of the dissolved and mechanically mixed platinum metals constituents of the lead button there are practically no data. The system of lead and the six metals is an exceedingly complex one, and information about its character must be derived from guesses about much simpler systems. It seems reasonably certain that iridium, in some forms at least, is mechanically mixed. This guess also applies to at least some of the iridosmines. Because these constituents have a high density (Ir = 22·42) they will be found concentrated at the apex of the button. Thus the traditional method of hammering the button to form a cube cannot be recommended, because mechanical losses may well occur. Normally the button should be bright, soft and malleable.

In those instances where slag adheres to the button it can be removed by gentle tapping with a thin metal rod.

Buttons which are obviously badly contaminated should be scorified. This contamination of buttons may arise from excessive proportions of base metals such as copper or nickel in the ore, together with an unsuitable choice of flux composition. " Dirty buttons " cannot be cupelled effectively because the base metals deposited on the surface of the cupel may carry " values ", and the cupelled bead will also be contaminated. Furthermore, when wet treatments of the button are contemplated the presence of excessive amounts of base metals will complicate the wet treatment, which is already usually fraught with sufficient unavoidable difficulties.

SCORIFICATION

The scorification process may sometimes be used as a substitute for a pot assay. It is used extensively for certain types of silver and gold assays. In these instances it involves mixing the ore sample with lead, and covering with borax. The reactions involved are similar to the pot fusion, but there is also a series of reactions between air and the constituents of the charge. The oxidized lead forms part of the fusion mixture, and the residual lead acts as a collector. The scorification assay is not, in general, recommended for noble metal determination. The process is essential, however, for the reduction of button size and, as stated above, for cleaning a badly contaminated button. In this instance the button is transferred to a scorifier (see Chapter 7, Equipment No. 14), and covered with a few g of borax, the amount depending upon the degree of contamination. At the required temperature of 1050–1100°C and in the presence of air the melted lead is oxidized, and together with the borax forms a slag with the oxidized base metal contaminants. The slag moves progressively to the periphery of the scorifier, and the molten lead forms the centre or *eye* of the fusion. The melt may be poured as in the pot fusion.

CUPELLATION

The classical fire assay with lead as a collector usually requires the presence of silver. Thus the lead button includes, in addition to noble metals, an amount of silver sufficient to collect the noble metals, and in proportions sufficient to allow parting procedures. The process used to produce this silver bead or *prill* is known as cupellation.

A second method of assay sometimes called the dry assay is best accomplished in the absence of silver, however, and involves a cupellation to produce a mixed residue of noble metals. In this instance the residue seldom takes the form of a spherical bead, and is usually found in a non-coherent deposit. Generally the method is used for the more common noble metals, and when accurate results are not required. The subsequent method of analysis involves the process of dissolution, e.g. chlorination, and then the application of one of the above separatory methods, the choice of which depending upon the composition of the residue.

The techniques and characteristics of cupellation have been studied in detail for silver and gold, particularly for the former. Detailed descriptions may be found in such standard texts as Bugbee,[234] Smith,[235] Fulton and Sharwood[14] and others.

Relatively little factual data have been recorded concerning the cupellation of buttons containing the platinum metals. Some of the characteristics of the cupellation for silver, however, apply also to platinum metals. As would be expected, the temperature variations and control, which are important factors for silver because of its volatility, are of relatively little importance for the platinum metals.

The process of cupellation is accomplished in vessels called *cupels*. The construction and desirable characteristics of these are discussed in Chapter 7, Equipment No. 15.

Under suitable conditions of temperature and air exposure the lead button in the cupel is oxidized to form litharge, which is liquid at its formation temperature. Differing from the noble metals constituents, the litharge wets the cupel and is absorbed, carrying with it such base metals as copper and nickel. In general suitable cupels will absorb about 98·5 per cent of the litharge formed, the remaining 1·5 per cent being volatilized. The process is an interesting one; under the correct conditions the lead melts quickly and then forms a grey scum of lead oxide over the surface of the melted metal. This fuses rapidly, and the melted alloy is quickly exposed, this phenomenon being known as " uncovering " or " opening ". If this does not take place during the initial stages after melting, the button is said to be " frozen ". Sometimes the frozen alloy may be " driven " or " cleared " again by raising the temperature, and placing a piece of charcoal adjacent to the cupel. The present author prefers to discard frozen buttons.

Freezing is usually due to low temperatures prior to the transfer of the button. It is also sometimes caused by a temperature drop during cupellation. With the progress of the cupellation the liquid litharge flows over the surface of the melted lead and is absorbed by the cupel. This appears as a dull red or black ring on the surface of the cupel. Feather-like crystals of litharge may also appear on the sides of the cupel above the lead. At lowered temperatures these feathers accumulate and eventually cover the melted alloy, and this process results in freezing. It is generally advisable to increase the temperature toward the finish of the cupellation process. Theoretically, this is justified by the increase in noble metal proportions as the lead is removed. Whereas this precaution is an important factor in the assay for silver and to a lesser degree for gold for the removal of traces of lead, it is the present author's experience that lead is not thus entirely removed, and in the subsequent wet treatment of the noble metal residue there is nothing to be gained by merely reducing the amount of the lead trace. Concerning gold and silver, but not always the platinum metals, the final stage of cupellation is marked by a sudden clearing of the previously driving bead. This brightening follows the removal of the final very thin layer of litharge over the surface of the bead.

The resulting play of colours is followed in a few seconds by a dullness in the bead and then a sudden brightening. With the platinum metals the final stage of cupellation is not usually clearly defined. The platinum metals, if present, will display a variety of effects on the surface of the cold silver bead. These are discussed below.

Improper or hasty cooling of silver–noble metal beads will result in the sudden expulsion of oxygen, which is quite soluble in molten silver. The result of this action is one or more protruberances of silver from the bead. The process is called " sprouting " or " spitting ". With gold–silver beads the excrescences are objectionable, because the necessary coherence of the gold during the parting process is prevented. With the platinum metals violent spitting may result in mechanical loss; the various processes of parting, however, invariably produce at least a partially disintegrated residue, which introduces no particular difficulties in the wet methods of determining the platinum metals.

It may be emphasized here that the silver bead collection and its subsequent wet treatment, when properly applied, serves as an excellent method for the determination of gold, palladium and platinum together with traces of rhodium, iridium and ruthenium. It is quite unacceptable for osmium. For larger proportions of the more insoluble platinum metals, and where the amount of osmium is required, the direct wet treatment of the lead button is preferable. Unfortunately the wet methods at present available for lead buttons are complicated by the persistent presence of lead salts. Precipitation of lead as its sulphate from a nitric acid parting solution is by no means an effective procedure, because the evaporated filtrate yields significant amounts of the lead sulphate mixed with the palladium, traces of platinum and perhaps rhodium, etc. Furthermore, the re-treatment of the lead sulphate to recover traces of platinum metals either by extraction with ammonium acetate or by scorification is cumbersome and attended by uncertain accuracy. Because the direct treatment of the lead–noble metals button offers advantages over the silver bead method, one may hope that the newer techniques will provide improved methods of separating lead from parting acids. In so far as an immediate recognition of the presence of platinum metals is concerned, however, the silver bead, as compared to the lead button, is a much better basis from which to learn not only the presence of the platinum metals but, within limits, to make reasonable guesses as to practical values.

Surface Effects of Platinum Metals in Silver Assay Beads

Several authors have suggested that by a classification of the surface effects of the platinum metals on the silver assay bead, a surface examination might yield not only qualitative but also approximately quantitative data.

Bannister and Patchin[237] investigated the binary systems platinum metals–gold and platinum metals–silver, and not only dealt with the qualitative effects but also attempted to determine the minimum percentage of each of the platinum metals which would yield specific surface phenomena. Byers[238] described surface effects on the binary systems platinum metals–silver, stating that characteristic effects are visible in silver beads containing as low as 0·1 per cent of platinum. The present author has made some one thousand platinum metals–silver cupellations with subsequent examinations for surface phenomena, and has not been able to confirm this conclusion. Byers[238] described the effects of osmium on silver beads, but did not state how the composition of the beads was determined; it is probable that the proportions of osmium and silver stated to be present were those added to make the bead. Full cupellation of silver–osmium beads will result in an explosion of the bead if the osmium content is high, and the almost complete loss of small proportions of osmium.

Byers[238] discussed also the surface effects of the binary systems platinum metals–gold, and stated that the various members of the platinum group are more often associated with gold than with silver. According to Langer and Johnston,[239] a Sudbury precious metal residue contained about 372 parts of silver and 13 parts of gold to 100 parts of platinum metals. Placer deposits very often carry gold in predominant proportions mechanically mixed with native platinum, and in instances such as these the data given by Byers[238] may be of considerable value, because unlike silver the surface of a pure gold bead is normally smooth with a characteristic colour.

In the fire assay for platinum metals, silver is usually added to the charge in the proportion of 15–20 parts per 1 of total platinum metals, in order to facilitate parting by means of sulphuric or nitric acid. Therefore the data given below are confined to the discussion of the surface phenomena of the silver–platinum metals within these proportions.

In the examples reported below the proportions of platinum metals were determined by the analysis of the bead. The reported compositions can be considered accurate to about 0·5 per cent. The cupellation temperature recorded was that of the wall of the bone-ash cupel, and was determined by means of an optical pyrometer. No attempt was made to determine the actual temperature of the cupelling bead. In each example, unless otherwise recorded, the cupellation temperature was 950 ± 25°C. After completion of the cupellation process the beads were removed slowly in order to avoid spitting.

These salted beads were arranged in sets, associated with a number of pure silver beads prepared under identical conditions, and were examined by three operators experienced in this work who had no previous knowledge of the bead composition. The beads were brightly illuminated, and were examined by means of a microscope with a ×40 magnification.

BINARY SYSTEMS

Platinum–Silver

For high percentages of platinum (Fig. 3) the surface character is a somewhat regular pattern of pits with a continuously smooth surface. As the percentage of platinum is decreased, these pits become less frequent.

The bead in Fig. 4, containing 1 part of platinum to 50 parts of silver, shows very slight platinum effects, while in Fig. 5 the platinum effects are more marked, in spite of the fact that this bead contains 1 part of platinum to 60 parts of silver. This indicates that the intensity of specific platinum effects under the condition specified above could be only very roughly proportional to the percentage of platinum present. When the proportion of platinum to silver was less than about 1 part of platinum to 90 of silver, the operators were unable to distinguish such beads from silver beads made up to the same size and subjected to identical conditions. A comparison of Fig. 6, a pure silver bead, and Fig. 4, which is near the border area of sensitivity, will indicate the difficulty in identifying beads which contain a much lower percentage of platinum. Figure 7 is also a silver bead. The lower, extremely rough portion of the bead is the area that was attached to the cupel.

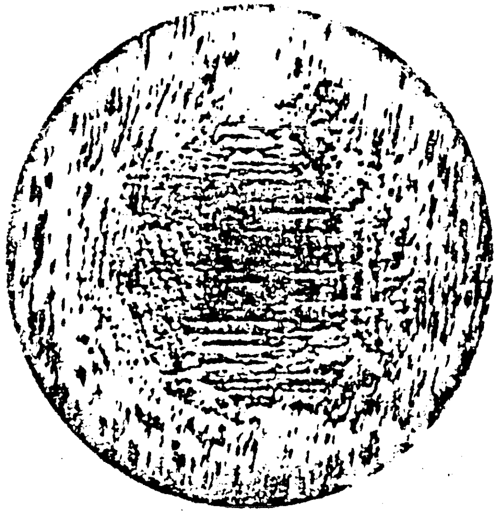

FIG. 3. 1 Pt : 12 Ag, magnification × 40, weight 30 mg.

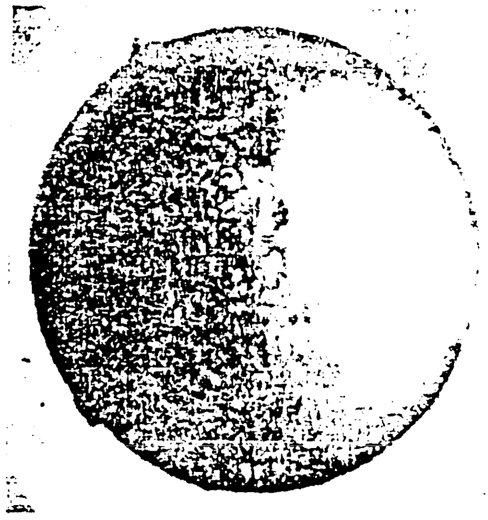

FIG. 4. 1 Pt : 50 Ag, magnification × 30, weight 40 mg.

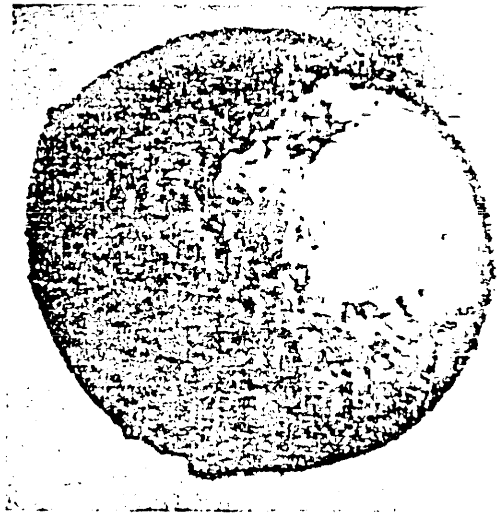

FIG. 5. 1 Pt : 60 Ag, magnification × 30, weight 40 mg.

FIG. 6. Ag, magnification × 30, weight 40 mg.

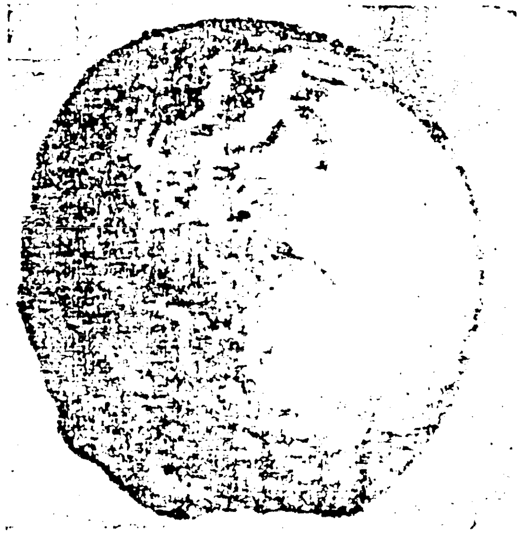

FIG. 7. Ag, magnification × 30, weight 40 mg.

Palladium–Silver

When palladium is present in high percentages (Fig. 8) the beads resemble those of platinum–silver in that the surface is covered with smooth-surfaced pits. These pits are much smaller than with platinum, and are less regular in pattern.

Iridium–Silver

When iridium is present in high percentages (Fig. 9) the bead forms an irregular, often elongated black mass spread over a considerable surface of the cupel. Very often numerous small particles of the bead can be found separated from the main body. As the proportion of the iridium is decreased the bead assumes a more spherical shape, and projections of blue-black crystalline clumps appear, scattered over the surface. The bead finally assumes a form similar to low percentage platinum beads.

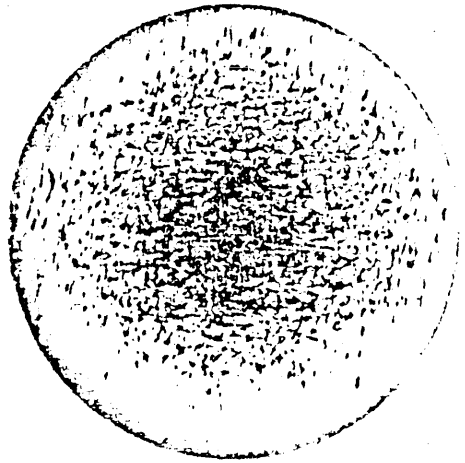

FIG. 8. 1 Pd : 10 Ag, magnification × 40, weight 30 mg.

Rhodium–Silver

With large percentages of rhodium (Fig. 10) the bead assumes an irregular shape and is coke-black with an extremely rough surface.

It is the present author's opinion that under the conditions described above the presence of platinum and palladium can be detected with certainty only when present in proportions of 1 or more parts of platinum or palladium to about 70 of silver. Additional tests made on beads of about 500 mg and 10 mg indicate that the limit of sensitivity with respect to platinum is also 1 part of platinum to about 70 of silver.

FIG. 9. 1 Ir : 7 Ag, magnification × 20, weight 30 mg.

POLYCOMPONENT SYSTEMS

Buttons were made containing approximately the relative proportion of each of the platinum metals often found in norite deposits, i.e. 8·3 parts of platinum, 9·4 parts of palladium, 0·6 parts of rhodium, 0·6 parts of iridium and 3·0 parts of gold. These buttons were cupelled, and the beads examined exactly as described for the binary systems.

Figure 11 illustrates the surface phenomenon, which is different from that of platinum–silver. An examination indicated that under the conditions described above it was possible to detect the platinum metals when the proportion present was about 1 or more parts of total platinum metals to 150 of silver. Figure 12 indicates the decrease in the intensity of surface effects upon reduction of the platinum metals content.

Beads containing the same percentage of silver and platinum metals but weighing approximately 8 mg were prepared as described above: the limit of sensitivity was about the same as with those weighing 40 mg.

Buttons were made containing the following relative proportions of platinum metals: 23·1 per cent gold, 3·2 per cent iridium and 73·7 per cent platinum. The beads were prepared and treated exactly as described above. The surface phenomena characteristic of platinum could be detected when the percentage of platinum metals was high, but disappeared when the ratio of platinum metals to silver was about 1 to 80: the operators were then no longer able to distinguish beads containing platinum from pure silver beads.

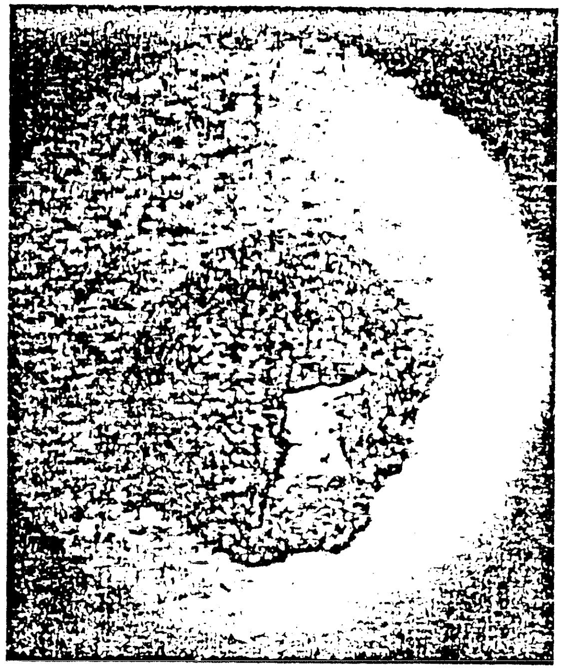

FIG. 10. 1 Rh : 10 Ag, magnification × 17, weight 30 mg.

Because so very little information is recorded about the properties of the polycomponent platinum metals–silver systems, the present author feels that more emphasis than is reasonable has been placed upon the value of the surface effects on assay beads for the detection and rough estimation of their platinum metals content.

A number of platinum–silver beads cupelled with a finishing temperature of about 1300°C gave surface effects of an entirely different character to beads of similar composition cupelled at 950°C. The rate of cooling also seemed to exert a marked effect on the character of surface phenomena.

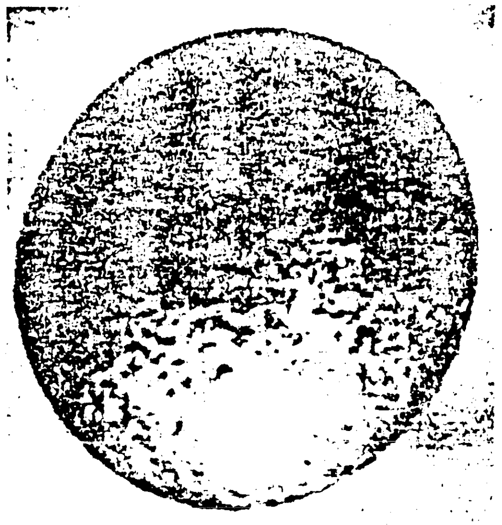

FIG. 11. 1 Pt metals : 30 Ag, magnification × 30, weight 40 mg.

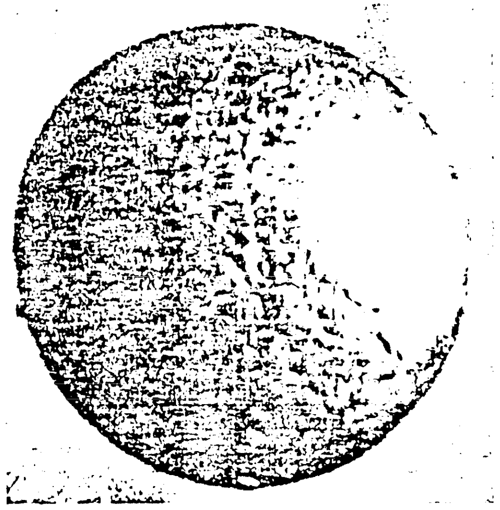

FIG. 12. 1 Pt metals : 140 Ag, magnification × 30, weight 40 mg.

The present author's experience has borne out Stanley's statement[240] that " sometimes one bead will be free from surface effect while others from the same sample show signs ".

By reducing the percentage of silver in the bead an experienced operator can sometimes determine that the ore under examination is of commercial value with respect to total platinum metals, but the absence of specific surface phenomena does not necessarily mean the absence of commercial values of platinum metals. Only an analytical chemist thoroughly familiar with the appearance of platinum metals–silver beads, as well as pure silver beads, can make even approximate guesses concerning the qualitative composition of the platinum metals assay bead.

Slag Losses of Noble Metals

Considerable confusion arises from published assay procedures that describe the acidity and basicity of constituents of pot charges. Unfortunately, some of the present author's own procedural descriptions have added to this confusion in that it was not always made clear that the losses of platinum metals to the slags should be related to the acidity of the final slag and not to the silicate degree of the added fluxes. Furthermore, the acidity of the slag can seldom be calculated with more than approximate accuracy. To accomplish an accurate description one must have knowledge not only of all of the major constituents of the flux, but also of the types of reactions between the acid and basic constituents of the complete charge. Because the solution composition of practically all assay slags is very complex, and the reactions are appreciably dependent upon the temperature attained and the time and rate of heating, one can only approach within very approximate limits the potential acidity of the full charge. Thus a reported neutral slag may actually be considerably acid or basic. In all of the discussions described below an attempt is made to assign the terms acid or basic on the basis of simple reactions between the acid and basic oxides of the complete charge, e.g. ore and flux. The reader is cautioned here against a misinterpretation of the terms basic, acid and neutral. None of the various definitions for these terms used by the analytical chemist may apply to the slag constituents. Thus a neutral slag is not one that reacts as a neutral salt, e.g. $Na_2O{\cdot}SO_3$ but one which contains an equal number of basic and acidic oxygens, e.g. $2Na_2O{\cdot}SiO_2$. To state that a platinum metal is readily lost to a basic slag does not mean that the slag yields the ordinary basic reactions, e.g. the slag could correspond to $3CuO{\cdot}SiO_2$. For those who wish to use other conceptions of acidity, re-calculation of the proportions of flux and ore can be made. For this reason and others, the full composition of a recommended charge should be included in published procedures for the fire assay methods.

In a series of investigations the present author has attempted to find the relationships between slag composition and the losses of each platinum metal to the fused slag. From the point of view of the most effective practical applications, researches of this type require an accurate and extensive knowledge of the varieties of forms in which the platinum metals occur in ores. Unfortunately, insufficient information is available about the mineral types in even the commercially valuable ore deposits. For any given deposit, general statements can be made about the mode of occurrence of the more common platinum metals, but for a metal such as osmium it is a good guess that the platinum metals producers are unaware of the mineral origin of the metal. One need only examine the published literature concerning the character and the analysis of iridosmines to realize this situation. The mineralogy of this mineral is practically unknown, and in so far as other natural sources of osmium are concerned, even less is known.

A further complicating factor in predicting slag losses is the possibility that the degree of extraction by the slag for any one platinum metal may be influenced by associated platinum metals, e.g. the amount of osmium in the slag may be influenced by the presence of iridium in the slag.

These and other factors introduce difficulties in attempts to simulate ores by the direct additions of platinum metals. Thus one cannot assume that the losses of iridium to various slags from mixtures containing iridium added as a mechanically mixed constituent will be quantitatively indicative of iridium losses for ores containing iridium as iridosmine. In some instances at least, however, the tendency to slag losses will be encouraged when the metal is present in a form which provides for intimate contact with the fused slag. In these instances, at least when the observed losses are small, one may expect that the losses will represent the maximum losses for the assay of a natural ore or concentrate. Also, the present author has found continued confirmation that the losses observed in each of these investigations represent the trend for each metal. Furthermore, there is value in those data that indicate sources of loss.

In all of the fire assay investigations described below, the general heating pattern involved placing the charge in the furnace at 975°C, then raising the temperature at the maximum rate to 1150° or 1200°C at the pouring. The furnace used for all the classical fire assays was a pyrometrically controlled Williams and Wilson 15 KVA Globar-type; see Chapter 7, Equipment No. 16A.

FIRE ASSAY FOR RUTHENIUM

Thiers, Graydon and Beamish[41] determined the sources of ruthenium loss during the classical fire assay. The compositions of the slag varied from acid to basic, and included slags from the nitre and iron nail methods.

The acid flux had an acidic oxide to basic oxide ratio of 2 : 3, the constituents being silica (20 g), borax glass (4 g), calcium oxide (5 g), litharge (78 g) and flour (3·5 g). Twenty-seven g of the litharge was required for the button. The basic flux had an acidic oxide to basic oxide ratio of 0·62, and contained silica (10 g), borax glass (2 g), calcium oxide (21 g), soda ash (52 g), litharge (81 g) and flour (3·5 g). Twenty-seven g of the litharge was required for the button.

The second acid flux had an acidic oxide to basic oxide ratio of 1·8, and contained silica (17 g), borax glass (7 g), calcium oxide (3·5 g), soda ash (23 g), litharge (52 g) and flour (3·5 g). Twenty-seven g of the litharge was required for the button. Oxidizing fluxes were used for pyrite ores whose reducing power was 9·5 on a scale where FeS_2 = 12·0 (see Procedure 54). The composition of the flux was silica (19 g), soda ash (25 g), litharge (54 g), potassium nitrate (26 g) and ore (0·5 assay ton).

Iron nail assays were also examined. The authors determined the ruthenium content of the gases from the pot fusion and the cupellation processes, as well as that of the slags and cupels. The method involved the use of radioactive ruthenium as a tracer, supplemented in some instances by classical methods of analysis. It should be noted here that the mixing of active and non-active ruthenium is not accomplished by simple shaking, two successive distillations of the mixed solutions being required to produce homogeneity. Tables 19 and 20 provide a summary of the data obtained.

The above data indicate that even under somewhat idealized conditions serious losses of ruthenium will occur. Surprisingly, there seems to be little difference in losses for acidic, basic or other fluxes, except that the iron nail assay is inadmissible. Slag losses seem to be reduced at the higher temperature and with extended periods of fusion.

It is particularly important to note that cupellation losses may be high. They are not due, as is commonly assumed, to air volatilization. Practically all of the loss is due to the cupel. These data suggest that the not uncommon practice of partial cupellation of ruthenium–lead buttons is inadvisable. In the present author's opinion the only safe method of determining ruthenium and osmium after an assay lead collection is a direct wet treatment of the lead button, with no cupellation. A method is provided in Procedure 28. It is perhaps surprising that the gas losses for ruthenium during both fusion and cupellation are negligible, and furthermore that the nitre assay, essentially oxidizing in nature, is applicable.

FIRE ASSAY FOR OSMIUM

The various sources of loss of osmium during fire assay with lead as a collector were examined by Allan and Beamish.[241] As with ruthenium a fire assay for osmium carried out under optimum conditions can result in losses as great as 6 per cent. Contrary to the findings for ruthenium the magnitude of osmium losses varied with the composition of the slag and with the amount of osmium present. Like ruthenium assays the rate of fusion seemed to affect the recovery. A variety of fluxes were used; they

TABLE 19. FIRE ASSAYS FOR RUTHENIUM[21]

No.	Flux	Wt. of flux (g)	Ratio of acid oxide to basic oxide	Buttons wt. (g)	Slag wt. (g)	Time in muffle (min)	Temperature Start (°F)	Temperature Finish (°F)	Remarks
1	Bisilicate	100	1·8 to 1	24	70	40	1500	1800	
2	Bisilicate	100	1·8 to 1	25	70	50	1700	2000	
3	Bisilicate	100	1·8 to 1	28	65	60	1500	2000	Test of borax wash, and of partial cupellation to 6·5 g.
4	Bisilicate	100	1·8 to 1	26	60	60	1500	2000	Test of partial cupellation to 6·5 g.
5	Nitre assay	100	SiO_2 2 g $Na_2B_4O_7$ 25 g Na_2CO_3 50 g PbO 40 g Flour 1 g 0·5 assay ton ore (R.P. 9·5)	16	90	60	1500	2000	These buttons were all borax washed to remove sulphide slag.
6	Nitre assay	100		24	85	60	1500	2000	
7	Nitre assay	100		22	85	60	1500	2000	
8	Bisilicate	107	0·77 to 0·33	34	55	60	1600	2000	
9	Subsilicate	130	0·49 to 0·79	30	85	120	1400	2200	
10	Subsilicate	130	0·49 to 0·79	32	90	180	1400	2400	
11	Bisilicate	107	0·77 to 0·33	30	70	40	1600	2000	
12	Iron nail	133	SiO_2 2 g	42	110	75	1600	2100	These slags were mostly iron sulphide.
13	Iron nail	132	$Na_2B_4O_7$ 25 g Na_2CO_3 50 g PbO 40 g Flour 1 g 0·5 assay ton ore (R.P. 9·5)	38	105	75	1600	2100	

TABLE 20. THE DISTRIBUTION OF RUTHENIUM IN FIRE ASSAYS[21]

No.	Counts found* In button	In slag	In assay gases	In borax wash	In cupel	In cupel gases	Total†	Remarks
1	380 ±2	144 ±15	0·6 ±2	..	..	..	525 ±19	
2	472 ±3	57 ±10	4 ±3	..	..	..	533 ±6	
3	428 ±2	38 ±8	..	7 ± 3	53 ±4	0·0	526 ±17	Assay gases not checked as such.
4	428 ±2	53 ±6	..	..	53 ±4	0·0	534 ±12	Other data give 0·05 mg or less.
5	450 ±2	55 ±3	1 ± 3	20 ±4	..	..	526 ±12	
6	398 ±2	100 ±3	1 ± 3	13 ±4	..	..	512 ±12	
7	382 ±2	129 ±3	1 ± 3	11 ±4	..	..	523 ±12	
8	498 ±2	29 ±7	0·0	..	..	..	527 ±9	
9	457 ±2	38 ±12	0·0	..	..	..	495 ±14	38 ± 8 counts or 0·41 mg found in thionalide filtrate.
10	490 ±2	34 ±10	..	..	..	..	524 ±14	
11	436 ±2	117 ±10	..	..	..	..	553 ±12	No known reason for anomaly.
12	358 ±2	12 ±2	0·0	10 ±3	..	93‡	470	Nail counts are rough.
13	290 ±2	34 ±15	0·0	11 ±3	..	188‡	520	

* Counts corrected for decay and absorption and are referred to standard.
† 523 ± 3 counts taken.
‡ Found on iron nail.

are recorded in Table 21. It should be noted that, for all except the oxidizing flux and the iron nail assay, the flux composition would be approximately that of the slag composition, e.g. no ore is added.

It was found that the osmium losses varied with the viscosity of the slag. In those instances where fluxes of identical acidity were used, the slag of lower viscosity provided the more complete recovery. Slow fusions with acid fluxes tended to increase the losses, thus differing from ruthenium assays. In general basic fluxes produced higher losses even though the slag was quite fluid. Losses by volatilization from basic pot mixtures were also higher than with most acid fluxes, particularly when the charge contained much osmium. Fusions of the basic charge (No. 4, Table 21) for 4–5 hr increased the losses of osmium, both as gas and slag losses. Viscous, slightly acid fluxes (No. 2, Table 21) behaved like the basic flux No. 4, five re-assays of the slag being required to recover the osmium.

There seems little doubt that under certain conditions osmium, like iridium (see below), can enter into combination with slag constituents and subsequently resist recovery by lead. Samples of osmium salt fused with the basic flux No. 4 in the absence of a lead collection produced a slag from which only 50 per cent of the osmium added could be recovered with three re-assays.

Fire assay recoveries of osmium seem to be influenced by the presence of silica in the slag. A neutral slag (No. 5, Table 21) containing no silica gave the best recoveries of osmium on the initial lead extraction. The neutral slag (No. 6, Table 21) containing silica also gave good recoveries, but was less effective than the slag without silica. It is significant that of all the slags used the neutral slag without silica was the superior one. The platinum metals ores practically always contain silica, and furthermore, fluxes that have a high borax glass content as a substitute rapidly destroy the clay pots.

Unexpectedly, it was found that a nitre assay may be used for sulphide ores. For small amounts of osmium (2 mg or less) this assay may allow a 99 per cent recovery. It is recommended that the charge be poured at about 1200°C. As for ruthenium the iron nail method is inadmissible. Much of the osmium is picked up by the nails, and the iron is difficult to recover because some of it sticks to the pot wall as scale.

The weight of the lead button seems to have little effect provided at least 25 g of lead are collected. In excess of this amount there is little or no improvement in collection. With buttons of less than 20 g there seems to be an increase in gas losses. Cupellation of lead buttons containing osmium is inadmissible. The removal of as little as a few g of lead by cupellation may result in losses of osmium. Most of the losses occur at weights of lead below 10 g, and complete cupellation to a silver bead *may* result in the complete disintegration of the bead and anyway an almost complete loss of osmium. It should be noted here that when the native source of osmium is an iridosmine

TABLE 21. THE COMPOSITION OF FLUXES[241]

Flux No.	Flux type	Ratio of acidic oxide to basic oxide	Silica (g)	Borax glass (g)	Calcium oxide (g)	Sodium carbonate (g)	Litharge (g)	Potassium nitrate (g)	Ore (g)
1	Glazing flux		8	3	2	11	16	0	0
2	Very acid (medium viscosity)	0·75 to 0·32	19	4	5	0	46	0	0
3	Very acid (very fluid)	0·95 to 0·37	10	21	0	19	20	0	0
4	Basic flux	0·3 to 0·6	13	2	3	23	72	0	0
5	Neutral flux (without silica)	0·65 to 0·59	0	22	5	35	20	0	0
6	Neutral flux (with silica)	0·58 to 0·54	12	6	5	35	20	0	0
7	Oxidizing flux		0	9	0	21	70	17	15*
8	Iron nail assay		2	25	0	50	40	0	15*
9	Cupel assay flux		16	0	0	40	40	0	0

* Reducing power, R.P. = 6·9.

TABLE 22. THE DISTRIBUTION OF OSMIUM IN FIRE ASSAYS[241]

Assay No.	Type No.	Osmium taken (mg)	Wt. of button 1st (g)	Wt. of button 2nd (g)	Osmium found: In 1st button (mg)	Osmium found: In 2nd button (μg)	Osmium found: In 1st gas (μg)	Osmium found: In 2nd gas (μg)	Total osmium recovered (mg)	Osmium unrecovered (mg)
1	3	5·37	36	49	5·20	8	0	0	5·21	0·16
2	3	5·39	41	40	5·10	31	0	0	5·13	0·26
3	3	5·36	40	40	5·04	28	3	0	5·07	0·29
4	3	5·39	37	43	5·13	8	5	0	5·14	0·25
5	4	5·41	44	31	5·04	12	25	2	5·08	0·33
6	4	5·40	43	34	5·19	10	23	1	5·22	0·18
7	4	5·36	40	43	5·07	1	13	8	5·09	0·27
8	4	5·38	42	36	4·98	18	1	0	5·00	0·38
9	4	5·37	43	36	4·95	10	5	8	4·97	0·40
10	4	5·38	42	39	5·04	27	8	15	5·09	0·29
11	5	5·37	43	47	5·28	63	0	20	5·36	0·01
12	5	5·38	46	35	5·28	2	7	0	5·29	0·09
13	5	5·37	45	41	5·25	2	12	0	5·26	0·11
14	5	5·37	41	43	5·30	15	0	0	5·32	0·05
15	5	5·40	44	41	5·30	15	3	0	5·32	0·08
16	5	5·39	43	39	5·25	10	1	0	5·26	0·13
17	6	0·194	45	42	0·193	1	0	1	0·195	−0·001
18	6	0·222	40	40	0·212	2	0	0	0·214	0·008
19	6	0·172	40	38	0·169	0	2	0	0·171	0·001
20	6	0·508	45	41	0·493	3	5	6	0·507	0·001
21	6	0·482	38	40	0·470	0	3	5	0·478	0·004
22	6	0·535	47	40	0·523	1	0	0	0·524	0·01
23	6	2·00	44	38	1·98	0	0	0	1·98	0·02
24	6	2·10	45	40	2·09	0	0	0	2·09	0·01
25	6	2·25	35	43	2·17	16	3	0	2·19	0.06
26	6	2·25	45	35	1·92	239	0	3	2·16	0·09
27	6	2·55	40	42	2·40	3	0	0	2·40	0·15
28	6	3·20	40	39	3·02	3	0	0	3·02	0·18
29	6	4·34	38	39	4·14	3	0	0	4·14	0·20
30	6	5·41	40	50	5·28	40	24	8	5·35	0·06
31	6	5·39	45	32	5·16	8	12	8	5·19	0·20
32	6	5·35	43	43	5·16	10	0	0	5·17	0·18
33	6	5·37	42	46	5·16	2	4	0	5·17	0·20
34	6	5·36	43	41	5·20	0	0	0	5·20	0·16
35	6	5·38	44	41	5·18	5	0	0	5·19	0·19

Nitre assay of pyritic ore (R.P. = 6·9)

Assay No.	Type No.	Osmium taken (mg)	Wt. of button 1st (g)	Wt. of button 2nd (g)	Osmium found: In 1st button (mg)	Osmium found: In 2nd button (μg)	Osmium found: In 1st gas (μg)	Osmium found: In 2nd gas (μg)	Osmium found: In 1st nails (mg)	Osmium found: In 2nd nails (mg)	Total osmium recovered (mg)	Osmium unrecovered (mg)
36	..	5·40	45	38	5·19	31	18	0	..	..	5·24	0·16
37	..	5·36	38	42	5·13	68	0	0	..	..	5·20	0·16
38	..	5·35	36	41	5·11	40	0	0	..	..	5·15	0·20
39	..	5·38	40	43	5·13	49	0	0	..	..	5·18	0·20
					Iron nail assay of pyritic ore (R.P. = 6·9)							
40	..	5·39	10	36	1·65	0·12	0	0	1·87	0·10	2·74	2·65
41	..	5·36	40	33	0·825	0·35	8	10	1·10	0·49	2·81	2·55
42	..	5·36	40	38	1·77	0·66	3	25	0·510	0·52	3·48	1·88

TABLE 23. THE DISTRIBUTION OF OSMIUM IN FIRE ASSAYS USING ACID FLUX 2[241]

Assay No.	Osmium taken (mg)	Osmium found					Osmium found					Total osmium recovered (mg)	Osmium unrecovered (mg)
		In 1st button (mg)	In 2nd button (mg)	In 3rd button (mg)	In 4th button (μg)	In 5th button (μg)	In 1st gas (μg)	In 2nd gas (μg)	In 3rd gas (μg)	In 4th gas (μg)	In 5th gas (μg)		
43	5·38	3·98	0·67	0·13	22	38	88	122	116	48	40	5·25	0·13
44	5·36	4·46	0·20	0·16	40	20	60	40	40	20	20	5·06	0·30
45	5·40	4·18	0·31	0·22	20	14	110	66	40	26	32	5·02	0·38
46	5·36	4·70	0·24	0·08	16	..	36	48	16	8	..	5·14	0·22
47	5·34	4·22	0·48	0·16	44	..	27	110	24	0	..	5·07	0·27
48	5·38	3·98	0·67	0·13	22	38	88	122	116	48	40	5·26	0·12
49	27·71	25·12	0·51	0·05	94	20	196	24	36	24	10	26·08	1·63

The weights of the buttons obtained above ranged from 40 to 45 g.

TABLE 23A. THE CUPELLATION OF OSMIUM-LEAD BUTTONS OBTAINED FROM NEUTRAL FLUX 6[241]

Assay No.	Osmium taken (mg)	Wt. of button (g)	Osmium found			Wt. of partially cupelled button (g)	Osmium found in partially cupelled button (mg)	Osmium recovered (mg)
			In gas from cupellation (mg)	In bead (μg)	In cupel (μg)			
50	5·38	48	4·47	8	188	..	..	0·71
51	5·35	45	4·11	0	70	..	..	1·17
52	5·40	45	4·77	0	72	..	..	0·56
53	5·36	45	0·121	..	42	5	4·92	0·28
54	5·40	44	0·133	..	..	40	..	..
55	5·35	46	0·063	..	20	7	5·04	0·22

the above statements do not necessarily apply. The iridosmines are of such varied compositions that no general statement can be made.

In general the most satisfactory fire assay for osmium with lead as a collector involves a quick fusion with a neutral flux (No. 6, Table 21) or a nitre flux (No. 7, Table 21), and a finishing temperature of about 1200°C. It is advisable to make one re-assay of the slag. The button should be analysed by wet methods, as for ruthenium (Procedure 28).

The various sources of osmium loss were recorded by Allan,[241] and are summarized in Tables 21–23.

FIRE ASSAY FOR RHODIUM

Allan and Beamish[242] determined the losses of rhodium to the slag. Whereas this investigation was relatively incomplete in detail, sufficient evidence was accumulated to indicate that rhodium is one of the well-behaved platinum metals in so far as lead collection is concerned. No data were recorded to determine cupellation losses, but from an examination of the surface effects of rhodium–silver beads one may expect at least small amounts of rhodium to be recoverable with an accuracy comparable to that with palladium and platinum. With mg amounts of rhodium mechanical loss is probable.

The flux and slag compositions used for rhodium[242] are listed in Table No. 24. Over the range of slag compositions which varied from subsilicate to an approximate bisilicate, the losses of rhodium indicated independence of the proportions of slag constituents. Furthermore, in most instances a single re-assay of the slag was found to be sufficient for complete recovery. In those instances where losses amounted to as much as 0·5 per cent, the re-assay of the second slag failed to account for the rhodium. It was assumed, without sufficient evidence, that these small losses were due to adsorption on the pot. It is unfortunate that no data were provided to indicate the possibility of rhodium in slags unrecoverable by fire assay. This phenomenon occurs with iridium as stated below.

It should be noted that high nickel slags were not particularly detrimental to the recovery of rhodium as they were with platinum and palladium. The few data for these assays indicated acceptable recoveries. Consistent with other platinum metals the nitre assay for sulphide ores is quite acceptable, and for rhodium the salt cake is not objectionable. As expected, a large decrease in button size is detrimental to rhodium recovery; its reduction to about 10 g of lead results in losses of about 1 per cent.

FIRE ASSAY FOR IRIDIUM

In a fire assay, iridium does not alloy with lead but is collected as a suspension in the molten metal. In order to avoid mechanical losses during the

TABLE 24. THE RECOVERY OF RHODIUM FROM ORES BY FIRE ASSAY[242]

No.	Ore type	Ratio of acidic oxide to basic oxide	Button wt. 1st (g)	Button wt. 2nd (g)	Parting method	Rhodium added (mg)	Rhodium recovered 1st button (mg)	Rhodium recovered 2nd button (mg)	Rhodium recovered Total (mg)	Error (mg)
1	Silica	0·514 to 0·349	27	30	$HClO_4$	12·64	12·18	0·15	12·33	−0·31
2	Silica	0·514 to 0·349	28	29	$HClO_4$	16·26	16·31	0·08	16·39	+0·13
3	Silica	0·514 to 0·349	27	27	$HClO_4$	17·69	17·29	0·32	17·61	−0·08
4	Silica	0·514 to 0·349	24	21	HNO_3	11·17	10·52	0·22	10·74	−0·43
5	Silica	0·514 to 0·349	24	23	HNO_3	11·21	10·60	0·35	10·95	−0·26
6	Silica	0·514 to 0·349	23	23	HNO_3	10·71	10·35	0·17	10·52	−0·19
7	Silica	0·514 to 0·349	9·6	20	HNO_3	10·68	7·54	2·15	9·69	−0·99
8	Sulphide*	0·34 to 0·85	23	25	HNO_3	10·69	10·06	0·44	10·50	−0·19
9	Sulphide*	0·34 to 0·85	23	25	HNO_3	10·69	9·51	0·54	10·05	−0·64
10	Sulphide†	0·30 to 0·88	20	27	HNO_3	10·69	10·84	0·20	11·04	+0·35
11	Sulphide†	0·30 to 0·88	20	26	HNO_3	10·69	10·45	0·15	10·60	−0·09
12	Nickel oxide	0·42 to 0·85	26	20	$HClO_4$	10·69	9·96	0·78	10·74	+0·05
13	Nickel oxide	0·42 to 0·85	29	26	$HClO_4$	10·69	10·21	0·41	10·62	−0·07

* Treated by preroasting procedure.
† Treated by nitre assay procedure.

pouring of melts containing iridium, Davis[244] recommended that the fusion be cooled in the pot. Even greater losses may occur, however, in attempting to break the pot away sufficiently to free the lead button. Iridium is generally concentrated near the bottom of the button or at the apex of a poured lead melt. Barefoot and Beamish[243] examined the relationships between losses of iridium and composition of slags. Table 25 includes a list of the types of charges used. Table 26 describes the proportions of recovery of iridium in buttons from a sequence of assays with a variety of slag compositions.

It is noted in Table 26 that the collection of iridium in a single assay is not complete, except when the quantity of iridium is small. Two re-assays of acid slags are sufficient to collect most of the iridium not collected in the first assay. Basic or subsilicate slags result in serious losses of iridium. Furthermore, there is some evidence that iridium slagged off into a basic slag is not completely recoverable by a subsequent re-assay of the slag. In some instances a recovery of only 80 per cent of the iridium was thus obtained. It is not improbable that iridium enters into some stable combination with basic slag constituents maintained at a high temperature.

Barefoot and Beamish also noted that there were no significant differences between the losses of iridium in nitre assays and assays of a preroasted ore, and that the period of fusion beyond that normally used appeared to play no part in the completeness of the collection of iridium. Losses of iridium were comparable for charges heated at 1200°C for 40 min and charges heated from 815°C to 1200°C over a period of about 1·5 hr.

Good recoveries can be made from ores with a high iron content by using a slag whose composition approaches that of a bisilicate. Ores high in copper and nickel present serious problems. The usual precaution of using a high litharge charge for these ores does not improve the collection of iridium, and the button contamination is increased. For ores of high copper–nickel content a combination assay is recommended. A suitably chosen prior acid treatment of the ore will then allow the use of a bisilicate slag.

Despite the mechanical characteristic of the lead–iridium collection, a satisfactory assay can be made, but the subsequent determination of iridium should be made with the lead alloy, for cupellation processes are often attended by large mechanical losses. This fact seems not to be recognized, for most text-books on fire assaying include procedures for the determination of iridium in the silver bead.

Plaksin and Marenkov[245] reported that almost 4 per cent of a 5 mg sample of iridium was lost from a 75 mg bead obtained by cupellation.

Table 27 includes data obtained by the author for the cupellation process. All of the silver bea[illegible] black scales at various places on their surfaces (see Fig. 9). As the ratio of silver to iridium is increased the scales appear only near the base of the bead, just above the cupel. Furthermore, almost

TABLE 25. FLUX AND SLAG COMPOSITIONS FOR IRIDIUM[243]

Flux No.	Ratio of acidic oxide to basic oxide	Parts by weight								
		Flux (g)	Ore (g)	Silica (g)	Borax glass (g)	Calcium oxide (g)	Sodium carbonate (g)	Litharge (g)	Potassium nitrate (g)	Flour (g)
1	0·72 to 0·4	100	..	25	10	5·0	35	78	..	4·5
2	0·84 to 0·452	107	..	80	16	20	..	312	..	14
3	0·26 to 0·575	114	..	8·0	3·0	7·4	28	65	..	3·5
4	0·435 to 1·05	122	..	12	6·0	50	35	61	..	3·5
5	0·635 to 0·681	126	..	..	22	5·0	35	61	..	3·5
6	0·24 to 0·60	141	¼ A.T.*	7	..	..	18	112	4	..
7	0·694 to 0·778	114	¼ A.T.*	6	4	..	20	65	19	..
8	0·37 to 0·542	123	¼ A.T.†	11	..	..	7·5	100	..	4·2
9	0·43 to 0·85	198	½ A.T.‡	..	..	..	15	180	..	3·5
10	1·22 to 0·57	80	⅓ A.T.§	5	5	..	15	51	..	3·6

* Chalcopyrite; 23% of Cu, 20% Fe, 15% SiO_2, R.P. = 6·9

† Roasted chalcopyrite.

‡ Nickel oxide ore; 20% Ni, 80% SiO_2.

§ Iron oxide ore; 40% Fe_2O_3, 60% SiO_2.

TABLE 26. THE RECOVERY OF IRIDIUM FROM ORES*[243]

Flux No.	Ratio of acidic oxide to basic oxide	No.	Button wt. (g)			Iridium recovered (mg)			Total (mg)	Error (mg)
			1st	2nd	3rd	1st	2nd	3rd†		
6	0·24 to 0·60	1	39	31	..	2·742	0·439	..	3·18	−1·86
		2	35	30	25	3·720	0·378	0·03	4·10	−0·94
		3	39	30	26	2·958	0·594	0·01	3·55	−1·49
		4	42	28	25	3·394	0·369	0·07	3·76	−1·28
8	0·37 to 0·542	5	35	23	20	3·636	0·047	0·01	3·68	−1·36
		6	35	20	24	3·228	0·075	0·04	3·30	−1·74
7	0·694 to 0·778	7	30	15	..	1·849	0·382	..	2·23	−2·81
		8	30	13	..	2·843	0·243	..	3·09	−1·95
9	0·43 to 0·85	9	26	32	22	1·797	0·054	0·01	1·86	−3·18
		10	28	32	21	2·130	0·035	0·00	2·17	−2·87
		11	54	20	..	1·508	0·460	..	1·97	−3·07
		12	57	23	..	2·234	0·223	..	2·46	−2·58
10	1·22 to 0·57	13	29	31	..	5·129	0·00	..	5·13	+0·09
		14	28	30	..	5·054	0·045	..	5·10	+0·06

* 5·04 mg of iridium taken.

† Colorimetric estimation, not included in gravimetric value.

invariably, black particles of iridium oxide can be found scattered about the surface of the cupel, close to the bead itself. These phenomena may be observed even when the ratio of silver to iridium is as high as 200 to 1.

Despite the fact that the cupellation of the lead button to produce a silver–platinum metals alloy has been used at least for the past century, the method is not recommended for the determination of iridium, osmium or ruthenium. It is stated here again that one may hope for improved methods of analysing the lead–platinum metals button.

TABLE 27. THE CUPELLATION OF LEAD–IRIDIUM BUTTONS*[243]

No.	Silver taken (mg)	Iridium taken (mg)	Ratio	Iridium recovered (mg)	Loss (mg)
1	100	4·19	25	3·94	0·25
2	125	4·24	30	4·02	0·22
3	150	4·52	40	4·32	0·20
4	100	1·50	70	1·23	0·27
5	100	0·88	100	0·75	0·13
6	150	0·86	150	0·79	0·07

* 30-g buttons.

FIRE ASSAY FOR PALLADIUM

Fraser and Beamish[246] determined the distribution of losses of palladium during standard fire assay procedures. Table 28 describes the composition of the fluxes used. These are also the compositions of the slags. For each type enough litharge and flour were added to produce a 25-g button.

Tables 29 and 30 indicate the amounts of palladium found in successive lead buttons for samples of 5 mg and 1 mg of palladium respectively.

From these tables it is apparent that no one flux or slag is preferable for the over-all recovery of palladium. There is a distinction, however, between the recovery made in the first button and the number of re-assays required to give adequate collection. In Table 29 it can be seen that only acid fluxes caused any appreciable quantity of palladium to come down in the third button.

With the very acid flux of only medium viscosity considerable palladium remained even in the fourth button when 5·00 mg were present in the flux. For 1·0 mg of palladium present originally, this acid flux was the only flux in which virtually complete collection of palladium was not obtained in the first button.

A flux of some interest contained no silica; the palladium recovery was excellent; however, a flux of this type is scarcely practical because most noble metal ores will contain significant amounts of silica and some associated base metals such as copper, nickel, iron, etc. Generally, these base metals are slagged off by a flux containing a high proportion of litharge. Flux No. 8 is suitable for high iron–copper ores containing silica. The slag, however, is corrosive, and a slightly lower finishing temperature is recommended.

For the nickel ores there was a significant loss of palladium to the slag. Two re-assays of the slag were found to give a total recovery of 83 per cent of the palladium present. As stated above, this loss to nickel slags is serious for iridium also.

As the platinum metals are often encountered in sulphide ores one should note the results of the nitre assay with flux No. 7 (Table 28). Almost complete recovery was obtained with only one re-assay.

The assayer must, from time to time, answer the criticism that the classical lead collection will not respond to certain types of ores. Various explanations for this supposed situation are presented. It has been reported that slags may be made to contain certain platinum metals which are difficult to recover by any number of re-assays. If this resistance to lead collection can be demonstrated by artificial means then one can scarcely claim that natural fusion processes could not produce a similar retention. At the present time there is no positive answer to this problem. From the negative point of view the present author has not encountered noble metal ores whose value cannot be determined with reasonable accuracy by the classical fire assay process. In this connection some effort has been made to learn the degree of resistance to the collection of palladium from slags prepared by a pre-fusion in the absence of metallic lead. Table 31 illustrates the distribution of palladium in the various buttons obtained initially from pre-fused samples of slag containing palladium but no metallic lead.

It will be noted again that neutral flux No. 5, which contained no silica, was the only one which accomplished a reasonable recovery.

In the almost complete absence of descriptions of these very complicated systems any attempt to explain these phenomena is most difficult. Whereas experiments with slags pre-fused with a platinum metal have indicated a resistance to a subsequent collection by lead, the low recoveries for such re-assays may be attributed to factors other than resistance to extraction from slags of platinum metal compounds. For platinum, data are presented below to prove that, in some instances, the method of preparing the pre-fused slag encourages the migration of platinum to the pot wall, and when this occurs simultaneously with creeping to the rim of the pot one may expect large percentage losses.

Because palladium lends itself so readily to fire assay collection it was used to learn something of the mechanism of lead extraction during the progress of the fire assay. Generally, it is considered that the falling of lead through the molten slag is a necessary mechanism for the recovery of the

TABLE 28. THE COMPOSITION OF THE FLUXES(246)

Flux No.	Type of flux	Silica (%)	Borax glass (%)	Calcium oxide (%)	Sodium carbonate (%)	Litharge (%)	Potassium nitrate (%)	Wt. taken per assay* (g)
1	Glazing flux	20·0	7·5	5·0	27·5	40·0	..	35
2	Very acidic (medium viscosity)	25·7	5·4	6·7	..	62·6	..	80
3	Very acidic (low viscosity)	14·3	30·0	..	27·2	28·5	..	70
4	Basic	11·5	1·8	2·7	20·3	63·7	..	113
5	Neutral	..	26·8	6·1	42·7	24·4	..	80
6	Neutral	15·4	7·7	6·4	44·9	25·6	..	78
7	Oxidizing (nitre assay)	4·0	2·6	..	16·9	58·8	17·7	133†
8	Basic (extra litharge)	3·5	4·6	..	7·1	84·8	..	220
9	Cupel assay flux	..	14·9	..	28·4	56·7	..	140

* Enough litharge and flour were mixed with the flux to produce a 25-g button before salting.

† This flux was mixed with 0·5 assay ton of pyritic ore (reducing power = 6·9) and 28 g of litharge before salting.

TABLE 29. THE DISTRIBUTION OF PALLADIUM IN FIRE ASSAYS*(246)

Assay No.	Flux	Flux No.	Button weights (g)					Palladium found (mg)							Palladium unrecovered (mg)
			1st	2nd	3rd	4th	Silica residue	In 1st button†	In silica residue	Total in 1st button	In 2nd button	In 3rd button	In 4th button	Total recovered (mg)	
91	Acidic	2	27	17	22	23	24	4·415	0·025	4·440	0·306	0·130	0·026	4·90	0·10
92	Acidic	2	28	16	27	21	22	4·441	0·090	4·531	0·203	0·107	0·052	4·89	0·11
93	Acidic	2	27	19	25	22	27	4·418	0·065	4·483	0·301	0·090	0·036	4·91	0·09
72	Acidic	3	20	23	20	..	21	4·774	0·060	4·834	0·063	0·027	..	4·92	0·08
73	Acidic	3	17	21	18	..	21	4·809	0·045	4·854	0·069	0·041	..	4·96	0·04
74	Acidic	3	20	22	20	..	21	4·550	0·046	4·596	0·080	0·040	..	4·72	0·28
54	Basic	4	25	22	17	..	14	4·436	0·038	4·474	0·298	0·002	..	4·77	0·23
55	Basic	4	22	21	14	..	15	4·597	0·041	4·638	0·245	0·009	..	4·89	0·11
56	Basic	4	23	21	17	..	18	4·532	0·032	4·564	0·360	0·000	..	4·92	0·08
63	Neutral	5	24	22	21	..	19	4·880	0·048	4·928	0·012	0·002	..	4·94	0·06
64	Neutral	5	24	23	20	..	16	4·804	0·036	4·840	0·048	0·000	..	4·89	0·11
65	Neutral	5	20	23	20	..	19	4·881	0·064	4·945	0·038	0·004	..	4·99	0·01
48	Neutral	6	26	20	19	..	24	4·747	0·017	4·764	0·125	0·014	..	4·90	0·10
49	Neutral	6	27	18	20	..	22	4·749	0·009	4·758	0·088	0·003	..	4·84	0·16
50	Neutral	6	26	18	20	..	23	4·334	0·000	4·334	0·156	0·007	..	4·50	0·50
88	Oxidizing	7	28	25	27	..	21	4·654	0·066	4·720	0·124	0·003	..	4·85	0·15
89	Oxidizing	7	26	26	26	..	27	4·663	0·067	4·730	0·165	0·010	..	4·91	0·09
90	Oxidizing	7	27	25	27	..	25	4·727	0·064	4·791	0·190	0·009	..	4·99	0·01

* 5·00 mg palladium taken.

† Determined gravimetrically.

TABLE 30. THE DISTRIBUTION OF PALLADIUM IN FIRE ASSAYS*[246]

Assay	Flux	Flux No.	Button weights (g)			Palladium found (μg)				Palladium taken (μg)	Difference (μg)
			1st	2nd	3rd	In 1st button	In 2nd button	In 3rd button	Total recovered (μg)		
94	Acidic	2	23	22	12	65	21	13	99	100	−1
95	Acidic	2	22	19	12	151	34	17	202	250	−48
96	Acidic	2	27	23	21	439	31	17	487	500	−13
97	Acidic	2	24	21	20	953	19	21	993	1000	−7
75	Acidic	3	21	28	..	90	2	..	92	100	−8
76	Acidic	3	21	28	..	240	1	..	241	250	−9
77	Acidic	3	25	28	..	500	2	..	502	500	+2
57	Basic	4	27	19	..	100	5	..	105	100	+5
58	Basic	4	27	20	..	247	3	..	250	250	0
59	Basic	4	27	20	..	505	13	..	518	500	+18
66	Neutral	5	25	21	..	103	2	..	105	100	+5
67	Neutral	5	26	19	..	230	2	..	232	250	−18
68	Neutral	5	24	18	..	497	8	..	505	500	+5
30	Neutral	6	23	23	..	100	3	..	103	100	+3
31	Neutral	6	25	22	..	242	2	..	244	250	−6
32	Neutral	6	25	22	..	477	12	..	489	500	−11
84	Oxidizing	7	23	15	..	96	2	..	98	100	−2
85	Oxidizing	7	27	18	..	238	7	..	245	250	−5
86	Oxidizing	7	22	20	..	511	3	..	514	500	+14
87	Oxidizing	7	22	20	..	1012	2	..	1014	1000	+14

* Samples of 1 mg and under.

TABLE 31. THE DISTRIBUTION OF PRE-FUSED PALLADIUM SAMPLES IN FIRE ASSAYS[246]

Assay No.	Flux	Flux No.	Button weights (g)				Palladium found (μg)					Palladium taken (μg)	Difference (μg)
			1st	2nd	3rd	4th	In 1st button	In 2nd button	In 3rd button	In 4th button	Total recovered (μg)		
98	Acidic	2	25	23	20	19	48	66	39	26	179	250	71
99	Acidic	2	24	25	21	20	64	109	82	55	330	400	70
100	Acidic	2	23	27	27	22	94	..	93	43	..	500	..
101	Acidic	2	25	26	21	18	215	332	192	80	819	1000	181
78	Acidic	3	27	20	22	19	178	37	7	2	224	250	26
79	Acidic	3	28	19	22	19	256	37	8	4	305	400	95
80	Acidic	3	27	19	21	19	284	90	14	2	390	500	110
60	Basic	4	18	15	8	..	217	10	1	..	228	250	22
61	Basic	4	23	18	15	..	334	16	5	..	355	400	45
62	Basic	4	25	19	15	..	375	30	6	..	411	500	89
69	Neutral	5	23	20	21	..	205	39	14	..	258	250	−8
70	Neutral	5	23	22	21	..	361	41	14	..	416	400	−16
71	Neutral	5	23	19	22	..	400	43	18	..	461	500	39
23	Neutral	6	23	24	23	23	163	38	11	2	214	250	36
24	Neutral	6	22	23	23	23	234	77	22	6	339	400	61
25	Neutral	6	23	23	23	23	251	136	36	8	431	500	69

noble metal. To examine this theory Fraser[246] avoided the usual fall of lead, and placed the lead in the bottom of the pot. The only method of collecting the palladium would then be by interfacial diffusion of the palladium in the fluid flux.

Table 32 includes data to indicate that well over 50 per cent of the palladium present can be collected by this method. This table also includes data dealing with the recovery of palladium from prefused slags. One may guess from the data in the above table that the *in situ* production of lead throughout the whole charge is a required condition, and therefore in the initial stages of the reactions between flux constituents and ores the viscosity of the charge should be such that intimate contact between all constituents is maintained until the noble metal has been freed. Furthermore, the charge should be suitably fluid during the collecting stage; this should assist in the gravity collection of the lead alloy particles, as well as in collecting the noble metals, which also have high densities.

TABLE 32. COLLECTION BY LEAD THROUGH INTERFACIAL DIFFUSION[246]

Flux No.	Palladium found* (μg)	
	Normal flux	Pre-fused flux
2	54	35
3	535	201
4	702	261
5	490	149
6	583	164
8	676	346

* In these assays 25 g of lead were placed in the bottom of the pot and salted flux placed above the lead. The fusions were made in the usual manner. 1·000 mg of palladium were taken.

A potentially important factor in slag losses in general has received insufficient attention. This is loss by adsorption onto the pot wall, which can be of importance in specific instances. Nothing has been recorded which would quantitatively relate these losses to the rate of heating or to the viscosity of the flux. The discussion of platinum losses includes some data dealing with this problem.

The marked difference in the collection of palladium by interfacial diffusion when fusing with a normal flux and fusion with a pre-fused flux (see Table 32) may be due simply to the absence of the stirring effect with the latter, because carbon dioxide is not produced.

Fraser[246] also examined the efficiency of the cupellation process for palladium. The data obtained indicate that losses to the cupel are not significant and that good recoveries may be obtained.

It is emphasized here again that the classical fire assay for gold, platinum and palladium in ores, and the subsequent concentration by cupellation with silver is far superior to any other analytical method with respect to speed and simplicity of operation, accuracy of recovery and general reliability. Improvements over the classical wet treatments of the silver–noble metals bead are being introduced, and further improvements will be forthcoming. Suitable methods of bead treatment are described in Procedures 33, 34, 35 and 36.

FIRE ASSAY FOR PLATINUM

Hoffman[247] examined the effects of various conditions on the accuracy of the recovery of platinum by fire assay. To determine losses of platinum to the slag, the flux compositions recorded in Table 33 were used. These also represent the slag compositions.

Table 34 records the platinum content of successive lead buttons; in some instances as many as three re-assays of slags were made. In addition to the re-assay of slag the nitric acid parting solutions of the first and second buttons were assayed to produce additional buttons.

The data in Table 34 indicate that there is no outstandingly successful type of flux or slag for the overall recovery of platinum. Nevertheless, it was confirmed that a flux or slag such as No. 2, Table 33, having a high silica content and being viscous during the fusion, is detrimental to good recovery; although even in this instance the platinum may be recovered by three re-assays of the slag. For sulphide ores the nitre assay may be applied successfully.

The effects of associated base metals on slag losses and on platinum recovery were also investigated by Hoffman.[247] One must bear in mind that these metals may influence the efficiency of parting processes as well as the retention of platinum by the slag. Excessive copper in the lead button may encourage the dissolution of platinum by nitric acid parting solutions.

In so far as slag losses are concerned, it has been found that an excess of litharge flux (No. 8, Table 33) is suitable for copper and iron, but with nickel the losses of platinum persist beyond two slag assays.

An examination of the effectiveness of recovery from samples of slag previously fused with platinum led to a discovery which can be of significance with other platinum metals. In the absence of the lead collecting techniques platinum shows a strong tendency to migrate through the flux to the pot wall and sometimes to creep to the lip of the pot. When this occurs losses may be quite high, and a recovery by a washing flux may fail to recover the platinum. It is not inconceivable that this migration of platinum to the pot wall may occur even during a normal assay where lead is produced *in situ* by the reaction of flour and litharge. In those instances where no creeping has occurred the adsorbed platinum is probably recovered by the ensuing fusion, but when creeping has occurred the adsorbed metal may be carried beyond the fluxing medium. There is some evidence to suggest that creeping beyond the meniscus of the fluxing medium is at a minimum with such acid fluxes as No. 2 or 3 (Table 33).

An examination of the cupellation process for platinum indicates that under proper conditions losses are negligible. Whereas differences in the size of beads do not appear to be an important variable, losses to the cupel may become significant with small beads (e.g. 10 mg) when the ratio of platinum to silver is increased much beyond that required for suitable partings (e.g. 1 to 20).

In so far as fluxes of optimum efficiency for any one platinum ore are concerned the results of the investigations support the opinion of some assayers that there is no slag composition of maximum effectiveness. For each ore one may expect a rather wide range of optimum proportions of constituents. It is evident, of course, that viscosity plays an important role in the recovery of noble metals, and viscous slags are to be avoided. The addition of borax glass or sodium carbonate may effectively regulate the viscosity. In general excessively basic slags are to be avoided.

For ores low in sulphur, neutral to fluid bisilicate slags may be effective. For oxidized ores a similar range of slags may be applicable.

In general a nitre assay is quite suitable for high sulphide ores, although there may be some slight loss of ruthenium and iridium. It should be emphasized here that these losses were made evident under the conditions of salting with platinum metals or salts; they may not occur, or occur only to a lesser degree, in a normal assay of an ore.

In no instance can the iron nail method of assay be recommended. All of the above researches indicated that platinum metals may cling to the iron nail and to the disintegrated parts of the nail. Gray and Toombs[248] stated that the iron nail method resulted in the retention by the iron of 70–80 per cent of iridium in an ore.

No fully acceptable explanation for slag losses has been recorded. It is clearly evident that the complexity of the fused systems makes any guessing an uncertain undertaking. It is not out of the question that in some instances the so-called slag losses may in reality be mechanical losses or losses by adsorption on the pot. It seems obvious that this cannot fully explain the detrimental effects of nickel. High nickel slags do seem to resist the transference of platinum to the lead button. Additional support for this statement may be taken from the success of the iron–copper–nickel recovery of noble metals by the new method described in Procedure 60. Here the nickel is almost completely removed from the slag, and losses of platinum metals to the slag are negligible. Anyway, chemical reactions which could account for these losses in the presence of nickel have not been postulated. The whole problem of slag losses has been examined empirically, and indeed,

TABLE 33. THE COMPOSITION OF THE FLUXES[247]

Flux No.	Type of flux	Silica sand (%)	Borax glass (%)	Calcium oxide (%)	Soda ash (%)	Litharge (%)	Potassium nitrate (%)	Wt. taken per assay (g)
1	Glazing flux	20·0	7·5	5·0	27·5	40·0	. .	35
2	Very acidic (medium viscosity)	25·7	5·4	6·7	. .	62·6	. .	80
3	Very acidic (low viscosity)	14·3	30·0	. .	27·2	28·5	. .	70
4	Basic	11·5	1·8	2·7	20·3	63·7	. .	100
5	Neutral (without silica)	. .	26·8	6·1	42·7	24·4	. .	80
6	Neutral	15·4	7·7	6·4	44·9	25·6	. .	78
7	Oxidizing (nitre assay)	4·0	2·6	. .	16·9	58·8	17·7	133*
8	Base metals flux	14·9	. .	. .	7·5	77·6	. .	200

* Sulphur (6·2 g) and litharge (28 g) were mixed with this flux before salting in a cellophane liner.

TABLE 34. THE DISTRIBUTION OF PLATINUM IN FIRE ASSAYS*[247]

Flux No.	Button weights (g)								Platinum found (mg)		
	1st button	Parting acid assay	Re-assay of parting acid	Re-assay of slag from parting acid	2nd button	Parting acid assay	3rd button	4th button	1st button†	Parting acid assay	Re-assay of parting acid
2	25	29	27	30	25	29	27	23	4·283	0·133	0·122
	25	30	25	28	25	29	28	28	4·339	0·205	0·079
	27	27	28	29	26	27	28	25	4·436	0·135	0·149
3	27	28	26	29	30	27	30	..	4·737	0·093	0·051
	27	29	28	29	29	28	28	..	4·708	0·100	0·064
	26	27	27	29	26	28	27	..	4·723	0·105	0·070
4	30	28	28	30	25	29	21	..	4·894	0·046	0·030
	29	27	28	29	24	28	20	..	4·803	0·063	0·042
	31	26	30	30	25	27	21	..	4·814	0·045	0·040
5	27	26	31	29	32	23	24	..	4·738	0·070	0·082
	27	27	30	29	31	22	24	..	5·038	0·068	0·138
	28	26	30	28	32	21	25	..	4·707	0·087	0·100
6	28	26	31	27	31	23	23	..	4·703	0·080	0·060
	29	27	30	27	29	24	23	..	4·621	0·075	0·000
	28	27	27	27	29	22	21	..	4·616	0·085	0·059
7	26	28	30	28	36	21	24	..	4·060	0·430	0·363
	26	29	29	27	37	18	25	..	4·453	0·243	0·255
	24	28	29	28	36	21	24	..	4·376	0·262	0·370

* Platinum taken = 4·99 mg.
† Found gravimetrically.

TABLE 34—*continued*

Flux No.	Platinum found (mg)									
	Re-assay of slag from parting acid	Benzenethiol filtrate test	Total in 1st button	In 2nd button	Parting acid assay	Total in 2nd button	In 3rd button	In 4th button	Total recovery	Platinum un-recovered (mg)
2	0·088	0·000	4·546	0·101	0·025	0·126	0·028	0·005	4·71	0·28
	0·005	0·000	4·628	0·072	0·030	0·102	0·017	0·005	4·75	0·24
	0·002	0·001	4·723	0·015	0·015	0·030	0·012	0·002	4·77	0·22
3	0·000	0·003	4·884	0·007	0·000	0·007	0·000	..	4·89	0·10
	0·000	0·000	4·872	0·010	0·000	0·010	0·003	..	4·89	0·10
	0·000	0·000	4·898	0·005	0·000	0·005	0·000	..	4·90	0·09
4	0·004	0·000	4·974	0·033	0·015	0·048	0·007	..	5·03	−0·04
	0·007	0·000	4·915	0·032	0·008	0·040	0·007	..	4·96	0·03
	0·003	0·000	4·902	0·033	0·009	0·042	0·008	..	4·95	0·04
5	0·003	0·000	4·893	0·048	0·035	0·083	0·008	..	4·98	0·01
	0·004	0·000	5·248	0·040	0·010	0·050	0·008	..	5·31	−0·32
	0·003	0·000	4·897	0·033	0·012	0·045	0·008	..	4·95	0·04
6	0·001	0·002	4·846	0·115	0·017	0·132	0·002	..	4·98	0·01
	0·000	0·003	4·761	0·189	0·012	0·201	0·001	..	4·96	0·03
	0·004	0·001	4·765	0·148	0·013	0·161	0·001	..	4·93	0·06
7	0·005	0·000	4·858	0·043	0·011	0·054	0·003	..	4·92	0·07
	0·000	0·000	4·951	0·025	0·010	0·035	0·003	..	4·99	0·00
	0·002	0·000	5·010	0·035	0·018	0·053	0·004	..	5·07	−0·08

even agreement as to the existence of slag losses through chemical reactions of the platinum metals is not conclusive.

In an informative article Adams[228] dealt with the claim that platinum metals may be dissolved in the slags, and that once in this condition they are not recovered by a subsequent assay of the slag. Among various methods synthetic samples containing platinum and palladium were assayed, presumably with no slag losses. Adams reached the conclusion that " when good fusions are obtained no serious errors are caused by losses in slags ". This claim is somewhat vitiated, however, by the subsequent statement that " when the greatest accuracy is aimed at, slags and cupels are again fused with a suitable flux ". Anyway, only palladium and platinum were investigated, and furthermore, no results were provided.

Fire Assay Procedures

The preliminary approach to the problem of a fire assay of an ore for platinum metals is of the utmost importance. In those instances where the samples are derived from established mines, and the laboratories and staff are relatively permanent, the successive steps involved in the preparation for the assay are of a more or less routine nature. The only problems are technical, and no moral overtones are involved.

The situation may be quite a different one for a consulting institution. Not infrequently the arrangements for the analysis are preceded by an interview. In the present author's opinion this can be, and usually ought to be, an important part of the investigation. One must assume that the consulting interviewer is one with a wide experience in the analytical chemistry of the platinum metals. For the ultimate reputation of the laboratory this experience is essential. A second factor involves the safety of the investing public. Not infrequently, the need for a sense of moral responsibility is rejected as incompatible with business success and competition. There can be no doubt that for a limited period the indiscriminate acceptance of consulting projects in this field will bring some considerable monetary reward. It will also bring, however, an ultimate lack of confidence and in some instances the elimination of the consulting service.

SAMPLING

The importance of proper sampling methods is nicely illustrated by Bugbee[234] who states that " when it is considered that the final sample for fire assay usually weighs somewhat less than 15 g. and that each must truly represent from 1 to 5 car-loads of ore weighing from 50 to 250 tons, the enormous practical difficulty of the problem may be appreciated ".

The problem of ore sampling prior to the appearance of the sample in the laboratory is not considered here. Excellent discussions of this important aspect of assaying are given in such text-books as those of Bugbee,[234] Smith,[235] etc. These authors and others also deal more adequately with laboratory sampling in general, which of course may involve techniques not required for the assay only of platinum metals. The analytical chemist more or less permanently associated with an assay laboratory need feel little or no concern with respect to the sampling methods used in the collection from field exploration. This comforting situation seldom applies to the consulting assayer. In general he has little control over the origin of the sample, and to avoid the possible complications arising from this lack of information the assayer should only report values on the samples as they have been received. In this instance the sampling technique is usually confined to the crushing and mixing of the coarse sample and finally to securing a representative sample by some process of selection.

Among the factors to be considered is particle size. Richards[249] stated that the weight taken for an assay should be approximately proportional to the square of the diameter of the largest particle, i.e. $W = Kd^2$. By determining the proportionality constant K one could then calculate a suitable sample weight for an ore of a specific fineness. The ore, of course, should be an average type free from malleable minerals, etc. The constant for the above equation may be calculated from the size of sample normally used for an ordinary ore of about 100 mesh. This sample size is one assay ton. The maximum diameter of a particle passing through a 100 mesh screen will be the aperture of the opening, i.e. $5{\cdot}5 \times 10^{-3}$ in. Thus substituting 1 for W and $5{\cdot}5 \times 10^{-3}$ for d, K becomes 30,000 assay tons/in^2. By applying the above rule Richards[249] provided the data in Table 35.

Columns 1 and 2 apply to low-grade ores and to ores in which the valuable constituents are homogeneously distributed; columns 3 and 4 apply to ores similar to 1 and 2 but of higher grade. Gold ores may be included under the title of low-grade ores when the gold is combined with pyritic material that is more or less evenly disseminated throughout the ore.

Columns 5 and 6 correspond to ores of the precious metals in which the latter are present in a non-homogeneous scattering of relatively rich particles. Bugbee[234] has pointed out that the table leaves the inference that a low-grade ore is necessarily uniform. This is not necessarily so. This table can be of value when the sample for examination weighs a hundred pounds or more.

It has been generally accepted that the optimum size of sample for assay is related to the ratio of the relative proportion of the richest mineral to the average value of the ore. As the ratio of the latter two values increases, the size of the sample should increase. This means, of course, that a homogeneous deposit of platinum metals containing a high content of iridosmine as compared to a low total value requires a relatively large sample for assay, to ensure representative values. Brunton[236] examined these relationships

TABLE 35. WEIGHTS TO BE TAKEN IN SAMPLING ORE[249]

Weight		Diameter of largest particle					
(g)	(lb.)	Very low-grade or very uniform ores 1 mm	Low-grade or uniform ores 2 mm	Medium-grade ores 3 mm	High-grade ores 4 mm	Rich or "spotted" ores 5 mm	Very rich or excessively "spotted" ores 6 mm
—	20,000	207·00	114·00	76·20	50·80	31·60	5·40
—	10,000	147·00	80·30	53·90	35·90	22·40	3·80
—	5,000	104·00	56·80	38·10	25·40	15·80	2·70
—	2,000	65·60	35·90	24·10	16·10	10·00	1·70
—	1,000	46·40	25·40	17·00	11·40	7·10	1·20
—	500·0	32·80	18·00	12·00	8·00	5·00	0·85
—	200·0	20·70	11·40	7·60	5·10	3·20	0·54
—	100·0	14·70	8·00	5·40	3·60	2·20	0·38
—	50·00	10·40	5·70	3·80	2·50	1·60	0·27
—	20·00	6·60	3·60	2·40	1·60	1·00	0·17
—	10·00	4·60	2·50	1·70	1·10	0·71	0·12
—	5·000	3·30	1·80	1·20	0·80	0·50	
—	2·000	2·10	1·10	0·76	0·51	0·32	
—	1·000	1·50	0·80	0·54	0·36	0·22	
—	0·500	1·00	0·57	0·38	0·25	0·16	
90·0	0·200	0·66	0·36	0·24	0·16	0·10	
45·0	0·100	0·46	0·25	0·17	0·11		
22·5	0·050	0·33	0·18	0·12			
9·0	0·020	0·21	0·11				
4·5	0·010	0·15					
2·25	0·005	0·10					

N.B. This table indicates measurement of 20,000 lb to the nearest 1/1000th lb.

with a view to determining the fineness to which crushing must be carried out in order to obtain acceptable accuracy and to establish a formula by which the optimum ratio of grade of the richest mineral to the average grade could be attained. Initially Brunton found that:

$$d = 0{\cdot}65\left(\frac{WCp}{fsn\,(K - C)}\right)^{\frac{1}{3}}$$

where

W is the weight of the sample in pounds,
K is the value of the richest mineral in ounces per ton,
C is the average value of the ore in ounces per ton,
s is the specific gravity of the richest mineral, and
n is the number of maximum-sized particles of the richest mineral in excess or deficit in the sample.

f is a factor expressing the ratio of the actual weight of the richest mineral in the largest particles which will pass a screen of a given size to the weight of the largest cubes of the same mineral which will pass the same screen,
p is the allowable per cent error in sample, and
d is the diameter in inches of the holes in the screen, or the nominal diameter to which the ore is crushed.
n was determined experimentally by assaying one assay ton ($W = 0{\cdot}0064$ lb) of two different lots of high-grade silver ore, crushed to 100-mesh ($d = {\cdot}0055$ inches) thus obtaining C and K. s and f were obtained from tables. The allowable error p, 0·88, was taken as the average deviation from the mean assay values. By substitution of these values, n was found to be approximately 3. Using these values for n and p,

$$W = \frac{10{\cdot}8\,fsd^3\,(K - C)}{C}$$

Thus, after ascertaining the data required by the formula for a given ore, the safe sample weight in lb, W, may be calculated for any ore whose largest particle is inches in diameter.

The above relationships of the optimum size of the sample to the physical characteristics of the ore constituents can be of value when large ore deposits are to be evaluated and a planned approach to sampling is required. A concise description of these relationships is described in *The Theory and Practice of Ore Sampling*.[250]

The assayer normally will have little need for this approach, however. The size of sample, i.e. the multiple of the assay ton, is determined principally by the proportion of total platinum metals present, the proportions of each platinum metal, the accuracy required for each metal and the availability of a suitable method of determination. A properly trained analytical chemist may work efficiently with a total of 1 mg of noble metals with amounts of noble metal constituents as low as 5–10 μg. In general a total weight of 10 mg of platinum provides for easier manipulation, and weights up to 1 g may be treated with the efficiency and ease of a base metal analysis. For high grade, non-homogeneous samples the effectiveness of representative sampling should not be sacrificed to allow for easy analytical techniques, and in general not less than one half an assay ton of sample should be used.

Ore samples in excess of about 100 lb should be mixed, crushed and ground by standard methods with suitable mill equipment. This aspect of sampling is described adequately in most text-books on fire assaying.

If the ore sample presented for assaying is of the order of 100 lb or less and consists of large pieces, the whole of the sample should be crushed and ground to between 100 and 200 mesh. No residue should fail to pass the

100-mesh screen. Prior to this process it is well to clean the crusher and the grinding mill by processing a known blank rock. The mill should also receive a prior cleaning by hand. The present author uses a crusher and mill of the types illustrated in Chapter 7, Equipment No. 17. Ground samples of more than 100 lb are best mixed and sampled by a suitable splitter or sampler. The present author uses the rolling technique, Procedure 53, for amounts of 100 lb or less, ground to pass a 100-mesh screen.

Procedure 53—Mixing

Place on the desk or floor a square sheet of cellophane sufficiently large to retain the sample spread over the centre of the sheet, with clear borders of at least 16 in. Transfer a suitable portion of the sample from the disk pulverizer to a 100-mesh screen, and sift over the centre of the cellophane sheet. Repeat this to remove the complete sample from the pulverizer. Finally, allow the pulverizer to run dry for a few min, stop it, and lower the grinding disc. If a suitable brush is available, brush off the disc into the screen with its retaining pan in place. Then uncover the opening above the grinding disc, and with a carefully adjusted air stream blow the adhering ore into the screen; then sift into the main sample.

Lift the four corners of the cellophane sheet alternately or in opposite pairs in such a manner that the whole sample of ore is thoroughly mixed. Several hundred full rollings, depending upon the size and homogeneity of the sample, should secure a suitably mixed sample. Then spread the latter evenly over almost the whole sheet area by means of a large blade spatula. Make divisions of about 1·5 in^2 through the layer of ore by a spatula or any suitable instrument.

If the original sample is of the order of 1 lb the assay sample may be measured directly. Do this by transferring to a porcelain evaporating dish a small amount of ore from each of the marked squares. With some practice this can be accomplished to secure an approximately equal amount from each square to provide the fraction of the assay ton required.

If the original sample is much larger than 1 lb, transfer a relatively larger amount of the sample, removed from each square, to a second cellophane sheet. By repetition of the above process the required splitting may be accomplished.

THE CALCULATION OF FLUX COMPOSITION

In this area of assaying there is no substitute for experience. The most suitable flux for any specific sample is then a matter of good judgment. There can be no doubt that the trained intuition of the assayer may, in many instances, suggest a suitable flux composition through a mere visual examination of the ore. This approach is assisted by the fact that there is perhaps no single optimum flux for any particular ore. Rather wide variations in proportions of constituents may produce comparable results. Obviously one can fall back upon such general principles that ores with high nickel–copper contents require litharge, and other relationships can be recalled from one's own experience. Nevertheless, no competent assayer should lack the knowledge of some methodical approach to securing a suitable flux or charge.

In order to calculate the composition of a suitable flux some knowledge of the proportions of the basic and acidic constituents of the ore or concentrate is required. In general this is obtained by a chemical analysis. The example given below illustrates one approach to the calculation of an applicable flux.

The following is the composition of a sample which is an oxidized, sulphide concentrate:

copper	5·0%
nickel	6·0%
iron	41·1%
silica	5·1%

The basic oxygens from the ore are derived from CuO, NiO and Fe_2O_3. The acidic oxygens from the ore are derived from the silica. Assuming that one assay ton is to be used, the amounts of basic oxygens are:

from copper oxide,

$$\frac{5{\cdot}0}{100} \times 29{\cdot}166 \times \frac{\mathrm{CuO}}{\mathrm{Cu}} \times \frac{1}{\mathrm{CuO}} = 0{\cdot}023 \text{ g-atom}$$

from nickel oxide,

$$\frac{6{\cdot}0}{100} \times 29{\cdot}166 \times \frac{\mathrm{NiO}}{\mathrm{Ni}} \times \frac{1}{\mathrm{NiO}} = 0{\cdot}030 \text{ g-atom}$$

from iron oxide,

$$\frac{41{\cdot}1}{100} \times 29{\cdot}166 \times \frac{\mathrm{Fe_2O_3}}{2\mathrm{Fe}} \times \frac{3}{\mathrm{Fe_2O_3}} = 0{\cdot}321 \text{ g-atom}$$

total,

$$0{\cdot}023 + 0{\cdot}030 + 0{\cdot}321 = 0{\cdot}374 \text{ g-atom}$$

The amount of acidic oxygens, from the silica, is

$$\frac{5{\cdot}1}{100} \times 29{\cdot}166 \times \frac{2}{\mathrm{SiO_2}} = 0{\cdot}05 \text{ g-atom}$$

From the data recorded above for fire assay slag losses, it is advisable to use a slag of between neutral and bisilicate composition. In this instance, the use of a bisilicate slag for the ore alone will require the addition of silica, for such a slag requires two acidic oxygens per basic oxygen. In this example, therefore, 0·374 g-atom of basic oxygens requires 0·748 g-atom of acidic oxygens, i.e. an additional 0·698 g-atom to that already present as silica. Such an amount of oxygen is supplied by 0·698 × $SiO_2/2$ = 21·3 g of silica. The total weight of sample and added silica is then 29·2 + 21·3 = 50·5 g. To this sample must be added a suitable amount of flux, and preferably a bisilicate flux. The basic relationship of 1 weight of ore to 1 weight of sodium carbonate has proved generally acceptable. The addition of 29·2 g of sodium carbonate to 50·5 g of the sample will require additional silica to maintain the bisilicate relationship.

The number of basic oxygens in 29·2 g of sodium carbonate is

$$29{\cdot}2 \times \frac{\mathrm{Na_2O}}{\mathrm{Na_2CO_3}} \times \frac{1}{\mathrm{Na_2O}} = 0{\cdot}28 \text{ g-atom}$$

The weight of silica required to react with the sodium carbonate to produce a bisilicate is

$$0{\cdot}28 \times 2 \times \frac{\mathrm{SiO_2}}{2} = 16{\cdot}8 \text{ g}$$

Thus far, the charge contains, therefore, 29·2 g of ore, 38·1 g of silica and 29·2 g of sodium carbonate.

A second general rule which can be applied here involves the ratio of total flux to ore. For many fusions 3 parts of flux to 1 part of ore is quite sufficient. Because the above ore contains appreciable amounts of nickel and copper it may be advisable to use a ratio of 4 to 1 to provide the litharge required to slag off the base metals.

For the above 29·2 g of ore 67·3 g of fluxes have been added. Thus, for a ratio of 4 to 1 (4 × 29·2) − 67·3 = 49·5 g of flux are still required. This 49·5 g of flux will consist of litharge and silica; it should be noted here that the choice of constituents is made arbitrarily. In order to produce a bisilicate, in this instance $PbO{\cdot}SiO_2$, the proportion of litharge will be

$$\frac{PbO}{PbO{\cdot}SiO_2} \times 49{\cdot}5 = 38{\cdot}9 \text{ g}$$

The weight of silica will then be 49·5 − 38·9 = 10·6 g. In order to produce a 25-g lead button the amount of litharge required will be

$$\frac{PbO}{Pb} \times 25 = 27 \text{ g}$$

The oxygen derived from this portion of the litharge is lost during the fusion, and thus need not be balanced by silica.

Thus far the charge contains:

Ore	29·2 g
Sodium carbonate	29·2 g
Silica	21·3 + 16·8 + 10·6 = 48·7 g
Litharge	27 + 38·9 = 65·9 g
Flour*	10 g

The above charge derives its acidic oxygens solely from the silica. This would probably produce a slag whose viscosity was detrimental to the lead extraction of noble metals. To increase the fluidity one may substitute borax glass for silica. The degree of substitution is again largely a matter of experience.

Assuming that 10 g of the silica is replaced by borax glass, the acid oxygen ratio of SiO_2 to $Na_2O{\cdot}2B_2O_3$ is 2 to 6. Thus the borax glass required will be

$$10 \times \frac{Na_2O{\cdot}2B_2O_3}{3 \times SiO_2} = 11 \text{ g}$$

Borax glass also contains a basic oxygen. Whereas the amount of this oxygen can be readily calculated, the amount is relatively small and will have little effect on the silica degree of the above charge. Moreover, it will reduce the acidity slightly, a condition that is quite acceptable for noble metal assays.

The final charge for one assay ton of the above roasted concentrate is then

29·2 g of ore
29·2 g of sodium carbonate
65·9 g of litharge
38·7 g of silica
11·2 g of borax glass
10 g of flour

If a trial of the above fusion indicates that the button is insufficiently free from copper and nickel, or if the slag is non-homogeneous it will be advisable to increase the amount of litharge. One may then proceed to calculate the additional amount of both litharge and silica on the basis of a flux to ore ratio of 1 to 5, etc. For such a ratio, the addition should be of 29·2 g of flux containing a litharge to silica ratio of one PbO to one SiO_2, if the bisilicate is required. The calculation is made as above:

$$\frac{PbO}{PbO{\cdot}SiO_2} \times 29{\cdot}2 = 23 \text{ g litharge}$$

and 29·2 − 23 = 6·2 g silica.

---

* For non-oxidizing ores, 3 g of flour will produce about 25 g of lead. For oxidized ores, the 10 g added is a guess from experience. One cannot calculate the flour to litharge ratio for the fusion of this type of ore. The reason for this is, at least partly, the existence of some localized oxidizing reactions between flour and oxides other than those of lead. The degree to which this takes place cannot be calculated, but it is generally sufficiently constant for any one type of ore.

For ores that contain very high proportions of nickel and copper, an excess of litharge or basic charge is required. It should be recalled, as discussed above, that with this charge one may expect losses at least of iridium and ruthenium. Furthermore, the charge will damage the pot extensively. For ores of this type a preliminary wet treatment is desirable. Procedure 58 is applicable in these instances.

It is always advisable to make at least one assay of the slag. This is accomplished by grinding the slag to about 100 mesh, mixing with sufficient litharge (27 g) to form a button, adding 3 g of flour, and returning the charge to the original pot. The method is included in Procedure 56.

THE CALCULATION FOR FLUX AND SLAG FOR A FUSION OF AN IRON ORE

Assuming that the composition of the ore is 40 per cent iron (as Fe_2O_3) and 60 per cent silica, that a monosilicate slag is required, and that one assay ton is to be used, the number of basic oxygens is

$$\frac{40}{100} \times 29{\cdot}2 \times \frac{Fe_2O_3}{2Fe} \times \frac{1}{Fe_2O_3} \times 3 = 0{\cdot}312 \text{ g-atom}$$

In the case of black sand the iron oxide is taken as Fe_3O_4 instead of Fe_2O_3.

The number of acidic oxygens is

$$\frac{60}{100} \times 29{\cdot}2 \times \frac{1}{SiO_2} \times 2 = 0{\cdot}584 \text{ g-atom}$$

Thus the number of excess acidic oxygens is

$$0{\cdot}584 - 0{\cdot}312 = 0{\cdot}272 \text{ g-atom}$$

Accepting again the optimum ratio of sodium carbonate to ore as being 1 : 1, the additional basic oxygens from this source is then

$$29{\cdot}2 \times \frac{Na_2O}{Na_2CO_3} \times \frac{1}{Na_2O} = 0{\cdot}275 \text{ g-atom}$$

Thus the ore sample plus the added carbonate is now a monosilicate, with the total number of basic oxygens being

$$0{\cdot}312 + 0{\cdot}275 = 0{\cdot}587 \text{ g-atom}$$

as compared to 0·584 g-atom of acidic oxygens.

Assuming again that an acceptable ratio of sample weight to flux weight is about 1 to 4, the amount of flux to be added to the sample is then 29·2 × 4 = 116·8 g

Therefore 116·8 − 29·2 (weight of soda ash)

= 87·6 g of flux are still required.

The additional flux will be made up from litharge and silica. The monosilicate will be $2PbO{\cdot}SiO_2$. The weight of litharge to be added will then be

$$\frac{2PbO}{2PbO{\cdot}SiO_2} \times 87{\cdot}6 = 77{\cdot}20 \text{ g}$$

and the weight of silica will be

$$87{\cdot}6 - 77{\cdot}20 = 10{\cdot}4 \text{ g}$$

In order to provide the 25-g button the weight of litharge will again be

$$\frac{PbO}{Pb} \times 25 = 27 \text{ g}$$

The composition of the charge will then be:

Ore	29·2 g
Sodium carbonate	29·2 g
Litharge	77·20 + 27 = 104·2 g
Silica	10·4
Flour	4 g

If the fusion of the above charge is excessively viscous, some or all of the added silica may be replaced by borax glass. If the litharge proves excessive one may use a proportion of charge to ore of 3 to 1, etc. instead of the 4 to 1 used above.

THE NITRE ASSAY

Ores of the platinum metals which contain high proportions of associated base metal sulphides present a special problem. Unless the assay is properly carried out the sulphides may form a matte that will be a third phase in the final slag. The matte, made up of base metal sulphides, is an excellent carrier of platinum metals. In fact, a reasonably good assay can be made in which the matte is the sole collector. With lead as the collector the presence of the matte must be avoided. This can be accomplished by the use of various fusion charges. Not infrequently, excess of litharge charges are recommended. These involve the presence in the fusion of relatively large amounts of litharge with a deficiency of acid constituents. The result is a subsilicate or basic charge. Aside from the fact that these fusions may involve losses of iridium, ruthenium, etc., there is the objectionable feature that corrosion of the pot becomes excessive, and in fact a single fusion may destroy the pot.

In so far as the platinum metals are concerned the present author recommends either of two methods for the assay of high sulphide concentrates; the roasting procedure or the nitre* assay. The nitre assay involves the partial oxidation of the sulphides by the addition of potassium nitrate; the excess of base metals sulphides is then used to produce the lead button. In a nitre fusion the formation of a matte seems to be encouraged by an excess of acidic oxygens over basic oxygens and also by a slow fusion at a low temperature. These suggestions may find support in the relatively low formation temperatures of lead silicates and the higher temperatures required for the oxidation of sulphides by the litharge or nitrate. It is desirable to arrange the rate of heating so as to avoid reactions with the acidic constituents until oxidation of the sulphide by nitre and by litharge has been completed. In general it has been recommended that, with the nitre fusion, the pots should be placed in the furnace at 800°C, heated rapidly for about 30 min, and then removed at about 1000°C.

The most generally suitable slag composition is a monosilicate. Prior to the nitre assay one must determine experimentally the amount of the sulphide ore constituents that must remain unoxidized by the nitre in order to provide for a lead button of suitable size. The methods used are described below in Procedure 54. It should be noted that the weight of lead produced by 1 g of sulphide ore, i.e. " the reducing power ", will depend to an appreciable degree upon the composition of the charge. Fulton and Sharwood[14] state that " the range of reducing power for pyrite is from about 9 to 12·2 g of lead, according to whether the charge is acid and contains little soda or is of the litharge–soda type ". Thus it is essential that the conditions used for determining the reducing power should be a close duplicate of the conditions used during the assay.

Here there exists a strange anomaly. Whereas the above condition is generally recognized, few text-books on fire assaying recognize the condition in the proposed procedures. In some instances the compositions of the flux used for the determination of the oxidizing and reducing powers differ only in the addition of nitre but with no variation in compositions to allow for the reaction products of the reaction with the nitre. In certain instances the addition of nitre is accompanied by an increase in the silica proportions despite the accompanying claim that the addition of nitre requires an increase in the proportion of soda ash, which reacts with a portion of the sulphate[234] formed by the reaction between nitrate and sulphide.

It is in these areas of fire assaying that a discriminating knowledge of how chemicals behave becomes of considerable significance. The reactions involved during the fusion of these complex systems present one of the most fertile fields of research. Many of the recorded reaction equations are derived from an integration of simple systems, and the variations in these equations suggested for comparable systems and fusion conditions provide convincing evidence that stoichiometric calculations for reducing and oxidizing powers are quite impractical. One must suspect that too many of the proposed equations, while perhaps self-satisfying to the specific author, have little basis in experimental data. The two following equations, pertinent to the calculation of flux and slag compositions for nitrate fusions, were suggested by Bugbee.[234]

$$\text{(A)}\quad 2FeS_2 + 14PbO + 4Na_2CO_3 + SiO_2 \rightarrow FeSiO_4 + 14Pb + 4Na_2SO_4 + 4CO_2$$

$$\text{(B)}\quad 10FeS_2 + 28KNO_3 + 6Na_2CO_3 + 5SiO_2 \rightarrow 5FeSiO_4 + 14K_2SO_4 + 6Na_2SO_4 + 14N_2 + 6CO_2$$

One must not conclude that the relationships in equations A and B can be used indiscriminately or even that acceptable proof exists for their validity. They are included here because their use has provided satisfactory fluxes and slags.

In practically all instances trial assays are necessary to determine the amount of nitrate required for the flux, and even with an experienced assayer, re-adjustments of flux constituents are frequently necessary. Various

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* " Nitre " is a trivial name for potassium nitrate.

methods may be used to determine the amount of potassium nitrate required to oxidize the sulphide in excess of that required for the production of the button.

The conventional procedure involves the determination of the " reducing power " of the ore and simultaneously the " oxidizing power " of nitrate for the particular charge to be used in the assay. In principle the *reducing power* of the ore is obtained by fusing a portion of the ore with the flux to be used, and weighing the lead button. The reducing power is then the weight of the lead button divided by the weight of the ore. The oxidizing power of the nitre for the particular fusion is obtained by adding a suitable amount of nitre to the charge used for determining the reducing power and thus producing a smaller button, owing to the oxidizing action of the nitrate on the sulphide. The *oxidizing power* of the nitrate is then calculated in terms of the lead obtained, i.e. it is the difference in weight of the two lead buttons divided by the weight of nitrate used. Obviously the reducing power of the ore, the oxidizing power of the nitrate and thus the amount of nitrate required could be calculated theoretically if the exact constituents of the charge and the resulting chemical reactions are known. These data are seldom if ever known for natural ores or concentrates. It should be emphasized again that the conditions for determining the required data must approach as closely as possible the conditions used for the assay.

It was stated above that, for the nitre assay, the development of a matte is encouraged by low temperatures and prolonged fusions. There is some evidence to indicate that under these conditions the data obtained for the reducing and oxidizing powers results in excessively large buttons. This may be the result of a low value for the reducing power. Anyway, some considerable difficulty may be experienced when the reducing and oxidizing powers are determined from prolonged fusions at low temperatures.

THE DETERMINATION OF THE REDUCING POWER OF ORES AND THE OXIDIZING POWER OF NITRE

Procedure 54

Determine by suitable analytical methods the proportions of base metals and acid constituents, including sulphur, in the ore sample.

Using 5 g of ore, calculate the proportions of the flux constituents required for a monosilicate, including the sodium carbonate required to form sodium sulphate, the silica needed to form iron silicate, and sufficient excess of litharge to form 10 g of lead (Note 1). Fuse exactly as required for the final assay, and weigh the button (wt. = L_1).

The reducing power is

$$\frac{\text{Button weight (g)}}{5}$$

Repeat the above procedure but in this instance add 3·00 g of potassium nitrate (Note 2).

Notes—1. The weight of this litharge for a given sample may be determined by one or two preliminary trial fusions. One may arrive at a suitable amount of litharge, however, by calculating from the equation A, recorded above, and suggested by Bugbee[234] for the reactions between litharge and sulphide, the sulphur being obtained by a preliminary analysis.

2. In general no adjustment of flux composition is made to allow for the reaction products of the nitrate that will affect the acidity of the slag. Bugbee[234] recognizes the presence of the nitrate in the determination of the oxidizing power by increasing only the silica content of the flux used for the reducing power. This is in contradiction to the reactions recorded by equation B. Assuming that this equation approximates the effect of nitrate it is seen that some sodium carbonate is used to form sodium sulphate. The sodium carbonate thus used will therefore deplete the proportions calculated for the flux, and if this shift toward acidity is inadvisable one must provide additional sodium carbonate which in the calculations recorded below is obtained from equation A. Furthermore, additional sodium carbonate, as well as silica, is also required to complete the reaction with the sulphate or sulphite arising from the oxidation of the sulphide by the litharge in forming the lead button. These additions are recommended particularly in those instances where it is desirable to retain an optimum silicate degree.

Weigh the resulting button (wt. = L_2).

The lead equivalent of 3 g of nitrate is $L_1 - L_2$. The oxidizing power of the nitrate expressed in terms of a lead equivalent is then

$$\frac{L_1 - L_2}{3{\cdot}00}$$

Assuming that one assay ton of ore is to be used for the assay, calculate the nitre required thus:

(a) Multiply the reducing power of ore by 29·2 g.

(b) Subtract the desired weight of the button.

(c) Divide the result of (b) by the oxidizing power of the nitre.

Now recalculate the charge for the monosilicate slag on the basis of 29·2 g of ore in place of the 5 g used for the preliminary assays. These calculations are illustrated below.

Note—The present author has used a simplified method of determining the amount of potassium nitrate required to secure a button of suitable size. This method requires an experimentally determined quantitative relationship between the increase in button size and the decrease in weight of potassium nitrate for a particular charge.

An arbitrarily chosen amount of potassium nitrate is added to the properly calculated charge of flux and ore, and, after the fusion, the lead button is weighed. A suitable amount of potassium nitrate may be estimated roughly from the per cent of sulphur in the ore (see equations A and B). The charge must, of course, correspond in acidity and excess of litharge to the composition used for the final assay.

A second assay is made as described above but in this instance a somewhat smaller amount of potassium nitrate is added to produce a larger button. From the desired weight of the final assay button, the difference in the amounts of potassium nitrate used and in the lead produced in the two preliminary assays, the weight of potassium nitrate to be used in the final assay can be calculated.

Thus if a 25-g button is required for the final assay and if:

(*a*) 45 g of potassium nitrate produce a lead button of 40 g and 40 g of potassium nitrate produce a lead button of 50 g, a 10-g decrease in lead corresponds to an increase of 5 g of potassium nitrate. Thus, a 25-g decrease of lead (50 − 25) corresponds to an addition of $5 \times \frac{25}{10} = 12{\cdot}5$ g of potassium nitrate. Therefore, the total amount of potassium nitrate to be used is 40 + 12·5 = 52·5 g

or

(*b*) A 10-g decrease of lead corresponds to an increase of 5 g of potassium nitrate. To produce a 25-g button, a decrease of (40 − 25) = 15 g of lead is required. Thus, a 15-g decrease of lead corresponds to $5 \times \frac{15}{10} = 7{\cdot}5$ g of potassium nitrate.

The amount of potassium nitrate to be used is again 45 + 7·5 = 52·5 g.

It will be noted that these calculations are based on the assumption that the oxidizing power of the nitrate and the lead produced is a straight line relationship. This assumption is also made for the classical method of applying the oxidizing and reducing power to arrive at the required amount of potassium nitrate.

THE CALCULATION OF THE FLUX COMPOSITION FOR A NITRE CHARGE

Whereas one cannot calculate in advance the acidity for a nitre assay, one can calculate the acidity of the charge after finding the amount of potassium nitrate required, and minor adjustments of the constituents can then be made if they are desired. Furthermore, small variations from the generally suitable monosilicate are not objectionable because equally good recoveries can be made from charges slightly on the sesquisilicate side.

It is generally accepted that in basic charges the result of the oxidation of sulphur is the formation of sulphur(VI), whereas oxidations in the bisilicate charge form sulphur(IV). It is generally assumed also that the associated basic metals in the more basic slag are converted to their higher oxides, and the calculation included below is based on this somewhat questionable assumption.

A certain sulphide ore concentrate of platinum metals has the following composition:

iron	40·7%	silica	5·10%
copper	5·2%	calcium oxide	2·00%
nickel	6·14%	aluminium oxide	4·50%
sulphur	34·00%	magnesium oxide	2·00%

With this concentrate a 25-g button requires 52 g of potassium nitrate.

One part of concentrate to one part of sodium carbonate is the accepted ratio, and the accepted ratio of flux to ore is 11 : 1. This large ratio is used to assist in slagging the high proportions of base metals and thus providing a relatively clean button. Attention is directed again to the fact that during the nitric acid parting the dissolution of platinum metals is encouraged by the presence of copper in the button.

Calculation

Basic oxygens from the concentrate for one assay ton (29·2 g) are:

$$\frac{40{\cdot}7}{100} \times 29{\cdot}2 \times \frac{Fe_2O_3}{2Fe} \times \frac{1}{Fe_2O_3} \times 3 = 0{\cdot}319 \text{ g-atom}$$

$$\frac{5{\cdot}2}{100} \times 29{\cdot}2 \times \frac{CuO}{Cu} \times \frac{1}{CuO} = 0{\cdot}0239 \text{ g-atom}$$

$$\frac{6{\cdot}14}{100} \times 29{\cdot}2 \times \frac{NiO}{Ni} \times \frac{1}{NiO} = 0{\cdot}0305 \text{ g-atom}$$

$$\frac{2{\cdot}00}{100} \times 29{\cdot}2 \times \frac{1}{CaO} = 0{\cdot}0104 \text{ g-atom}$$

$$\frac{4{\cdot}5}{100} \times 29{\cdot}2 \times \frac{1}{Al_2O_3} \times 3 = 0{\cdot}0387 \text{ g-atom}$$

$$\frac{2{\cdot}0}{100} \times 29{\cdot}2 \times \frac{1}{MgO} = 0{\cdot}0145 \text{ g-atom}$$

Total basic oxygens from the ore = 0·438 g-atom

Acidic oxygen from ore

$$\frac{5{\cdot}1}{100} \times 29{\cdot}2 \times \frac{1}{SiO_2} \times 2 = 0{\cdot}0496 \text{ g-atom}$$

Basic oxygen in excess = 0·388 g-atom

Thus for a monosilicate, e.g. ($2Na_2O{\cdot}SiO_2$), the weight of silica which must be added to the concentrate is

$$0{\cdot}388 \times \frac{SiO_2}{2} = \underline{11{\cdot}66 \text{ g}}$$

Because the 25 g of lead button is derived from an oxidation of sulphide presumably to form sulphate, sodium carbonate may be added to react with this sulphate. Bugbee[234] states that in the presence of sufficient alkali carbonates the sulphur is oxidized to sulphur trioxide, which combines with the alkali to form sulphate according to equation A, described above. Thus the sodium carbonate required to react with sulphate formed by the reaction of sulphide with litharge will be:

$$25 \times \frac{4Na_2CO_3}{14Pb} = 3{\cdot}7 \text{ g}$$

According to equation A the following additional silica is also required:

$$25 \times \frac{SiO_2}{14Pb} = 0{\cdot}52 \text{ g}$$

From equation B it can be seen that additional sodium carbonate is required as a result of the reaction with potassium nitrate. Because a 25-g button is produced from 52 g of potassium nitrate, the weight of soda ash required is thus:

$$\frac{6Na_2CO_3}{28KNO_3} \times 52 = 11{\cdot}68 \text{ g}$$

Again additional silica is required to complete the reaction. This is also calculated for equation B thus:

$$\frac{5SiO_2}{28KNO_3} \times 52 = 5{\cdot}5 \text{ g}$$

Accepting again the usual ratio of 1 : 1 for sodium carbonate and the sample, the weight of silica which must accompany the carbonate to produce the monosilicate ($2Na_2O{\cdot}SiO_2$) is

$$29{\cdot}2 \times \frac{SiO_2}{2Na_2CO_3} = 8{\cdot}26 \text{ g}$$

Excluding the sodium carbonate used as a result of the addition of potassium nitrate, the constituents added thus far to produce the monosilicate are: 11·66 g of silica (equivalent to the excess basic oxygen), 29·2 g of sodium carbonate (to maintain the ratio of 1 of carbonate to 1 of sample) and 8·26 g of silica (to produce the monosilicate from the above 29·2 g of carbonate). Total flux thus far added = 49·12 g. To obtain the ratio of 11 of flux to 1 of ore the total amount of flux added must be 11 × 29·2 = 321·2 g. The excess flux needed is, therefore:

$$321{\cdot}2 - 49{\cdot}12 = 272{\cdot}08 \text{ g}$$

If the flux constituents are litharge and silica the weight of litharge required to form the monosilicate is:

$$\frac{2PbO}{2PbO{\cdot}SiO_2} \times 272{\cdot}08 = 239{\cdot}5 \text{ g}$$

$$\text{The weight of silica} = 272{\cdot}08 - 239{\cdot}5 = 32{\cdot}58 \text{ g}$$

The weight of litharge required to form the 25-g button is

$$\frac{PbO}{Pb} \times 25 = 27 \text{ g}$$

The total charge is then:

Concentrate	29·2 g
Silica, 11·66 + 8·26 + 0·52 + 5·5 + 32·58	= 58·52 g
Sodium carbonate 29·2 + 3·7 + 11·68	= 44·58 g
Litharge, 239·5 + 27	= 266·5 g
Potassium nitrate	52·0 g

PROCEDURE FOR NITRE ASSAY

Procedure 55

Add to the mixing sheet the properly sampled ore or concentrate, together with the calculated fluxes, the excess litharge for the button, the potassium nitrate and its corresponding weight of sodium carbonate and silica. It may be preferable to screen prior to mixing.

Transfer the mixture to an assay pot of an appropriate size (see Equipment No. 18, Chapter 7). When a silver bead is required, add the silver powder or solution to the pot mixture. Place the pot in the muffle at 1100°C, and fuse for about 45 min. Continue as described below in Procedure 56, pouring the fused mixture into the iron mold.

In general this nitre assay is comparable in accuracy of recovery of platinum metals to any other type of fusion.

PROCEDURE FOR ASSAYING ROASTED SULPHIDE ORES

Procedure 56

Grind, mix, and sample the ore as described above. Transfer the weighed ore to a 6-in. porcelain evaporating dish, and place for a few min at the front of the furnace with the door open. The initial temperature should be about 600°C. Over a period of about 5 min move the dish to the furnace centre, stirring intermittently. Partially close the door, and allow to roast for 2 hr at 950°C, frequently stirring for the first 30 min to avoid agglomeration of the concentrate. Remove the dish, cool, transfer the contents to a mortar and grind to a fine powder. Take care to avoid any loss of powder.

From the necessary analytical data calculate a suitable flux composition. In general a bisilicate slag is a suitable medium for the collection of platinum metals in oxidizing ores. For samples with high proportions of associated base metals—copper, nickel, etc.—it may be desirable to increase the proportion of litharge. This can be done by using an increased ratio of flux to ore. For ores of the non-oxidizing or non-reducing types a flux ratio of 2 or 3 to 1 of ore is usually satisfactory. This may be increased considerably to provide a satisfactory slag. Decide on a proper ratio of flux to ore. If a silver bead is to be prepared, add to the flux an amount of silver powder or silver in solution to give a ratio of approximately 20 of silver to 1 of total platinum metals expected.

Arrange a cellophane sheet in a suitable position, and pass the roasted ore through a 45-mesh sieve to the centre of the sheet. Add a portion of the flux to the sieve to remove any traces of ore. Transfer most of the remaining flux to the mixing sheet, and mix thoroughly. Place the mixture in an assay pot of an appropriate size. Add the remaining flux to the sheet, mix, and transfer to the pot, taking care to brush the sheet free of the mixture.

Place the pots in the furnace at about 950°C, and raise the temperature at the maximum rate to 1200°C. This fusion period should be approximately 1 hr. Remove the pots, pour the mixture into conical iron moulds, and allow to cool. (The iron moulds, equipment for handling pots and technique of pouring are illustrated in Chapter 7, Equipment Nos. 19, 19a and 20.) Remove the button, taking care to retain all of the slag. Free the button of slag by gentle tapping with a small iron rod. Set the button aside. Transfer the slag to a grinding mill or to a mortar, grind to pass a No. 45 standard sieve, and place the sample on the original mixing sheet. Clean the mill, mortar and screen with sufficient litharge to produce a second button, then transfer to the slag on the sheet. Mix well as before, and transfer the mixture to the original pot. Fuse as before, and clean the lead button as described above. If necessary a fusion of the second slag can be made to produce a third button.

Transfer the two or three lead buttons to a 3- or 4-in. scorifier previously heated to about 300°C (see Chapter 7, Equipment No. 14). If there is evidence of copper or nickel in the buttons, a few g of borax may be added to the buttons on the scorifier. Continue the scorification at about 1000°C to secure a button of about 25–30 g, and then pour into the iron mould.

When the lead button is to be analysed for osmium and ruthenium, part and treat it as described in Procedure 28. For iridium in the presence of platinum or palladium only, use Procedure 38.

When the noble metals are to be concentrated to form a silver bead clean the button thoroughly by gentle tapping with an iron rod, and transfer it to a bone-ash cupel which has been preheated at 900°C for at least 10 min (see Chapter 7, Equipment 15). Continue heating the cupelling button at about 1000°C, with a plentiful supply of air. Remove the cupel over a period of a few min after the completion of the cupellation process (see the description of the cupellation process in Procedure 57). The determination of platinum metals in the silver-assay bead may be accomplished by any one of Procedures 32, 33, 34, 35 and 36.

Note—It should be stressed here that the classical methods of cleaning either a button or a bead by hammering it to form a square button or to flatten the bead are not recommended. The more insoluble platinum metals, e.g. iridium, are usually mechanically mixed with the silver or lead alloys, and losses will almost invariably occur through any interference with the shape of the alloy.

THE IRON NAIL METHOD FOR GOLD

In the iron nail method the lead button is obtained through the reducing action of iron nails. These also reduce lead minerals to metallic lead.

Because the proportion of litharge is reduced for the iron-nail assay the proportion of sodium carbonate must be correspondingly increased to provide sufficient basic oxygens.

The iron nail assay is quite suitable for the assay of gold in sulphide ores of moderately high sulphur content. The method is not at all applicable to similar ores for the assay of at least some of the platinum metals. In general, it is not recommended for ores containing high proportions of such base metals as copper, because these tend to contaminate the lead button.

Thiers *et al.*[21] state that the iron nail assay for ruthenium is completely useless because substantial amounts of ruthenium will adhere to the nails, and are then lost. Allan[241] stated that osmium is picked up by the iron nails partly because of the metallic lead which also adhered to the nails. Much of the iron scale adhered to the pot wall, and could only be incompletely removed. Whereas no data are available to indicate the efficiency of the iron nail method for all of the platinum metals, one may expect some difficulty in achieving complete recovery, owing to the presence of iron scale and to the subsilicate slag that is usually required. Moreover, one may suspect that the alkali metal ferrous sulphide complex in the slag may have some solvent action on some of the platinum metals. With the iron nail method it is particularly important to free the button from adhering slag, for the latter, with its high sulphide content, causes the precipitation of lead sulphide when the button is parted with nitric acid.

Usually the amount of ore per assay is limited to one-half of an assay ton in order to avoid the necessity of slagging off large amounts of sulphide. With larger amounts of ore the probability of matte formation and the resulting loss of noble metal is increased. Under optimum conditions part of the sulphide is converted to volatile sulphur dioxide, part is oxidized by the litharge in producing the button and, when the fusion is effective, the remaining sulphide is carried into the slag by sodium carbonate. Presumably the FeS_2 is reduced by the nails to ferrous sulphide which forms the complex sodium ferrous sulphide. The iron nail method involves a tendency toward the formation of a matte or of a speise which must be decomposed, because these materials will carry much of the platinum metal content.

In general a rather restricted range of flux compositions is used for the iron nail method. There is general agreement that the slag should be no higher in silica than a monosilicate, and preferably should be a subsilicate. It should be noted, however, that most assayers use a borax or borax glass cover in which instance, while the proportions of sodium carbonate and silica may provide a subsilicate, the inclusion of the acidic oxygens from the borax glass very often results in a slag in which the ratio of acidic oxygens to basic oxygens is greater than unity.

As stated above, one-half of an assay ton of the sulphide is recommended. The ratio of sodium carbonate to ore is usually 3 or 4 to 1. The amount of litharge added is restricted to that required for a button, generally about 30–35 g. The flux described below contains an acidic oxide to basic oxide ratio of 0·37–0·42. The acidity of the final slag will, of course, be influenced by the basic oxides in the ore sample, by the borax cover and by the reactions and destiny of the sulphur content.

The Iron Nail Method for Gold in High Sulphide Ores

Procedure 57

Mix 0·5 assay ton of the sulphide ore on a cellophane sheet with 45 g of sodium carbonate, 35 g of litharge and 2 g of silica or other suitable charges. Add sufficient silver as a powder or in solution to produce a ratio from 4 to 10 parts of silver to 1 of gold. Transfer to an assay ton pot, insert downward four 3-in. nails, cover the charge with 10 g of borax glass, and place in a furnace at low red heat. Fuse for 1 hr at 1000°C, and intermittently move the nails through the fused mixture to remove adhering lead. If the nails disintegrate during the fusion replace them with a few clean nails. Remove the nails at the completion of the fusion, and pour as usual.

Remove adhering slag from the lead button by gentle tapping with a small iron rod. Transfer the clean button to a bone ash cupel that has been preheated at 900°C for at least 10 min (see Chapter 7, Equipment No. 15). Heat at about 1000°C for 5 min, and then arrange a plentiful supply of air, but avoiding an excess that would cause the button to freeze through excessive cooling. Then continue heating at about 1000°C.

Note—The lead button may contain a higher proportion of base metals than is normally found with other methods of assay. In some instances the addition of about 1 g of flour to the charge prior to fusion will assist in providing a clean fusion.

Add to a 5–20-ml porcelain crucible about 4 ml of 1 : 4 nitric acid solution. Heat to incipient boiling, and transfer the bead to the acid. Continue careful heating to the completion of the reaction. Decant the acid, add a few ml of 1 : 1 nitric acid, and continue heating for 5–10 min. Decant the acid, and wash with water to remove the silver nitrate. Transfer the crucible with the gold to a cold muffle, and raise the temperature to about 700°C. Cool and weigh the gold bead. The accuracy, as indicated by salted samples, including both fusion and cupellation, is about 0·2 per cent.

Provided the cupels have been properly heated the lead alloy will have melted immediately and become quickly covered by a dark scum. This should disappear within a few min, the melted alloy assuming a bright surface. This process is appropriately known as *opening* or *uncovering*.

As the lead oxidizes, the melted alloy takes on a convex surface with the litharge " driving " over the surface. With a sufficiently high temperature most of this litharge is absorbed by the cupel, small proportions being volatilized. The absorbed litharge should appear a dark red. A bright red indicates an excessively high temperature. The optimum temperature is indicated by feather-like crystals of litharge forming on the surface of the cupel just above the lead. If sufficiently high temperatures are not maintained these crystals may cover the cupel and eventually the driving button, resulting finally in a frozen button that should be discarded.

As the cupellation approaches completion the temperature of the alloy will drop, owing to the decrease in the heat derived from the oxidation, and care must be taken to maintain the furnace temperature at 950–1000°C. One may notice a play of colours over the alloy at the final disappearance of the litharge. The silver–gold bead then becomes dull, and after a few sec one may observe the phenomenon of brightening. The cupel may now be slowly removed from the furnace. As the bead solidifies a flash of light is observed that is called the " blick ". This is due to the latent heat of fusion, which for a short period increases the temperature.

For gold-silver beads, as opposed to platinum metals–silver beads, it is important that the bead remains coherent. Too rapid cooling of the bead will result in the process of spitting, arising from the rapid evolution of oxygen dissolved in the gold–silver bead. One may avoid this by inverting hot cupels over the bead, allowing the cupels to remain near the muffle door, and then slowly withdrawing them from the furnace. The bead should appear smooth and free of protuberances, because on subsequent parting the gold is heated to form a bead which can be weighed directly. The surface of the bead adjacent to the cupel should appear frosted. If this surface is smooth, a too low temperature is indicated, and the bead may contain lead. This is of lesser consequence for platinum metals–silver beads because the latter must be chemically treated to effect dissolution.

For a more detailed account of cupellation, and the effects of impurities such as associated base metals on the recovery of gold, the reader is referred to text-books such as those of Bugbee[234] and Smith,[235] etc.

Combination Assay for Platinum Metals

It has been stated at times that the fire assay with lead as a collector may fail to reveal platinum metals values quantitatively or may even fail to indicate the presence of platinum metals. Until recently the only alternative procedure involved the prior wet treatment of the ores to convert the platinum metals to constituents such as relatively simple chlorides that are known to respond to the usual fire assay lead collection. These prior acid treatments are usually restricted to selective extractions by single or mixed acids, followed by some precipitating process applied to the leach liquids, and then a fire assay of the combined precipitate and leach insoluble.

A more thorough treatment requires a fusion of the leach insoluble prior to the final assay. In general the selective leaching is considered to be acceptable.

Reconnaissance surveys have been reported[229] to indicate the relative efficiency of the direct assay as compared to a combination of extractive procedures and a final fire assay. Unfortunately these surveys have included the relative recoveries of only platinum, palladium and rhodium. The results of these investigations indicate that prior leaching does not provide precision or accuracy greater than can be obtained under optimum conditions by a direct fire assay. More recently it has been found that there is indeed an improvement in the values obtained for rhodium, iridium, palladium and platinum by prior wet treatments and the chlorination of acid insolubles. The values obtained by classical assay for the above metals were, respectively, 3·5, 0·8, 14·5 and 24·0 μg per assay ton. By wet assay the corresponding values were 4·3, 1·9, 15·6 and 28·8 μg per assay ton.

Table 36. The composition of ores[229]

Ore No.	% Composition				
	Fe	Cu	Ni	S	Insoluble
1	23·10	0·90	1·53	12·63	
2	55·50	0·08	1·02	46·00	3·36
3	36·30	5·18	4·66	27·75	16·80

For any one sample, large differences in leachable platinum metals are not uncommon. Any competent assayer can devise a suitable wet extraction procedure, the details of which may vary considerably. In general, however, only two types of extracting liquids are used, viz., hydrochloric acid and various dilutions of *aqua regia*. The following procedures have been used with success for the ores whose compositions are recorded in Table 36.

Procedure 58

Weigh 1 assay ton of the ore sample, and place it in a shallow silica dish or a scorifier (see Chapter 7, Equipment No. 14). Roast overnight at 675 C in an electric muffle with the door slightly open. Transfer the oxidized sample to a 400-ml beaker, and add 50 ml of concentrated hydrochloric acid. Place the mixture on a steam bath overnight. Add 50 ml of water, and filter. Wash well with water, and repeat the hydrochloric acid treatment, filtration and washing. Burn the residue and paper in a porcelain crucible, and set the ash aside to be combined with the precipitate obtained by a precipitation from the leach liquid.

Two methods for the latter precipitation may be used. Method A involves the removal of metals by precipitation with hydrogen sulphide. Method B is a precipitation with zinc.

Method A. Combine the filtrates from the hydrochloric acid treatment, and evaporate to about 50 ml. Add 200 ml of water, and heat to boiling. Pass a stream of hydrogen sulphide through the solution while the solution is cooling to room temperature. Filter the sulphides, and wash well with a 1 per cent ammonium chloride solution. Transfer the paper and its contents to a porcelain crucible, and burn to an ash at 675°C.

Method B. Evaporate the filtrates from the hydrochloric acid treatments to dryness, and add 150 ml of water. Heat to boiling, and add sufficient hydrochloric acid to dissolve the residue. Add zinc dust to an excess of about 15 g. Boil the mixture for 30 min, filter, and wash well with water. Transfer the paper and precipitate to a porcelain crucible, and burn to an ash at a dull red heat.

The leached residue and the ash from the hydrogen sulphide treatment can be assayed by a neutral flux *A*.

The ash from the zinc treatment is best assayed with an excess of litharge charge *B*. The recommended composition of *A* for each determination is:

Leached residue and ash	x g
Sodium carbonate	37 g
Silica	12 g
Borax glass	6 g
Calcium oxide	5 g
Litharge	49 g
Flour	2·8 g
Silver powder	10 mg

The recommended composition of *B* for each determination is:

Sodium carbonate	24 g
Silica	48 g
Litharge	276 g
Flour	3 g
Silver powder	10 mg

Each charge is covered with the following mixture: 6 g of sodium carbonate, 12 g of silica and 60 g of litharge. The lead buttons may be cupelled according to Procedures 56 or 57, and the resulting silver bead may be treated according to Procedures 32, 33, 34, 35 or 36. The characteristics of the combination assay as applied to ore No. 3 are indicated in Table 37. Comparisons of the recoveries between a direct fire assay and the extractive procedures are also included.

Combination Assays for Gold

Assarsson, Peterson and Asklund[251] used a nitric acid extraction method for gold, the value of which is well supported by comparative data. Procedure 59 involves a nitric acid extraction in a specially constructed apparatus.

This extraction removes the associated base metals and provides a residue containing the gold, silica, sulphur and traces of iron oxide. The gold in the residue is dissolved in hydrochloric and nitric acids. Mercury(II) chloride,

TABLE 37. RESULTS OF LEACHING EXPERIMENTS[229]
(Figures represent troy ounces per ton of No. 3 sample)

Expt.	Treatment of filtrate	Platinum	Sum (a + b)	Palladium	Sum (a + b)	Rhodium	Sum (a + b)
1a	Method A	0·0170	0·0180	0·0067	0·0181	0·0031	0·0031
1b		0·0010		0·0114		. .	
2a		0·0202	0·0202	0·0027	0·0103	0·0027	0·0027
2b		. .		0·0076		. .	
3a		0·0191	0·0191	0·0036	0·0143	0·0029	0·0029
3b		. .		0·0107		. .	
4a	Method B	0·0161	0·0204	0·0017	0·0117	0·0015	0·0046
4b		0·0043		0·0100		0·0031	
5a		0·0221	0·0260	0·0034	0·0167	0·0031	0·0041
5b		0·0039		0·0133		0·0010	
6a		0·0195	0·0253	0·0014	0·0167	0·0021	0·0036
6b		0·0058		0·0153		0·0015	
			Av. 0·0215		0·0146		0·0035
Direct assay ——————→			Av. 0·0223 ± 0·0023		0·0143 ± 0·0009		0·0039 ± 0·004

a Leached residue.
b Leached precipitate.

hydrazine sulphate and sodium sulphide are added to the filtered gold extract. The mixed precipitate of gold and mercury sulphide is filtered, and the paper and residue are ignited. The ash is transferred to a lead sheet, and finally is cupelled. It is claimed that the method provides recoveries comparable in accuracy to those obtained by the classical assay. The method is recommended for ores containing μg amounts of gold per assay ton of ore, e.g. 30 g; however, with these amounts, because the final gold bead is weighed, one must expect appreciable inaccuracies. It would seem that a modification of the method in order to apply spectrophotometric methods of determination would be advisable. Errors will also result from the use of nitric acid containing chlorine, because the initial extraction of base metals may result in some dissolution of gold.

The interference of silver, which may contaminate the gold bead, is also a serious objection to the method.

Procedure 59[251]

Equipment. See Chapter 7, Equipment No. 21.

Transfer 50 g of the 100–200-mesh ore to the dissolution flask, and connect the water pump to the pressure flask. Add 70 ml of concentrated nitric acid, draw off the fumes, and allow the reaction to subside. Continue with intermittent additions of nitric acid until the volume in the flask is 200–300 ml. Heat the mixture to complete the reaction. Dilute the acid to 6 N with water. Heat to boiling, and allow to stand overnight. Filter the resulting mixture through a good grade of filter paper, and wash with cold water by decantation. Dry the paper, and ignite to remove the sulphur.

Transfer the ash to the initial beaker and add about 25 ml of concentrated nitric acid, heat to boiling, filter, and wash thoroughly. Ignite in a quartz crucible, add about 10 ml of 1 : 1 hydrochloric acid containing about 10 drops of concentrated nitric acid, and boil the solution (Note 1). Evaporate the filtrate to a volume suitable for the precipitation of the approximate amount of gold present. Filter the gold solution, wash well, and add to the filtrate 100 mg of mercury(II) chloride, 2 g of hydrazine sulphate and 5 g of sodium sulphide. Boil the mixture to precipitate the mercuric sulphide and the occluded gold. Filter, transfer the paper and precipitate to a small quartz dish, and ignite under a good draught of air.

Add the ash to a sheet of silver-free assay lead, fold, place on a cupel, and carry out the cupellation. In order to reduce the absorbing capacity of the cupel it is suggested that the latter be subjected to a prior cupellation with a small sheet of lead. After the cupellation, cool, and add a little water to the cupelled bead to facilitate its removal. Wash the bead with 1 : 1 nitric acid, ignite and weigh (Note 2).

Presumably the method allows the simultaneous treatment of 6 to 12 samples, and a set of 6 determinations can be made in 2 days.

Notes—1. The solution of gold will contain a trace of the iron oxide not extracted initially by the nitric acid. This introduces no difficulty and, in fact, assists in the complete removal of gold which may be adsorbed by the silica residue or the beaker wall.

2. Traces of silver may contaminate the bead; this may be detected by the lighter colour of the gold. It has been suggested that a correction for silver may be obtained through the preparation of standard gold beads containing known amounts of silver, and a subsequent comparison of colour. This method is unacceptable. Alternatively, the bead may be inquarted with 4 to 1 of silver, and parted with nitric acid in the usual manner (see Procedure 57).

A NEW FIRE ASSAY METHOD

Because of the non-quantitative collection of the more insoluble platinum metals in the classical fire assay and because, in a field which involves extensive financial implications, other proven methods of isolating precious metals from ores are required, the author has in recent years attempted to develop a fire assay extraction that makes use of the naturally occurring base metals associates. In the earlier experiments[252] the iron, copper and nickel in the roasted natural ore were reduced to form a button containing the platinum metals. The reduction was accomplished by the walls of the carbon pot placed in a high frequency furnace at 1450°C. With ores containing insufficient base metals, or with synthetic ores, the base metals were added in the form of oxides. Because the reaction time was short and difficult to control, thus producing excessively large buttons, and because the equipment was expensive and not readily available, efforts were made to devise an assay method based upon similar principles but which would allow control of button size and would require furnaces and pots of standard types. This aim was accomplished, and a procedure was developed[107] that was comparable in character with the classical lead collection. The base metal alloy button was prepared by reduction with mechanically mixed carbon, sodium carbonate, borax and ore, with base metal oxides added if they were required. The standard clay crucibles were heated in a gas/air furnace to 1450°C, as determined from the top of the melt by an optical pyrometer. Button size was controlled by the amount of carbon with an efficiency equal to that obtained with the lead button. The base metal button was then parted and treated as in Procedure 47.

In a series of papers, the above assay method has been proven for ores salted with each of the platinum metals. For either osmium or ruthenium[109] the iron–copper–nickel button is parted with 72 per cent perchloric acid in a standard distillation apparatus. The volatile oxide is distilled from the parting medium, collected in concentrated hydrochloric acid and precipitated by thionalide (Procedures 72 and 78 for osmium and Procedure 72 for ruthenium). For rhodium, the button is parted with hydrochloric acid and finally with a small addition of nitric acid. Base metals are removed by cation-exchange as described in Procedure 47. Rhodium is determined gravimetrically by precipitation with thiobarbituric acid (Procedure 82) and spectrophotometrically with the tin(II) chloride reagent (Procedure 157).

Buttons containing iridium and platinum with palladium are prepared and parted as indicated above. For iridium the gravimetric determinations are made with 2-mercaptobenzothiazole (Procedure 89) and spectrophotometric determinations are made with tin(II) chloride-hydrobromic acid (Procedure 163). Platinum is determined gravimetrically with thiophenol (Procedure 101) and palladium with dimethylglyoxime (Procedure 94). Spectrophotometrically, palladium is determined with *p*-nitrosodimethylaniline (Procedure 168) and platinum with tin(II) chloride (Procedure 179).

In addition to the successful collection of each of the six platinum metals, recent research has indicated that the most resistant iridosmines such as the Tasmanian variety, previously used for fountain pen tips, are collected by the iron–copper–nickel button, and, furthermore, that the alloy will dissolve completely in the acidic parting solutions.

The method has not yet been applied directly to sulphide ores and concentrates because the constituents of the charge would produce a matte. These concentrates are subjected to a prior roasting, and thus there is the possibility of losses of osmium and perhaps some ruthenium. Whereas the extent of these losses has not yet been investigated it is not unlikely that roasting under controlled conditions or under hydrogen will allow the collection of any volatilized osmium and ruthenium.*

The flux constituents are carbon, sodium carbonate and borax. The ratio of acidic oxygen to basic oxygen in the final charge will, of course, depend upon the proportions of the flux constituents and the degree to which each of the base metals is carried into the button. Because no method is yet available which allows even a reasonable prediction to be made of the distribution and destiny of base metals when they are in excess over the amount required for the button collection, one cannot calculate the final slag acidity. In the present instance the flux used contains an acidic to basic oxide ratio of 0·80 to 0·56.

While different forms of carbon such as flour, etc. may be used, graphite provides the most predictable weight of metal alloy. Flour is about 25 per cent as effective as graphite. Initially the graphite was obtained by grinding graphite rods, but aside from the dust problem the fineness of the particles made necessary some screening; commercially produced grade A-200 graphite proved consistently satisfactory, however. The relationship between the weights of the graphite and the button must be determined experimentally as in the classical lead method. The optimum button sizes or compositions have not yet been determined. The detailed characteristics of each of the three base metals as collectors of each of the platinum metals also awaits further research. Furthermore, there is the problem of the optimum temperatures for the alloy collection. Obviously an increase in the copper content of the button will allow lower fusion temperatures, but here again the relative effectiveness of copper as a collector will have a determining influence upon optimum conditions of assaying.†

The new assay procedure significantly effects the reduction of slag losses of platinum and palladium. Nickel is a selective and persistent carrier of platinum and palladium, and its presence in the slag from the classical fire assay increases the risk of some loss of platinum metals.[253] With high proportions of nickel this loss may be irrecoverable by fire assay with lead

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*A successful application to sulphide ores has recently been reported by Van Loon (*Analyt. Chem.* 1964, **36**, 892; 1965, **37**, 113).

†Recent researches in the author's laboratories have proved that copper collects quantitatively iridium rhodium, palladium and platinum.

as the collector.[246, 247] Because nickel and copper are preferentially reduced, the new method has the advantage of a practically complete transference of the nickel to the button. The slags resulting from the application of the new fire assay to a natural ore concentrate revealed the complete removal of platinum and palladium. Fire assays made on synthetic ores salted with platinum and palladium and containing very high proportions of nickel resulted in slags containing both nickel and platinum metals. These slags may be re-treated to remove completely the nickel and the remaining traces of platinum and palladium. With synthetic ores containing a high proportion of copper but no nickel or iron, the slag losses were small.

Some data dealing with the character of the alloys formed in the iron–copper–nickel button have been recorded by Plummer *et al.*[254] The button alloy with palladium appears to be a single phase solid solution. There is also good evidence that platinum, rhodium and osmium form solid solutions. The black residues recovered from buttons containing approximately 20 mg of iridium or ruthenium suggest that collections of this magnitude may be at least partly a mechanical process. This remains uncertain, however; anyway, amounts of the order of 10 mg each of ruthenium and iridium in iron–copper–nickel buttons are completely dissolved by the parting acid.

Procedure 60[107]

Transfer 100 g (3·43 assay tons) of ore or concentrate to a 6-in. porcelain dish, and roast in the assay furnace at 980°C for 2 hr. Stir intermittently to encourage the oxidation. Mix the cooled calcine with 42·4 g of sodium carbonate, 27 g of borax glass and 9·5 g of 200-mesh amorphous graphite. Crush the mix if necessary to pass a 45-mesh screen, and mix again on the mixing sheet (see Procedure 53). Transfer to a 30-g pot, and place in a gas furnace preheated to 1200°C (see Chapter 7, Equipment 22). Turn off the gas and air, the cooling period allowing the reactions to proceed without an overflow of the charge. When the volume of the pot mixture is reduced to about one-third of the original volume, re-ignite the gas–air mixture, and increase the temperature over a period of about 45 min to 1250°C. Then raise the temperature over 1·5 hr to 1450°C, at which time turn off the gas, and remove the pot. Break the cooled pot, separate the button, and remove adhering slag by gentle tapping with the end of a small iron rod.

The method of parting and subsequent analysis of the button are described in Procedure 47.

A Fire Assay Method Using Tin as the Collector for Platinum Metals and Gold
Its Application to Rocks, Ores and Concentrates

Procedure 61[255]

1. *Sample pretreatment*

Roasting. Place the sample (−200 mesh) in a shallow roasting dish, and roast at 750–800°C for approximately 1 hr with intermittent stirring.

The leaching of the copper–nickel matte. To remove the bulk of the copper and nickel, leach the sample in concentrated hydrochloric acid. Experiments showing that the platinum metals and gold remain insoluble during this treatment because reducing conditions prevail throughout.

Place the sample (up to 1 assay ton) in a 1-l. beaker, and treat with 25 g of ammonium chloride and 100 ml of 12 M hydrochloric acid. Heat the covered beaker and its contents until the amount of insoluble matter appears to be reduced to 1–3 g. (Further additions of hydrochloric acid may be required for large sample weights.) To avoid oxidizing the sample do not boil excessively after the evolution of hydrogen sulphide ceases.

Filter off the insoluble matter on a medium paper, dry for a short time in a drying oven, then place on a bed of silica (3–4 g) in a scorifying dish, and roast as described above.

2. *The preparation of tin assay buttons.*

Mix the roasted sample (up to 1 assay ton) thoroughly with a flux of the following composition:

Tin(IV) oxide	35 g
Sodium carbonate	50 g
Silica	10–20 g
Borax glass	10 g
Coke	6–8 g

Adjust the quantity of silica and coke to the amount of silica and iron respectively in the sample.

Place the charge in a 40-g assay crucible, and fuse at 1250°C for 45 min. Then pour the melt into a conical steel mould, and, when cool, separate the tin assay button from adhering slag by tapping with a small hammer.

When it is known that the sample taken for fusion contains more than 3 g of combined copper and nickel, add 15–25 g of stick tin to lower the melting point of the resultant alloy.

Melt the assay button under nitrogen (to prevent oxidation of the tin) in a Vycor melting tube using an open flame, or in a Jelrus Handy-melt portable furnace. To produce a spongy or granulated mass pour the melt into several l. of water in an enamel pail. Dispergate any large lumps produced in this operation with shears.

3. *The analysis of the assay button*

(*a*) *Parting the button.* Transfer the dried alloy to a 600-ml beaker, add 150 ml of concentrated hydrochloric acid, and cover the beaker with a watch glass. Heat until the excess of tin dissolves and the vigorous evolution of bubbles from the black insoluble residue ceases. After diluting to about 400 ml with water, stir the suspension with a motor-driven polyethylene coated stirrer, and add 7 g of powdered tin to precipitate the copper and any rhodium present in solution. Estimate the amount of copper precipitated, and when it is less than 0·3–0·4 g add 0·5 g of copper (as its chloride) to ensure that sufficient copper is present to act as an efficient carrier for rhodium. Stir the suspension for 20 min. Decant the supernatant solution through a pad of paper pulp (from Whatman No. 31 paper) supported on a filter disc. Wash the solids several times by decantation with 2 M hydrochloric acid, and pass the washings through the filter pad.

When rhodium is not to be determined, omit the treatment of the parting acid solution with tin powder and recover directly the parting residue by decantation as described in the preceding paragraph. Add about 50 ml of 12 M hydrochloric acid to the solids in the beaker. Follow this by cautious addition of small portions of a 30 per cent hydrogen peroxide solution until the solids appear to be dissolved and excess of peroxide is present. Heat the beaker for a few min to ensure the complete dissolution of the residue, place it under the filter pad, and wash the pad with 20 ml of a mixture of 3 parts of 8 M hydrochloric acid and 1 part of 30 per cent hydrogen peroxide, and dissolve any fines deposited during the decantation. Add about 100 mg of sodium chloride to the solution, and evaporate until salts begin to crystallize and the vapours of tin(IV) chloride appear.

To volatilize the tin, add 15 ml of a 7 : 2 mixture of concentrated hydrochloric and hydrobromic acids. Place the beaker in an aluminium evaporator under an infrared lamp, and evaporate the solution to dryness. Repeat this operation several times with further additions of the mixed acids until the removal of tin appears to be complete.

To ensure the complete dissolution of the precious metals treat the residue remaining after the volatilization of tin with a 3 : 1 mixture of 12 M hydrochloric acid and 30 per cent hydrogen peroxide solution. If only platinum metals are to be determined, evaporate the solution on the hot plate to dryness, or to 2 ml if gold is to be determined. In the latter instance, place the beaker in a water bath and, by using a jet of compressed air, gently evaporate the solution to dryness.

(*b*) *The extraction and determination of gold.* Take up the salts in the beaker in 5 ml of 2 M hydrobromic acid, and wash into a 60-ml separatory funnel with a further 10 ml of 2 M hydrobromic acid. Extract the gold according to the method of McBryde and Yoe[151] (Procedure 16) by shaking the solution with two 15-ml portions of diethyl ether (double the volumes of hydrobromic acid and ether when samples contain large quantities of base metals). Wash the combined ether extracts with three 5-ml portions of 2 M hydrobromic acid. Combine the washings with the aqueous phase, and reserve the whole for the determination of the platinum metals.

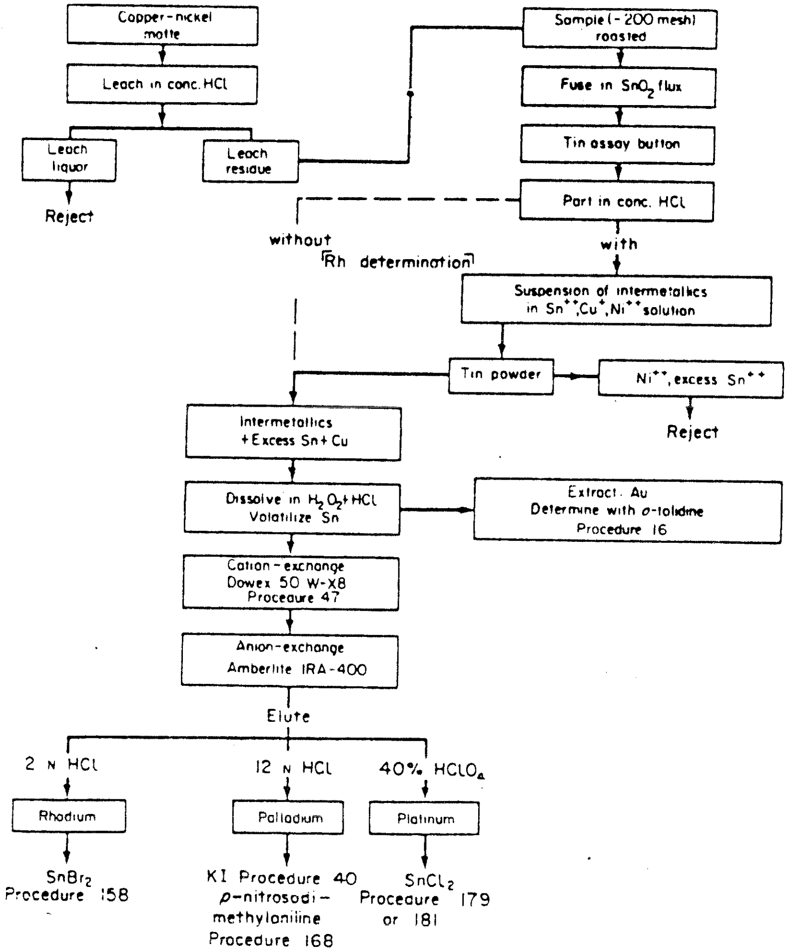

FIG 13. Flow sheet.

Strip the washed ether phase of its gold by shaking for 1 min each with three 15-ml portions of water. Treat the aqueous gold solution with about 50 mg of sodium chloride and 5 ml of *aqua regia*, and evaporate on a hot plate to 2 ml. Using a water bath and a jet of air, evaporate the solution to dryness. Determine the gold content of the residue either spectrophotometrically with *o*-tolidine according to the method of Clabaugh (Procedure 188) or gravimetrically with hydroquinone (Procedure 105).

Note—Attention is directed here to the discussion prior to Procedure 16. Little or no advantage is derived from the aqueous extraction of gold from the ether phase. An evaporation of the ethereal gold extract and a subsequent dissolution prior to the determination of gold provides excellent precision and accuracy.

(*c*) *The removal of base metals.* Evaporate to dryness the aqueous phase from which the gold has been extracted, and cautiously treat the residue with several 5–10-ml portions of a 3 : 1 mixture of 12 M hydrochloric acid and 30 per cent hydrogen peroxide solution (bromine is evolved vigorously when large quantities of base metal bromides are present), and then evaporate the solution to incipient dryness.

Take up the salts in either 0·25 or 0·50 ml of 12 M hydrochloric acid, and dilute to 50 or 100 ml with water (depending on the amount of base metals present) to give a solution with a pH of about 1·5. Remove iron, copper and nickel by passing the solution through a cation-exchange column (Dowex 50 W-X8) of appropriate size (see Procedure 47).

(*d*) *The separation and determination of platinum, palladium and rhodium.* Evaporate the effluent from the cation-exchange column to incipient dryness in the presence of a few mg of sodium chloride, take up the salts in 1·5 ml of 12 M hydrochloric acid, and dilute to 25 ml with water.

Separate platinum, palladium and rhodium from one another by the anion-exchange method (Procedure 42) using columns of Amberlite IRA-400 resin (0·3 × 2·5–3·0 cm). For each batch of resin it is suggested that experiments be made to determine the optimum resin particle size and column dimensions for the separations to be considered.

The first fraction stripped from the column contains rhodium; determine this metal spectrophotometrically with tin(II) bromide (Procedure 158).

Next remove the palladium. If more than 100 μg is present, determine it spectrophotometrically with potassium iodide (Procedure 40). Determine smaller quantities with *p*-nitrosodimethylaniline (Procedure 168).

Platinum elutes last. If more than 100 μg is present, determine it spectrophotometrically with tin(II) chloride (Procedure 179). A modification of this method involving the extraction of the coloured platinum complex into tributyl phosphate is used to determine less than 100 μg of platinum (Procedure 181).

The flow sheet (Fig. 13) provides an outline of the whole procedure.

THE DETERMINATION OF GOLD IN CYANIDE SOLUTIONS

Whereas a considerable variety of acceptable methods have been proposed for the determination of gold in cyanide solutions, there is a need, not only for a critical comparison of these methods, based on experimental data, but also for researches designed to apply some of the more recently developed separational techniques. It is not improbable that investigations such as these would add profitably to large scale separations.

In this context progress is being made towards the extraction of gold from cyanide solution by ion-exchangers. Whereas no generally applicable method has been proposed Fridman and Popova[256] used 5 g of the anion-exchanger AN-2F to remove 230 μg of gold from 2 l. of solution. It is significant that the presence of iron lowers the efficiency of the exchange. An unusual application of ion-exchange, viz., to the determination of gold in the filter cake from an extraction plant, was also described by these authors.[257] The anion-exchange resin AN-2F, in the chloride form was soaked in water for 2 hr and then mixed with a solution of the filter cake for 3 hr. The mixture was passed through a set of 35- and 100-mesh sieves. The material retained on the latter was mixed with a flux, and fire assayed.

From time to time adverse criticisms have been directed toward even the classical method of determining gold in cyanide solutions,[258] and there can be little doubt that some of the reactions involved in these methods are little understood. Here, then, is a potentially fertile field for fundamental and practical research.

Bugbee[234] stated that the Chiddy method with its numerous modifications is reported to be unpopular on the Rand on account of the care required to obtain satisfactory results and because it requires heating.

Alternative procedures, used in the absence of thiocyanates, involve the addition of copper(I) chloride in hydrochloric acid or the production of copper(I) ion *in situ* by adding consecutively a saturated solution of sodium cyanide, copper sulphate, sodium sulphite and sulphuric acid. Potassium ferrocyanide is usually added in small amounts to provide a carrier and to aid in filtering. With these two methods the gold is first precipitated as $CuAu(CN)_2$, and the excess of cyanide is removed simultaneously as copper(I) cyanide. The precipitations are accomplished in the cold. The use of potassium ferrocyanide as a coagulant was rejected by Creed and Clayton-Boxall[259] as unnecessary and leading to losses when excess is present. These authors stated that, when the ferrocyanide was to be used, the amount should be limited to 1 ml of a 5 per cent solution of ferrocyanide. The data provided indicated that the ferrocyanide reacted directly with the precipitated gold to produce a dissolved product.

The Copper(I) Chloride Method

King and Wolfe[260] provided the following modified method together with methods of making the copper salt solution, its effective storage, and a method of dispensing the unstable precipitant.

Procedure 62[260]

Reagents

Copper(I) chloride solution. To a suitably large pyrex Erlenmeyer flask fitted with a water-cooled condenser add crushed copper sulphate and concentrated hydrochloric acid in the proportion of 1 formula weight of the copper salt to 3 formula weights of hydrochloric acid. Into this mixture place a copper sheet extending to the surface of the liquid. It is preferable to use a large copper surface. Boil gently for a few hr to obtain a colourless solution. Remove the condenser, stopper the flask tightly, and allow to cool. The solution may darken as the copper(I) salt precipitates, but within 1 or 2 hr it will again become clear. Store the solution under hydrogen, and remove the necessary aliquots through an attached syphon.

An alternative method of preparing copper(I) chloride was described by Bettel.[261] The procedure, which requires the use of both a storage bottle and one for current use, is:

Add to the storage bottle an excess of high conductivity copper, and then fill it to the neck with 1 : 1 hydrochloric acid saturated with copper(I) chloride. Mix this solution with an equal volume of concentrated hydrochloric acid. When the resulting solution becomes colourless transfer a suitable amount to a small bottle containing copper foil. The solution is then available for current use. As the solution is removed from the stock bottle, refill the latter with the saturated hydrochloric acid-copper(I) chloride solution.

Stock flux.

Silica	8 parts
Borax glass	4 parts
Sodium carbonate	36 parts
Litharge	40 parts
Flour	1 part

Use about 90 g of the well-mixed flux for each fusion. Add silver as required. A 15-cm paper will produce about 10 g of lead, hence only a small amount of flour is required. This flux gives a good slag at about 1000°C.

Coagulant. The $CuAu(CN)_2$ precipitated by copper(I) chloride is pale green and sometimes very finely divided. Thus it may pass through filter paper. To assist the coagulation a dilute solution of potassium ferrocyanide is added to produce the flocculent copper ferrocyanide. Excess must be avoided so as to prevent the redissolution of the gold.

A 10 per cent solution of sodium sulphide may also be used. Five drops of this solution should suffice as a collector. There is the advantage with sodium sulphide that the formation of the copper sulphide indicates the necessary excess of copper(I), for the latter is not formed in the presence of cyanide. Too great an excess of sulphide must be avoided because the resulting excess of copper sulphide may produce high slag and cupel losses.

Filter paper pulp may also be used as a coagulant. The pulp should be added to the filter paper to form a uniform coating before filtering. In all instances the first 100 ml or so of the filtrate should be re-filtered.

Procedure. To 20 assay tons of the cyanide solution add 10 ml of the clear copper(I) chloride solution. If more than 20 assay tons are used add 2 ml of the copper solution for each additional 10 assay tons. Mix thoroughly, and leave the rod in the solution. Allow to stand for 5 min, and filter through a 15-cm No. 2 Whatman paper previously treated with paper pulp. Clean the beaker with a small piece of filter paper that is then added to the solid. Allow to drain, and transfer the precipitate and paper, apex down, to a 20-g crucible containing about 20 per cent of the flux. Add to the open cone the rest of the flux and sufficient silver for parting. Fuse, transfer the button to a cupel, and proceed according to the cupellation and parting technique described in Procedure 57.

Alternative Procedures (63 and 64) were given by Clayton-Boxall.[259]

Procedure 63[259]

Pour 1·5–2·0 l. of well-mixed slime pulp, thinned down to 1·40 density, into an enamel bucket or Winchester quart bottle. Add 15 ml of copper(I) chloride solution free of copper(II), and mix for at least 10 min.

Press off the liquor, and dry the sample in an enamel dish. Pass the dried sample through a 900-mesh screen, add silver for parting, mix well, and assay as described in Procedure 57.

Because of the inconvenience of preparation and the instability of the copper(I) chloride some assayers prefer the copper sulphate method (Procedure 64), in which the reagents are copper sulphate, sulphuric acid and sodium sulphite.

Procedure 64[259]

To a measured volume of solution, usually containing 10 or 20 assay tons, add 5 drops of a saturated solution of potassium ferrocyanide and a slight excess of 10 per cent copper sulphate solution. Stir or shake well. If the solution is low in cyanide it is advisable to bring it up to about 0·05 per cent in potassium cyanide before the precipitation. Then add in succession 10 ml of a 20 per cent sodium sulphite solution and 10 ml of 10 per cent sulphuric acid. Stir or shake well after each addition, and allow to stand for a few min until sulphur dioxide is being freely evolved and the precipitate is settling readily. 20 ml of the copper sulphate solution is usually sufficient, but a faint blue tinge to the filtrate is an assurance of it being in slight excess.

Filter through a 15-cm, rapid, folded filter. Wash out the beaker, then wipe the stirring rod and the beaker with a piece of moistened filter paper to ensure the collection of all the precipitate, and add to the contents of the filter. Allow the solution to drain; then dust a little mixed flux over the precipitate, and transfer the moist filter and its contents to a glazed 20-g crucible containing a little flux. Place the remainder and larger portion of a 100-g scoop of flux (see below) on top of the filter paper, add silver if the assay is for gold alone, and fuse, cupel, and part as in Procedure 57.

The following stock flux has proved satisfactory, although the flour content may need to be varied somewhat to secure a lead button of suitable size:

Sodium carbonate	15 g
Litharge	55 g
Silica	20 g
Borax	8 g
Flour	2 g

Gold and silver are precipitated, and may be determined in the same assay. Assays may be completed in 2 hr and with the reservations mentioned in the first paragraph the results are good for both low and high grade solutions.

Notes—1. The potassium ferrocyanide acts as a coagulant, and as a precipitant for silver. No more than the stated quantity should be added, however, because an excess leads to a loss of gold.

2. The sodium sulphite, an active reducing agent, is added to ensure complete reduction and the precipitation of all the gold.

3. The precipitate consists mainly of copper(I) cyanide; it is white, curdy and insoluble in weak acids.

4. If the precipitate tends to pass through the filter paper, pour a little suspended paper pulp into the latter. This will ensure rapid filtration and minimize the loss of fine precipitate.

In the determination of gold in oxidized tailings or slimes which may contain ferrocyanide, Bettel[261] obtained low values with the copper(II) sulphate–sodium sulphite–sulphuric acid method. This was attributed to the production of auricyanides that resist reduction. In these instances Bettel used a combination of the copper(I) salt and lead acetate–zinc methods, the latter being applied to the filtrate from the copper(I) precipitation.

The modification requires the application of the copper(I) method, with subsequent filtering and washing. The residue is opened up, and litharge is sprinkled over the surface. The filtrate is treated with lead acetate, zinc fume, and hydrochloric acid in sufficient quantities to dissolve the zinc after the lead sponge has been formed. The latter, containing the traces of gold and copper, is filtered off, washed, drained and added to the litharge-covered copper(I) precipitate. The whole is covered with litharge, dried, carefully heated to burn the paper and finally assayed with a suitable flux (see Procedure 57).

The Chiddy Method

This is one of the most widely used of the older procedures, and according to Bugbee[234] it is used almost always in North America for the assay of cyanide solutions. It works equally well on strong or weak, foul or pure solutions, and almost any quantity may be taken. The method was first reported by Chiddy in 1903 in a very short communication, with claims that he originated the method and that it improved on the existing methods.

The procedure has been changed very little during the past half century, although some modifications have been introduced. Wogrinz[262] rejected the method when the cyanide solutions contained ferrocyanide, but the latter, however, could be destroyed by evaporating to a residue and then fuming with sulphuric acid. Wogrinz recommended the addition of lead acetate, zinc dust and then hydrochloric acid until the mixture was strongly acidic. Subsequently, the lead was dissolved and the gold filtered, washed and weighed. Roodhouse[263] also slightly modified the Chiddy method by adding acetic acid to the reduced mixture, followed by boiling, decantation and the addition of hydrochloric acid.

Procedure 65[234]

Heat a solution containing from 1 to 20 assay tons in a beaker or an evaporating dish (Note 1). Add 10 or 20 ml of a 10 per cent lead acetate solution containing 40 ml of acetic acid per l. Then add 1 or 2 g of fine zinc shavings rolled lightly into a ball, or an equivalent amount of zinc dust in the form of an emulsion (Notes 2 and 3). Heat, but not to boiling, until the lead is well precipitated. This usually takes about 15 or 20 min. Then add 10–20 ml of strong hydrochloric acid to dissolve the excess of zinc. Continue heating until effervescence stops (Note 4). It is often found that action ceases while some undissolved zinc still remains. This is entirely covered and thus protected from the acid by the spongy lead. To be sure that all the zinc is dissolved, stroke the sponge with a stirring rod, and drop a little hydrochloric acid from a pipette directly on it.

As soon as the zinc is dissolved (Note 5) decant the solution and wash the sponge two or three times with tap water. Next, moisten the fingers, and press the sponge, which should be all in one piece, into a compact mass (Note 6). Dry by squeezing between pieces of soft filter paper or by placing on a piece of lead foil and rolling with a piece of large glass tubing. Finally, roll into a ball with lead foil, puncture to allow for escape of steam (Note 7), add silver for parting, place in a hot cupel, and proceed according to Procedure 57.

Notes—1. The solution must be clear and free from slime or colloidal matter or the sponge may break up. If not, add a little lime water, boil for a moment to coagulate the slime, and then filter if necessary before beginning the assay.

2. Some assayers bring to boiling after adding the zinc and the lead acetate solution, then decant the solution as completely as possible, after which they add an equal volume of dilute hydrochloric acid to dissolve the excess of zinc.

3. The gold, silver and lead will immediately begin to precipitate on the zinc. At first the solution may become cloudy, but will soon clear as more of the lead is precipitated.

4. When working with small quantities of solution it is best to add water occasionally to maintain the original volume of solution or else the hydrochloric acid will become too concentrated and cause the sponge to disintegrate.

5. Because the lead sponge begins to dissolve and break up as soon as all the zinc is dissolved, no time should be lost in decanting the solution after the zinc has disappeared.

6. In those rare instances where, because of special impurities or for other reasons, the sponge cannot be successfully collected by the above-described method, the solution may be filtered through rapid paper and quickly washed. The filter paper with precipitate is removed and the excess of water squeezed out. It is placed in a small scorifier with lead and borax glass together with silver for parting if gold only is sought. The filter paper is burned off, and the assay finished in the usual way.

7. Some assayers dry the assays before cupelling to avoid the danger of spitting caused by retained moisture.

The Analysis of Cyanide–Gold Plating Solutions

Whereas the problems associated with the determination of gold in mill cyanide solutions are somewhat comparable to those involved with plating solutions, with the former material the degree of contamination is subject to less control. Obviously the classical methods used for mill solutions are, in general, applicable also to plating solutions but are sometimes found to be unsuitable because of their difficulty or length of time. Thus, Kushner[264] recorded a relatively simple gravimetric method for plating solutions. The method proposed by him included the removal of free cyanide by the addition of silver nitrate and the subsequent fuming with sulphuric acid. In the presence of base metals and palladium, etc., the collected precipitate may be treated by an appropriate choice of wet methods to isolate and determine the gold content.

Procedure 66[264]

Use a 10-ml sample containing 0·5–20 g/l. of gold; for lesser contents, use a suitably increased sample. Transfer the sample to a 500-ml Erlenmeyer flask, dilute with 50 ml of water, and add sufficient 0·1 N silver nitrate solution from a burette to combine completely with the free cyanide, as indicated by 5 ml of a 2 per cent solution of potassium iodide. Place the flask in an efficient hood, and add cautiously concentrated sulphuric acid until vigorous action ceases. Add 50 ml more of the sulphuric acid, and boil, avoiding any violent reaction. Discontinue heating when the gold becomes light brown and the acid is quite clear.

Decant the supernatant liquid, treat the precipitate with an additional 50 ml of concentrated sulphuric acid, and boil to dissolve any silver sulphate. Decant the liquid, leaving as little as possible in the flask. Dilute the remaining acid with 200 ml of distilled water, and filter through a porcelain filtering crucible or a suitably prepared Gooch asbestos crucible. Wash the precipitate with hot dilute sulphuric acid and then with hot water to remove all acid. Dry, ignite to yellow gold, and weigh.

Evaporation Methods

With assay lead sheet, 0·005 in. thick, a boat suitable for the treatment of two assay tons of liquid can be made from a section 4 inches square. After the evaporation the folded boat is wrapped in a 2 × 4 in. sheet of lead, the total weight thus providing a button of 25–26 g.

In general two types of evaporation methods have been described. In one, the liquid is evaporated directly in a vessel made of an amount of lead sufficient to provide the optimum button weight for cupellation. In the second, the evaporation is made after admixture with the flux or its constituents. A fusion is then required to produce the lead button. The latter method is recommended only for rich liquids.

These methods provide the most accurate recoveries and may be used for the platinum metals as well as for gold. They are commonly used as the standards whereby one determines the effectiveness of new assay procedures for the noble metals. Whereas they are direct and simple of operation, great care must be taken to avoid losses by volatilization of the noble metals salts or, in the liquid fusion method, losses by the mechanical transference of the dried residues.

To apply the direct evaporation method, non-leaking lead vessels must be prepared; this requires a bit of practice. Furthermore, the noble metal solutions should be made neutral or basic if the acid present may attack the lead sheet. Evaporations should be carried out slowly at about 60°C, and when large volumes are to be treated this may extend overnight. More rapid evaporations will increase the probability of a loss of gold.

Procedure 67. The Direct Cupellation Method

Place the boat and the measured liquid in a good draught oven at 60°C, overnight evaporations being usually sufficient for up to 2 assay tons. Cool the boat, add silver for parting, and fold the vessel carefully to protect the residue. Wrap with the 2 × 4 in. strip of lead, cupel, and part as described in Procedure 57.

For the determination of platinum metals the evaporating solution should contain 20 parts of silver for each one of total platinum metals. The cupelled bead may be treated according to one of Procedures 32–36. If gold only is to be determined the methods of cupellation and parting are described in Procedure 57.

Procedure 68. The Fusion Method

In general a monosilicate flux (e.g. $2Na_2O \cdot SiO_2$) gives a clean button and a homogeneous slag. A bisilicate flux (e.g. $Na_2O \cdot SiO_2$) may also be successful.

Use 100 g of the following mixture:

Anhydrous sodium carbonate	38 g
Borax glass	10 g
Silica	25 g
Calcium oxide	5 g
*Flour	2–3 g

Prepare a cellophane sheet 8 in. × 8 in., and place on this [illegible] to [illegible] of the above flux. Fold the sheet and mixture into a 4-in. porcelain evaporating dish and add a solution containing 0·5 assay ton (for 1 assay ton about 150 g of the flux is recommended). If necessary add a silver salt or solution to give a gold : silver ratio of 1 : 10. Place the dish in a steam cabinet or oven at 60°C, maintaining a good air draught. Allow to stand overnight, then transfer the cellophane and its contents to a mortar, and grind carefully to a powder (alternatively only transfer the contents to the mortar, adding the cellophane separately to the pot.) Add the ground material to an assay ton pot in which has been placed 5 g of the flux, and clean the mortar with the remaining flux. Use this portion as a cover for fluxes which have been salted. Assay for gold as described in Procedure 57.

The Electrolytic Assay of Gold–Cyanide Solutions

This method has the advantages that, compared to other methods, relatively little attention is required during the course of the determination and both small and large volumes of cyanide solution may be analysed. Gold is quantitatively deposited as a bright yellow coating on the lead cathodes which are then folded and cupelled.

Procedure 69[265]

Use as anodes 5/16 in. arc lamp carbons held in place by clamps in the centre of the beaker. Use as cathodes strips of assay lead foil 2·5 × 9 in., with the lower edge notched to encourage the mixing of the solution. Make the battery connection by cutting the upper end of the cathode into a 1-in. strip. The latter is then turned to make the terminal. Connect the two sides of the foil by folding the edges to produce a cylinder 3 in. in diameter.

Add a 10-assay ton sample to a suitable beaker with the cathodes and anodes in place, and electrolyse with a 6-V accumulator source. Following complete deposition, which should require about 4 hr, remove the anodes, disconnect the cathodes and dry them on a hot plate. Fold the cathodes into a compact form with the gold protected within the fold,

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* The cellophane used has a reducing value equivalent to about 1 g of flour.

and cupel with silver added to obtain a gold to silver ratio of 1 : 10. Part with nitric acid as directed in Procedure 57.

Note—For cyanide solutions containing only traces of gold it is advisable to add a small quantity of cyanide solution to accelerate the deposition of the gold. Precautions must be taken against having the carbon anodes in contact with gold solutions in the absence of the current.

Other Methods

A number of methods have been proposed which involve the precipitation of gold from cyanide solutions in the absence of lead, followed by a filtration of the metal, which is then either purified and weighed, dissolved and re-precipitated, added to lead and cupelled or added to a flux and fused.

Fraser[266] added hydrochloric acid to 522·6 ml of a cyanide solution to give an acid reaction with litmus, then 1·25 or 1·5 g of 200-mesh charcoal to reduce the gold and to provide sufficient reducing power to produce a lead button in the subsequent fusion. The suspension was warmed, stirred, and filtered through paper. The latter was burned in an assay crucible and fused with suitable fluxes. Marenkov[267] used nitric acid to isolate gold from cyanide slimes, subsequently dissolving the metal in *aqua regia* and re-precipitating by using hydrazine hydrochloride.

Seath and Beamish[268] used zinc to precipitate collectively the gold tellurium and silver in mill cyanide solutions; the mixture was then dissolved and treated with hydroquinone to remove gold selectively. Shah[269] also used zinc, the excess being removed in a sulphuric acid solution. The gold was purified by nitric acid before weighing. Rochat[270] used aluminium foil to isolate the gold, which was then purified by nitric acid to within 99·5 per cent purity. Cadmium sulphide powder has been used to precipitate gold sulphide from an acidified solution of cyanide electrolyte.[271] The precipitate was then ignited, treated with nitric acid and finally converted to gold at 800–900°C. Wilson[272] provided simple details for the determination of gold in cyanide solutions by precipitation with ferrous sulphate and oxalic acid, after the elimination of hydrogen cyanide by hydrochloric acid.

The Mercury Amalgam Method

The simultaneous precipitation of gold and mercury has been used as an analytical method. In particular Caldwell and Smith[273] treated a cyanide solution with a large excess of ferrous sulphate to form ferrocyanide, then added mercuric chloride solution, magnesium powder and concentrated hydrochloric acid. Presumably there was no loss of gold, even in the presence of large amounts of ferrocyanide. The probability of such losses has been emphasized by assayers[230, 235] who advised only minimum amounts of ferrocyanide to provide a carrier in the copper(I) chloride method described above. Furthermore, Wogrinz[262] rejected the Chiddy method[274] as inapplicable in the presence of ferrocyanide. Caldwell and Smith,[273] however, provided data from their method which indicated recoveries comparable in accuracy to both the copper sulphate and Chiddy methods. The cyanide solutions used for the latter methods contained 20 assay tons as compared to approximately 66–330 assay tons for the proposed method. An objection to the method is concerned with the difficulty of burning the precipitated residue prior to cupellation, because mercury evolved may well carry gold unless extreme care is taken. There are also the acknowledged slightly low recoveries with 10-l. samples of the cyanide solution. The method described below can also be used to recover silver.

Procedure 70[273]

To 2-l. samples (about 67 assay tons) of the cyanide–gold–silver solution add a solution containing ferrous sulphate about ten times the weight of the cyanide in the sample. Add 50 ml of a saturated mercuric chloride solution, 5 g of magnesium powder and 60 ml of concentrated hydrochloric acid, adding the acid in portions to prevent bubbling over. If the volume of sample taken is much greater than the 67 assay tons, double the amount of mercuric chloride, magnesium and acid used. Allow to stand for 6–8 hr or overnight. Siphon off the clear liquid, and transfer the residue from the bottle into a beaker, rinsing out any residual material with small portions of water. Let it settle for a few min, then filter, using a rough quantitative filter paper. As the bulk of the residue is being washed onto the filter paper, sprinkle in about 20 g of granular test lead so that the two will become intimately mixed. Allow to drain and dry.

On a 60-g bone-ash cupel spread a layer of test lead, following the general concave shape of the cupel. Remove as much of the dried residue from the filter paper as is convenient, mash the lumps, and place in the centre of the cupel. With a little lead, cover the residue remaining on the filter paper, wad it up, and place on top of the cupel. Cover the residue with more test lead. The total weight of lead should not be much more than 45 g. Add silver to give a gold : silver ratio of 1 : 10.

Introduce the cupel slowly into the muffle so that the filter paper will be burned and mercury and its salts volatilized. This last-mentioned step must be executed cautiously and requires the close attention of the analytical chemist; otherwise, a too rapid volatilization of the mercurical residue will cause spitting and serious losses, or perhaps the salting of an adjacent cupellation. When the cupel has been placed in the hottest part of the muffle, increase the temperature to nearly 1000°C, and create a reducing atmosphere by putting near the cupel bits of wood, cork or like material. When the lead has "uncovered", as shown by its bright red appearance, cool the muffle to normal cupellation temperatures, and continue to the production of the bead. If gold only is to be determined, part and weigh as in Procedure 57.

Even more accurate results may be obtained by the scorification of the mercury-noble metal collection residue prior to cupellation. It is recommended that the filter paper with the residue be scorified in a 6·25-cm (2·5-in.) scorifier. Place in the bottom of the scorifier a 10-g sheet of lead moulded to the form of the scorifier. This prevents the absorbance of water and subsequent spattering during scorification. Add appropriate amounts of test lead and a little silica–borax glass. The scorification can be continued so as to yield an 18–30-g button, in which instance smaller cupels may be used.

A mercury–gold collection was also used by Lundquist.[275] He treated the cyanide solution with zinc dust and then with mercuric chloride. After warming the solution, hydroxylammonium chloride and ammonia were added, and the excess of zinc was dissolved by hydrochloric acid. The gold amalgam was treated with nitric acid to remove all traces of zinc and mercury, and the gold was then annealed and weighed.

Procedure 71[275]

To the cyanide solution (29·2 ml, containing 1 assay ton) add 300 mg of zinc dust, and mix well for a min. Add 500 mg of mercuric chloride, and heat the mixture on a hot plate. Add 500 mg of hydroxylammonium chloride and 3 ml of concentrated ammonia solution. Boil the mixture for a few min, cool, and acidify with 5 ml of concentrated hydrochloric acid. Boil until the solution is clear. If a flocculent precipitate appears add ammonia until the solution is alkaline to phenolphthalein and then 2–3 ml more. Add a further 500 mg of hydroxylammonium chloride, and boil until the solution is again clear (although mercury droplets will remain). Allow to settle, and decant the clear supernatant liquid. Add 10 ml of hydrochloric acid to the residue, and boil. Dilute to 50 ml, boil for 1 min, stir well, and collect the amalgam in a large globule with a stirring rod. Decant the clear liquid, and repeat the acid treatment of the residue. Then wash the globule several times with water, transfer to a porcelain crucible, and part with nitric acid (1 : 4). Cool and decant the clear liquid. Add 1 ml of concentrated nitric acid, heat, dilute with water, and decant. Repeat this process until the mercury and zinc have been removed. Wash with water, decant, dry anneal and weigh.

CHAPTER 3

GRAVIMETRIC METHODS FOR THE SEVEN NOBLE METALS

THE character of the natural sources of platinum metals and the requirements of the analytical laboratories involved in the determination of these metals have encouraged the development of the more rapid empirical analytical methods and the rejection of the relatively slow, but more accurate, precipitation procedures. Nevertheless, the gravimetric methods not only retain their status as the final arbiter of quantitative composition, but also provide a pool from which refining processes may be improved. Up to the present time, many of the large scale separational methods involve some type of selective precipitation and, of course, in most instances the isolation of each of the platinum metals requires an adoption of some gravimetric method. Although the separational value of precipitation methods will eventually give way to such techniques as ion-exchange separation, it is unlikely in the foreseeable future that either the platinum metals industries or the research analyst will be able to dispense with the good gravimetric methods. It is unfortunate that there are few available methods, either gravimetric or empirical, for the rarer platinum metals, while for palladium the surfeit of analytical methods is so great that even the specialists in this field are quite unable to choose with certainty the most generally useful procedure.

Ruthenium

Because no specific reagent is available for the determination of ruthenium, it is fortunate that this metal, along with osmium, may be isolated easily by the distillation of its volatile tetroxide. Whereas the relative merits of the various distillation processes are treated in Chapter 2, it may be recapitulated here that the most generally used procedures involve (*a*) the treatment of a caustic solution of the metals with chlorine; (*b*) the selective removal of osmium by nitric acid followed by the oxidation of ruthenium by bromate; (*c*) the collective distillation of both metals into a hydrogen peroxide solution by oxidation with perchloric acid, and the subsequent separation of osmium by selective oxidation with hydrogen peroxide. For very small amounts of the metal, a condition almost invariably found in ores and concentrates, the author prefers oxidation by perchloric acid. The use of nitric acid, which must be removed after the separation of osmium, sometimes encourages low values for osmium and ruthenium and introduces a greater number of technical difficulties into the determination of the remaining platinum metals. For each of these distillations, specific collecting liquids have been recommended, and the composition of these determine the treatment prior to precipitation and to a degree control the choice of precipitant.

Whereas caustic solutions are among the most efficient receivers for ruthenium tetroxide, there is the difficulty that almost all of the gravimetric reagents are either applied in acidic media or the preparation for precipitation involves an approach to neutrality from the acidic side.

In addition to the tendency for ruthenium and most other platinum metals to pass through a colloidal stage when one approaches the optimum acidity from the basic side, there is the inconvenience of the accumulating salts in the subsequent precipitation.

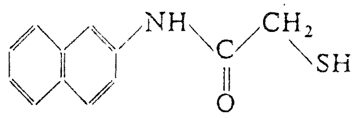
Because of these facts, a receiving solution of hydrochloric acid and sulphur dioxide is frequently used, but in this instance prior evaporation to remove the acid is required. Recently,[99] an aqueous solution of hydrochloric acid, without the addition of a reducing reagent, has been used successfully for μg amounts of ruthenium, but in general this adaptation is inadvisable because the range of metal concentration over which the acid alone can be used has not been determined.

To avoid the necessity of complete evaporation, hydrobromic acid solutions have been used effectively as collectors. In this instance the preparation for precipitation requires only a sufficient evaporation to obtain the required acidity.

Hydrogen peroxide has proved to be a useful collector, requiring little or no evaporation prior to the addition of the reagent. Specific difficulties associated with each of these reagents are discussed in greater detail in Chapter 2.

There exists for ruthenium the usual number of classical precipitants such as hydrogen sulphide, zinc, magnesium, ethanol, etc. In addition to these there are now available procedures for its gravimetric determination by thionalide and by hydrolysis to the hydrated oxide. In all instances the weighing form is the metal, and its preparation involves heating in air and hydrogen.

THIONALIDE



During the development of this method the quantitative recovery of ruthenium was confirmed directly by the examination of the filtrate by distillation and by radioactive tracer techniques.[21] It was concluded that the thionalide precipitation was, under the recommended conditions, complete to less than 1 part in 10,000 on 6 mg of ruthenium. Since that time many hundreds of determinations of ruthenium by thionalide have been made with excellent precision and accuracy by the author's colleagues. Recent literature, however, contains several references indicating that the determination of ruthenium may be attended by low results. These references have their origin in a statement[276] that " with semi-micro quantities the results tend to be low—the maximum error amounting to about 10 per cent." It would seem that this estimate is not based upon experience with the methods, but rather upon an indiscriminate use of values provided in the original publication[96] to indicate the adverse effects of certain dissolved constituents. Obviously the use of such exploratory data should eliminate any significance that may have been given to the above criticism. A second claim for ineffective precipitation by thionalide, however, has also been recorded.[277] In this instance the authors rejected thionalide for the standardization of ruthenium solutions, and stated that " precipitation with thionalide using samples containing about 20 mg of ruthenium gave extremely poor precision resulting from the rather high solubility of the precipitate; ruthenium could always be detected both in the mother liquid and in the solution ". Despite these adverse opinions thionalide is an excellent quantitative reagent, and the precision and accuracy are of a good order when the directions are carefully followed. It is well to realize, however, that thionalide is by no means a specific reagent and, in the presence of many associated metals, ruthenium must first be isolated. It should be emphasized that, as with most methods for the platinum metals, the presence of nitrates and nitroso species provides serious interference. Some of the resulting nitroso compounds have been described by Zvyagintsev.[278]

Quantitative precipitation by thionalide can be accomplished from practically all of the media used for receiving the tetroxide. Distillations in which the absorbing medium is a hot, acid-free solution of thionalide are not satisfactory because of mechanical difficulties. Whereas aqueous solutions of sodium hydroxide may be used, the subsequent preparation for precipitation is lengthy.[96] A collecting medium of hydrogen peroxide is particularly suitable, because by a proper adjustment of the volume and acidity of the absorbent, quantitative precipitation can be accomplished directly without evaporation. One should, of course, filter the solution prior to the precipitation. The ruthenium–thionalide complex does not coagulate well if hydrogen peroxide containing acetanilide as a stabilizer is used, low results always being obtained. In all instances a distillate must be heated to boiling before the addition of thionalide. If this is not done the residual hydrogen peroxide reacts with the precipitant. The product of this reaction is a white unidentified material with a melting range of 178–183°C.

The thionalide–ruthenium precipitate contains one atomic weight of ruthenium to two formula weights of thionalide. All efforts to use the precipitate as a weighing form have failed. There is some evidence to suggest that, although the reagent is soluble in hot water, the required excess is not selectively removed by washing. Alternatively the high results obtained by direct weighing may be due to the presence of a partially decomposed ruthenium(III) complex containing hydroxide. This would agree with the customary trivalency of ruthenium in its complexes.

Procedure 72[96]

To 50 ml of ruthenium chloride solution, containing from 2 to 20 mg of ruthenium, add 0·6 ml of concentrated hydrochloric acid. If the hydrogen peroxide collecting liquid is to be used, wash the latter into a 150-ml beaker, similarly acidify, and then boil to destroy the residual hydrogen peroxide. Weigh out the thionalide in excess of the calculated amount, dissolve in about 3 ml of ethanol, and add to the ruthenium solution by means of a capillary tube. (Note 1).

Boil until the precipitate is well coagulated. (Insufficient boiling results in low values—1 hr should be sufficient.) Filter through a 7-cm Whatman No. 42 paper or an A2 porcelain filtering crucible. In the latter instance, ignite carefully in order to avoid losses by volatilization. If paper is used, place the latter together with the funnel under an infrared lamp to remove excess of moisture prior to folding and transferring to the crucible, a suitable one being the high form, 1·3-ml capacity, 5/0 Coors porcelain crucible. Fold the paper carefully to protect the precipitate, and transfer to the crucible. Place the latter in a muffle, heat slowly from the cold in order to char, and then to ignite the organic matter. In the author's opinion ignition is more effectively controlled with a micro gas burner.

Transfer the crucible (several may be transferred at one time) to a porcelain boat, and place the boat in a Vycor tube, 750 × 25 mm (internal diam.) heated by a suitable tube furnace (Note 2). Allow hydrogen to pass through the cold tube at 2–3 bubbles per sec, as indicated by a water flow meter placed in series at the exit of the tube. Increase the temperature to 600–700°C over about 30 min, and continue the reduction for about 20 min, although a much shorter time is sometimes sufficient. Allow the furnace to cool somewhat, and replace the stream of hydrogen with nitrogen. Cool somewhat, move the tube from the furnace, and place it on a metal sheet to cool, maintaining the nitrogen flow. Cool to room temperature, transfer the crucible to a silver-plated brass block in a constant humidity desiccator for 10 min, place it on a balance pan for 10 min, then weigh it. A suitable humidity may be obtained by adding to the desiccator a saturated solution of calcium nitrate.

Notes—1. It is preferable to filter the enthanolic reagent solution; for a series of determinations a standard reagent solution can be prepared, and suitable aliquots used for precipitation.

2. The split type furnace allows visual observation, and is recommended.

Recently various organic thio compounds have been used for the precipitation of radio-ruthenium.[279] Thioacetamide, thiourea, thiophenol, β-mercaptopropionic acid and 2,3-dimercapto-1-propanol precipitate ruthenium carrier from a 2–3 M nitric or hydrochloric acid solution. The mixture is heated to 90–100°C for 30 min. The average recovery of Ru^{103} and Ru^{106} is 94 per cent.

β-Mercaptopropionic acid and 2,3-dimercapto-1-propanol[280] have also been proposed as precipitants for ruthenium from a nitric acid medium. Whereas these methods can be used effectively to provide a ruthenium carrier, they have not been examined for general gravimetric determinations, and anyway will offer no advantages over thionalide.

HYDROLYTIC PRECIPITATION

The earliest hydrolytic method for ruthenium involved the absorption of ruthenium tetroxide in a dilute solution of potassium hydroxide containing some ethanol, and the precipitation of ruthenium as an oxide by warming on a steam bath. This method encourages the adsorption of the alkali salt, and continued washing of the precipitate is generally ineffective for its complete removal. Although the evolution of these hydrolytic processes has been characterized by many contributions, a good degree of perfection has been reached through the researchers at the National Bureau of Standards. These advances involved the approach to neutralization from the acidic side, and thus more effectively avoided the occlusion of silica and the adsorption of alkali salts. The tendency toward contamination of precipitates formed in nearly neutral solution, however, is apparent here also, and becomes significant for very small amounts of ruthenium. A reduction in the weights and volumes of reagents in proportion to the smaller weight of ruthenium is not always feasible. Thus it would seem that a large proportion of the absolute error associated with the macrodetermination also applies to the microdetermination. The inaccuracies appear to be partly due to the inefficiency of the final leaching process. Where good accuracy is required the method is not recommended for determination of a few mg of ruthenium.

Procedure 73[90] (*Modified*)

Heat to boiling 100 ml of the ruthenium chloride solution containing 200 mg of ruthenium. If ruthenium has been distilled and then collected in a sulphur dioxide-hydrochloric acid solution (Chapter 2), evaporate the acid distillate to a moist residue. Repeat this procedure 3 times with hydrochloric acid, then add 25 ml of water, boil to the complete dissolution of the ruthenium salt, filter, and wash with 0·1 M hydrochloric acid to about 150 ml. Heat the solution to boiling, and add a 10 per cent solution of sodium bicarbonate to the appearance of a precipitate. This addition should be carried out slowly, and it is best accomplished by the use of a capillary tube or by a small bore pipette. Continue the heating and addition of the bicarbonate to a pH of 6. The optimum rate of neutralization is generally achieved only with some experience (Note 1).

Boil the solution at pH 6 to ensure coagulation. Filter the precipitate through an A2 porcelain filtering crucible and wash with 100 ml of a 1 per cent aqueous solution of ammonium chloride. Then add about 50 mg of wet, solid ammonium chloride to prevent decrepitation during the ignition. Slowly remove the ammonium chloride by heating in an atmosphere of hydrogen, and continue the heating in this atmosphere for 20 min. Cool the crucible for 20 min in carbon dioxide, and weigh the residue as metal (Note 2).

Notes—1. Too rapid an addition of the bicarbonate may result in local neutralization or in a final pH greater than 6. In both instances readjustment with an acid solution may result in low recoveries. The pH may be determined instrumentally or by the use of a suitable indicator. A 0·04 per cent solution of bromocresol purple may be used, and it is effectively added from a capillary onto the stirring rod after stirring the hot solution. A convenient rod is made by drawing the standard glass rod to provide a narrow neck, terminated by a knob about the diameter of a pea. A little practice allows an easy detection of the yellow to blue change.

2. The results are persistently a little high, so it is sometimes advisable to wash the metal with hot water before weighing. This leaching process may lessen the positive error, but it does not eliminate it. For the larger amounts of ruthenium, i.e. 50–200 mg, the hydrated ruthenium(III) oxide can be filtered through a 7- or 9-cm Whatman No. 42 filter paper. After its saturation with ammonium chloride, the paper is transferred to a porcelain crucible and charred very slowly, preferably over a bunsen flame. With proper care with the rate of heating, a

thin column of fume can be maintained. Rapid burning will result in decrepitation and mechanical carry-over of some precipitate. After charring, the precipitate is strongly ignited and reduced as described above.

For the larger amounts of ruthenium the hydrolytic precipitation provides very acceptable accuracy, and the precipitate is readily formed, filtered and washed. In the presence of nitric acid the precipitation is not complete, and if the ruthenium solutions have been treated with nitrate or nitrite, care must be taken to remove these completely. This can be accomplished by repeated evaporations with hydrochloric acid.

HYDROGEN SULPHIDE

Although ruthenium is a member of the acid-sulphide group, hydrogen sulphide is not an acceptable gravimetric reagent for this metal. The procedures included in various text-books direct that precipitation be made in a hydrochloric acid medium. The brown ruthenium(III) sulphide precipitates very slowly and incompletely. The application of pressure improves the precipitation, but in the opinion of the author the method is not a good one under any circumstances. Furthermore, the ignition of sulphides and the subsequent reduction to metal seldom provides a sufficiently pure metal.

Recently, a sulphide precipitation method has been recorded[281] that offers promises of useful applications. The procedure involves the addition of a large excess of sodium sulphide to a slightly ammoniacal solution of ruthenium chloride, followed by the addition of acetic acid and ammonium acetate. The precipitate of $Ru_2S_3 \cdot 2H_2O$, purified by successive washings with water, ethanol and ether, and dried *in vacuo*, is weighed directly. The results indicate high accuracy and precision; the errors over the range 18–86 mg of ruthenium were less than 0·1 per cent. An examination of the method by the present author showed that the weight of recovered ruthenium is actually 40–55 per cent. No explanation for these discrepancies in both precision and accuracy has been recorded.[282]

Thus, no sulphide method can be recommended as a gravimetric procedure for ruthenium. On the other hand, the proposed sulphide procedure[281] is potentially a useful separational method. To a degree it has been thus applied.[283]

REDUCTANTS

Ethanol has been used as a reductant of ruthenium tetroxide in alkaline solution. The method has practically nothing to recommend it.

The usual selection of metallic reductants has been proposed for ruthenium. Magnesium and zinc have been most frequently used. The problem presented by these theoretically attractive methods is concerned with the quantitative removal of excess of reductant. Because these metallic reductants are relatively easily attacked by dilute acids, and because ruthenium metal is considered to be inert to mineral acids, it would appear that selective leaching is a very simple purifying process. Some aspects of this technique have been discussed in Chapter 2, but aside from the susceptibility of finely divided platinum metals to attacks by acids, there is the difficulty that at least some of the platinum metals will form alloys with metallic reductants, particularly at ignition temperatures. One aspect of this difficulty is discussed with the zinc precipitation of platinum described in Procedure 103. Although no data have been provided to deal with this phenomenon where it concerns ruthenium, one may expect that the selective dissolution of zinc will introduce difficulties comparable to those found with platinum.

Ayres and Young[277] reject methods involving reduction by zinc or magnesium. Their work indicated that the precipitated ruthenium was in a very fine state that adhered to the beaker wall and contained the reductant metal. Iron as a reductant was also rejected. Even though insufficient data are available concerning the efficiency of metallic reductants, one would expect that magnesium would be relatively efficient. Even though both the hydrolytic and thionalide procedures are to be preferred, the application of reductants can be useful for preliminary separations and special adaptations. Kennedy and Fitzgerald[284] used magnesium to isolate ruthenium from solutions of vegetable matter, and applied radioactive techniques for its determination. Similarly, magnesium was used by Shannon[285] to determine radio-ruthenium gravimetrically in organic matter with a subsequent measurement of β-activity.

Magnesium was used by Pshenitsyn and Fedorov[286] to precipitate the ruthenium in copper–nickel slimes according to the following procedure:

Procedure 74[286]

To 150 ml of the slightly acidic solution containing 25–100 mg of ruthenium add an excess of powdered magnesium. Heat to dissolve the excess of magnesium, but note that prolonged heating in a slightly acidic solution may result in some dissolution of the finely divided ruthenium. Filter through an A2 porcelain filtering crucible, and wash with 0·1 N sulphuric acid, then with water. Dry at about 100°C, ignite in a current of hydrogen, cool in carbon dioxide, and weigh as the metal.

Osmium

In most natural occurrences of the platinum metals osmium forms a small part of the relatively small proportion of the material that is usually termed " the insolubles ". In this residue osmium is sometimes assumed to exist as some type of " iridosmium ". This nomenclature persists despite the fact that very little is known about the chemical or mineralogical properties of iridosmines, and even less is known about the properties of the assumed iridosmines in the " insoluble " encountered during the analysis of platinum ores and concentrates.

It is an astonishing fact that analytical chemistry literature contains no record of the successful application of any procedure for the direct determination of osmium in ores. It is a good guess that those industries concerned with the recovery of osmium in ores do not know their percentage recovery. Extractive processes which involve roasting may well influence adversely the osmium recovery.

Obviously, gravimetric reagents for osmium can find no direct application to the determination of the small amounts to be found in ores. From time to time, however, one is required to ascertain the composition of minerals or concentrates which do contain sufficiently high proportions of osmium. Most fortunately, one may isolate osmium easily from associated metals by the distillation of the tetroxide, and for such distillates gravimetric methods may be useful.

Various standard reducing reagents such as aluminium, hydrazine and formaldehyde have been applied. The most effective gravimetric methods involve precipitation by sodium hydrogen carbonate, strychnine sulphate, thionalide, acridine and 2-phenylbenzothiazole. Hydrogen sulphide and 1,2,3-benzotriazole have also been used as precipitants.

STRYCHNINE SULPHATE, $(C_{21}H_{22}O_2N_2)_2\cdot H_2SO_4$

Whereas many organic reagents have been found to precipitate osmium, none of the precipitates could be used as weighing forms. Because ignition in air is inadmissible, there has been little encouragement to seek quantitative organic precipitants. Strychnine sulphate was used by Ogburn and Miller[287] to quantitatively precipitate a canary-yellow complex that was used as a weighing form; but because the latter was not a pure substance the authors used an experimentally determined correction factor, a subterfuge that is seldom satisfactory and was not so in this instance.

Further work on strychnine as a precipitant was reported by Hoffman *et al.*,[288] who were able to use this reagent for quantitative purposes through their discovery that certain osmium–organic complexes could be ignited. An ignition in hydrogen was made possible through the catalytic influence of the metal in producing volatile organic compounds, presumably methane, etc. The red-brown complex of strychnine and bromo-osmate was produced quantitatively in neutral media, ignited in hydrogen to the metal and weighed as such.

Some controversy has existed concerning the composition of the precipitate and the effectiveness of strychnine as a quantitative reagent. Ogburn and Miller believed that the precipitate contained neither chlorine nor sulphate, and that it was probably composed of one atomic weight of osmium and three formula weight of strychnine. Gilchrist[100] found the precipitation to be incomplete, and stated that complexes formed from ammonium bromosmate and chlorosmate were different, and that the precipitates were probably the strychnine salts of the corresponding halo-osmate anions. The present author's data confirmed both the compositions reported by Gilchrist and Ogburn and Miller's contention that precipitation was complete, but only, however, with the bromosmate solutions. Inexplicably, the latter's value for the osmium content of the strychnine chlorosmate was also confirmed although these authors had reported the absence of halogen in the precipitate.

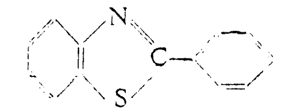
Unfortunately, the method has not been successfully applied to either the chlorosmate or to the osmium distillates in sulphur dioxide–hydrochloric acid solutions. In these media amounts of the order of 0·1–0·2 mg are found in the filtrate.

A further difficulty with the strychnine precipitation is associated with the requirement of a neutral or slightly acidic precipitating medium. Under these conditions associated base metals and some of the platinum metals are simultaneously precipitated. Even though osmium is always isolated before its determination, small amounts of impurities, such as iron derived from reagents or glass-ware, may contaminate precipitates obtained in nearly neutral solutions, and these become significant when mg amounts of precipitate are involved. It is this same difficulty that detracts from the generally useful hydrolytic method described below. In this connection one should bear in mind that among all gravimetric methods only osmium determinations may allow a direct determination of solid impurities in the metal precipitate. With few exceptions osmium may be removed in oxygen as the volatile tetroxide, thus exposing such impurities as iron, silica, etc. The few exceptions are concerned with the unexplained failure to volatilize osmium from certain silica residues, even at red heat.[102] There is evidence that this retention of osmium will vary with the character of the precipitating medium. It is more significant with absorbing liquids of hydrobromic acid than with hydrochloric acid–sulphur dioxide absorbants. As would be expected, however, errors of this type become significant only with mg amounts of precipitate.

Procedure 75[288]

Slowly evaporate the hydrobromic acid absorbing solution, after the distillation of osmium tetroxide, to a small volume. Dilute, filter, and add water to a volume of about 50 ml. Add to this solution a hydrobromic acid solution containing 3–20 mg of osmium (or a solution containing an equivalent amount of ammonium bromosmate) followed by an excess of an aqueous solution of strychnine sulphate, B.P. or U.S.P. grade. The red-brown complex forms immediately. Coagulate by heating on a steam bath for several min. Cool, allow to settle, and filter through a tared A2 porcelain filtering crucible. Transfer the last particles by repeated washing with small amounts of 0·02 M hydrochloric acid. Place the crucible in a clear quartz ignition tube, and allow hydrogen to flow for 5 min. Then ignite slowly over a low flame, and, after the removal of carbon, continue heating for 2 hr with the full heat of a Meker burner. Cool in hydrogen, then in nitrogen, and place the crucible for 10 min in a constant humidity desiccator containing a saturated solution of calcium nitrate, then allow the crucible to stand in the balance case for 20 min. Repeat the ignition in hydrogen to constant weight. Place the crucible in a protected position in a muffle at 750°C for 1 hr. Again ignite in hydrogen, and weigh as described above. Subtract this weight from the initial weight to obtain the blank.

2-PHENYLBENZOTHIAZOLE



By a procedure similar to that described above, 2-phenylbenzothiazole can be used to precipitate an osmium complex from a bromosmate solution, but, as with strychnine, there is an incomplete precipitation with the chloro complex or the sulphur dioxide–hydrochloric acid distillates. The method of ignition is that used for the strychnine complex, but with the thiazole there is a tendency to liquefy during ignition in hydrogen. Possible losses, due to this liquid passing through the porcelain filter, can be eliminated by the use of a small porcelain cap upon which the crucible is placed. The empirical formula for the osmium complex is OsL_2Br_6 (L = reagent). A corresponding chloro complex is also formed.

Procedure 76[288]

Add the weighed sample of ammonium bromosmate, containing from 3–25 mg of osmium, or the filtered hydrobromic acid receiving solution from the distillation of the tetroxide, to a 100-ml beaker. To the former salt add 25 ml of 4 M hydrobromic acid and an excess of 2-phenylbenzothiazole (m.p. 114–115°C) dissolved in 25 ml of 4 M hydrobromic acid. The dark red compound is formed immediately at room temperature. Allow the mixture to settle, and filter through a tared A2 filtering crucible. Transfer the fine particles with a feather or a glass rod drawn to a narrow stem, the end of which is fused to form a small glass globule. Wash with small amounts of 0·2 M hydrochloric acid. Place the crucible on a small porcelain cap, both of which are tared, burn the organic matter in hydrogen, ignite, and weigh as described in Procedure 75. For greater accuracy determine the blank by ignition in air as previously described in Procedure 75.

In a later application of this reagent to the hydrobromic acid distillates obtained from sulphuric acid–hydrogen peroxide oxidations and involving amounts of osmium as low as 2 mg it was found that additions of hydroxylammonium chloride were required to initiate the precipitation that then occurred slowly; about 24 hr were required to ensure quantitative recovery.[53] A modified procedure is therefore recommended for this distillation. In this connection it is well to note again the marked effect of the chemical history of the platinum metal solution on the analytical method.

Procedure 77[53]

Rinse the receivers with 1 : 4 hydrobromic acid into a beaker of suitable size, and add 200 mg of hydroxylammonium chloride. Place on a steam bath for 30 min. Precipitate with excess of reagent. Allow to stand for 45 hr, filter, ignite, and weigh as described in Procedure 75.

THIONALIDE

(For formula, see p. 250.)

This precipitant, whose application to ruthenium is described above, is the most generally applicable of the three organic reagents for osmium. Unlike strychnine and 2-phenylbenzothiazole, thionalide can be used for hydrochloric acid–sulphur dioxide distillates of osmium tetroxide. It is not recommended for hydrogen peroxide–sulphuric acid distillations, however, because the coagulation of the precipitate is incomplete. The cause of this is not known with certainty, and its circumvention would be advantageous. It may be noted that the blank residue from the thionalide precipitation obtained in the final volatilization of osmium may contain magnesium: the latter is present through its use as a reducing reagent for the preparation of thionalide. When thionalide cannot be readily purchased, one may prepare the reagent according to a recipe prepared by the present author.[289] The thionalide complex contains one atomic weight of osmium to three formula weights of thionalide, as opposed to ruthenium, which has one of ruthenium to two of thionalide.

Procedure 78[288]

Add to a 100-ml beaker either a sample of ammonium bromo- or chlorosmate containing 2–30 mg of osmium or the osmium distillate in a hydrobromic or hydrochloric acid–sulphur dioxide solution. If the latter is used the sulphur dioxide must be removed by the usual repeated evaporations with hydrochloric acid. Allow the distillates collected by the sulphur dioxide–hydrochloric acid solutions to stand overnight before evaporating them. Adjust to make the 50 ml of solution 0·5 M in acid (Note 1).

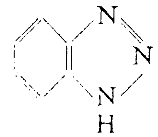
Add an excess of thionalide dissolved in 15 ml of ethanol. The method of this addition will contribute to the success of the determination. Gently boil the solution and initially add the thionalide effectively by means of a capillary tube, or anyway in small drops, over about 30 min. Alternatively, a burette with the tip extending into a hole bored in a borosilicate watch glass is convenient for the slow addition. Boil the contents of the beaker for 2 hr to give a well-coagulated precipitate and a clear supernatant liquid. Heat on a steam bath for another hr, keeping the volume constant by adding water when necessary. Decant the supernatant liquid through an A2 porcelain crucible previously heated in hydrogen to constant weight. Use the technique of filtration, ignition and weighing as described in Procedure 75.

Note—This solution is not filtered prior to precipitation because true blanks may be easily obtained by direct ignition in air of the osmium metal (see Procedure 75).

Comparing the above three reagents, the methods of determining osmium with strychnine sulphate and 2-phenylbenzothiazole present greater ease of operation and require less time than the thionalide method. The thionalide complex, however, coagulates particularly well, and less care need be taken with its ignition. The precipitation of strychnine sulphate has the disadvantage of being made in neutral or slightly acidic media, in which instance certain other trace metals may be simultaneously precipitated as their hydrated oxides. The procedure with 2-phenylbenzothiazole is made in a strongly acidic medium, and hence this difficulty is overcome. It is interesting to note that when osmium is precipitated by 2-phenylbenzothiazole from a weakly acidic solution, a black complex of unknown composition is formed.

It is unfortunate that none of the above three complexes, precipitated as described, are sufficiently pure to serve as weighing forms.

1,2,3-BENZOTRIAZOLE ($C_6H_5N_3$)

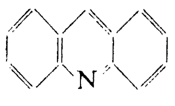


An osmium organic complex recommended as a weighing form was recorded by Wilson and Baye.[290] The method requires precipitation by

1,2,3-benzotriazole from an acetic acid–sodium acetate buffered medium, and involves the precipitation of $Os(OH)_3(C_6H_5N_3)_3$, a beige precipitate: it is washed with hot water and dried for 1 hr at 110°C. The method is applied directly to osmium(VIII) distilled into 0·1 M sodium hydroxide. The results reported by the authors on samples of 2–25 mg indicate excellent precision and accuracy.

Because the above method, as presented, appears to be the most effective of any recorded procedure, the present author has attempted its application under a variety of conditions, including those assigned by the authors. Unfortunately, neither the accuracy nor the precision indicated by the original report has been verified. Indeed, all of the data so far accumulated indicate that, whereas the precipitation is complete, the complex formed is either not a single substance or, more probably, it is admixed with an impurity not amenable to the recommended washing technique. Although the method is not recommended, one may hope that the failures experienced by the author may have resulted from some unacceptable technique.

ACRIDINE



Acetic acid solutions of acridine have been used to precipitate various weighing forms of osmium. Spacu and Gheorghiu[291] precipitated H_2OsCl_6 (acridine)$_2$ and H_2OsBr_6 (acridine)$_2$ from hydrochloric and hydrobromic acid solutions of osmium respectively. The methods are also applicable to hydrochloric acid solutions containing ethanol. The weighing forms are prepared by washing with ethanol, then with ether, and drying in a vacuum. There is no interference from copper, chromium, cobalt or iron for the chloro complex.

A third method produced the weighing form $[OsTu_6][Cr(SCN)_6]$* from hydrochloric or sulphuric acid solutions. A hydrochloric acid solution of thiourea and an excess of a concentrated solution of $K_3[Cr(CNS)_6] \cdot 4H_2O$ were added, and the precipitate was dried at 105°C. The method required a prior distillation to remove impurities. All three methods have been recommended for mg amounts of osmium.

Procedure 79.[291] *Acridine Method*

Add to 10–15 ml of the hydrochloric acid solution containing 0·6–5 mg of osmium, an excess of a 2 per cent acetic acid solution of acridine. Heat the yellow solution for a few min, cool, and filter the brown precipitate through a microfilter crucible. Wash initially with very dilute acetic acid, then with distilled water, then with 95 per cent ethanol and finally with absolute ethanol and ether. Dry for 5–10 min in a vacuum at room temperature, and weigh as H_2OsCl_6(acridine)$_2$.

Note. For $[OsBr_6]^{2-}$, the method of determination is comparable to the above procedure, except that washing is accomplished with acetic acid and water, and the precipitate is dried at 110°C.

The thiocyanate method requires the reagent $K_3[Cr(CNS)_6] \cdot 4H_2O$. Its preparation is included in the following procedure.

Procedure 80.[291] *Thiocyanate Method*

The Preparation of $K_3[Cr(CNS)_6] \cdot 4H_2O$. Mix 15 g of potassium thiocyanate and 12·5 g of chrome alum. The colour changes from violet to pink. Warm at 80°C for 2 hr, then cool to room temperature. Add ethanol to remove the sulphate, filter, and evaporate to incipient crystallization.

Procedure. Add to the hydrochloric or sulphuric acid solution of osmium tetroxide a hydrochloric acid solution of thiourea, and after 15–20 min add an excess of the concentrated chromium thiocyanate reagent. Allow to settle, and filter through an A2 or A porous-bottomed filtering crucible. Wash with water, dry at 105°C, and weigh as $[OsTu_6][Cr(SCN)_6]$.

HYDROLYTIC PRECIPITATION

The characteristics of this method have been discussed in Procedure 73. Emphasis is given here to the necessity of a carefully made initial precipitation, particularly when small amounts of osmium are to be determined. One may experience with the hydrolytic precipitation of osmium a phenomenon that is recognized by analytical chemists of long experience, viz., difficulties incident to inexperience with a method may be overcome with no clear recognition of the nature of the technical improvement. Most assuredly, once accomplished successfully, the hydrolytic precipitation is one of the most satisfactory methods of analysis. There is little doubt that some of these difficulties arise from our ignorance of the identities of the dissolved platinum metals constituents.

As for ruthenium, no method for osmium should be expected to apply to all of the various solution compositions normally obtained during the distillation and collection of osmium tetroxide. The receiving solutions used for osmium are generally those used for ruthenium, and each type requires some variation in technique before the precipitant is added. The hydrochloric acid–sulphur dioxide solution is a useful receiving liquid, but all types of following analytical gravimetric determinations require the removal of sulphur dioxide prior to precipitation. Gilchrist[100] removed sulphur dioxide by evaporation and subsequent boiling with hydrochloric acid. Various authors, however, have obtained low results for osmium by this process; these errors, although small, become significant with mg amounts of osmium. This error has been attributed by some[illegible] to the volatilization

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* Tu = Thiourea.

of osmium during evaporations, but other investigators[103] have found no loss of osmium during evaporations. Anyway it has been found that if the hydrochloric acid–sulphur dioxide distillates are allowed to stand for 12–16 hr at room temperature no loss of osmium occurs when the solution is concentrated by boiling. It is also a fact that while the addition of thiourea to fresh distillates results in the development of the intense rose colour of the osmium–thiourea complex, distillates several hr old give a colour of reduced intensity and distillates 24 hr old may yield no colour.

These observations have received various explanations. It has been suggested that the fresh distillates contain some dissolved osmium tetroxide that is lost when the solutions are heated before the reduction of the tetroxide is complete. Geilmann and Neeb[103] have shown that the evaporation of the sulphur dioxide–hydrochloric receiving solution does not result in loss of osmium. It is not improbable that the change in the thiourea reaction results from changes in the identity of the dissolved osmium complex.

The hydrolytic method described below is recommended for amounts of osmium of the order of 15–50 mg. It is not recommended for a few mg of osmium when high accuracy is required. By an appropriate adjustment of volume and reagents, amounts of osmium as large as 200–300 mg may be similarly determined. It may occur to the analytical chemist that the hydrolytic precipitation, with its relatively great advantage in the favourable physical characteristics of the precipitate, can be applied to even very small weights of metal, despite the significant accumulation of impurities. The application to mg amounts would merely require the determination of a true blank by a final oxidation to remove the osmium as the tetroxide. Some data have been recorded which bear upon this problem.[102] Spectrograms of these residues remaining after volatilization of the osmium revealed the presence of iron, silica and osmium. The oxidation of the residues at high temperature failed to remove the osmium. The treatment of these residues with nitric acid was also ineffective, although fusions with sodium carbonate released the osmium. The fact that osmium is sometimes retained even after ignition scarcely encourages the indiscriminate use of the " true blank " method to achieve improved accuracy.

Procedure 81[102]

To 50–75 ml of the boiling dilute hydrochloric acid solution of the osmium salt or the hydrochloric acid–sulphur dioxide distillate, treated as described above to remove sulphur dioxide, add, initially dropwise, a 10 per cent solution of sodium hydrogen carbonate. After the appearance and coagulation of the hydrated oxide of osmium, continue the addition of the hydrogen carbonate solution to a pH of 4, as indicated by adding a drop of 0·04 per cent bromophenol blue indicator solution to the stirring rod, as described for ruthenium in Procedure 72. Boil to complete coagulation. Add 10 ml of filtered 95 per cent ethanol to assist the coagulation. Place on a steam bath for at least 2 hr. Decant the supernatant liquid through a weighed porous A2 porcelain crucible. Add to the precipitate in the beaker 25 ml of a 1 per cent ammonium chloride solution and 10 ml of 95 per cent ethanol. Return the beaker to the steam bath for 15 min, and then decant as before. Wash the precipitate 4 times with the 1 per cent ammonium chloride solution, transferring each time to the crucible. Complete the transfer of the oxide with the assistance of a filtering feather, wash with a few ml of ethanol, and then cover with recrystallized ammonium chloride. Place the crucible in a quartz ignition tube through which hydrogen is allowed to flow. After 5 min, heat with a Meker burner until the ammonium chloride is volatilized. Ignite at full heat for 1 hr, cool in hydrogen for 5 min and then in nitrogen for 15 min. Place in a desiccator with a saturated solution of calcium nitrate for 10 min, and weigh after standing in the balance case for 20 min. Obtain the blank by igniting the osmium metal in air and repeating the heating and the weighing technique described above.

Table 38 indicates the effectiveness of the determination when it is applied to 5 mg of osmium. Because the blanks are not proportional to the weight of osmium metal, but are dependent largely upon the amount of reagents and the volume used, the accuracy obtained with large samples can be very acceptable.

TABLE 38. HYDROLYTIC DETERMINATIONS OF OSMIUM DISSOLVED IN SULPHUR DIOXIDE–HYDROCHLORIC ACID SOLUTIONS AFTER BEING DISTILLED FROM AMMONIUM BROMOSMATE SOLUTIONS BY NITRIC ACID[102]

Sample No.	Osmium taken (as ammonium bromosmate) (mg)	Total wt. of reduced precipitate (mg)	Wt. of residue after volatilization of osmium tetroxide (mg)	Osmium volatilized (mg)	Difference between osmium taken and volatilized (weight %)
1	4·893	5·441	0·716	4·725	−3·5
2	5·193	5·686	0·594	5·092	−2·0
3	5·051	5·638	0·704	4·934	−2·3
4	4·920	5·306	0·485	4·821	−2·0
5	5·236	6·129	1·372	4·757	−9·2
6	5·321	6·252	1·042	5·210	−2·1
7	5·219	5·791	0·745	5·046	−3·3
8	5·337	6·057	0·986	5·072	−5·0

OTHER ORGANIC REAGENTS

A number of organic reagents offer some promise of gravimetric application for osmium. One may entertain the hope that satisfactory directly weighable osmium complexes will yet be forthcoming. Table 39 records the results of an investigation designed to learn the functional organic group for a gravimetric application.

OTHER METHODS

It is necessary to deal with a seemingly obvious method for the determination of osmium in acid distillates. This procedure involves the evaporation of the volatile absorbent and the subsequent drying and ignition in hydrogen of the collected osmium. The difficulty with this simple procedure concerns the accumulation of the impurities that are not readily removed by selective leaching. Whereas the method may be used for approximate determinations, it has no advantages and is, of course, not recommended for accurate analysis.

TABLE 39. ORGANIC REAGENTS FOR OSMIUM[288]

Reagents	Hydrochloric acid strength of medium 0·05 M	4 M
Substituted thiazoles		
2-Aminobenzothiazole	col	
2-Aminothiazole	col	
6-Amino-2-mercaptobenzothiazole	D	C
2-Amino-4-(*p*-diphenyl)thiazole	B	D
2-Ethylmercaptobenzoxazole		D
2-Hydroxyphenylbenzoxazole	B	
2-Mercaptobenzoxazole	C	D
2-Mercaptobenzothiazole	C	
2-Mercapto-4,5-dimethylthiazole	col	
2-Mercapto-4-phenylthiazole	C	
3-Methylmercaptobenzothiazole		col
6-Nitro-2-mercaptobenzothiazole	B	
2-Phenylbenzothiazole	B	A
Substituted thioureas		
1,3-Diphenylthiourea	C	
Diphenylthiocarbazide	C	
1,3-Di-(*p*-tolyl)thiourea	C	
1-Acetyl-2-thiohydantoin	D	
5-Benzal-2-thiohydantoin	B	
1-Benzoyl-2-thiohydantoin	B	
5-Furfural-2-thiohydantoin	B	
5-(2-Hydroxybenzal)-2-thiohydantoin	B	
Other reagents		
Brucine	A	
p-Nitrophenylazo-1-naphthol	B	
1-Nitroso-2-naphthol	B	
1,10-Phenanthroline	A	
Strychnine sulphate	A	

A, B, C and D refer to the quantities of osmium found in the filtrate, viz., A, nondetectable; B, 20 to 40 μg; C, 40 to 100 μg; D, > 100 μg; col, colour.

A somewhat unusual approach to the determination of osmium is recorded by Musil and Pietsch,[292] who distilled osmium in a stream of oxygen into a previously weighed bulb containing potassium hydroxide. The method may have some value in specific instances where large amounts of osmium are to be determined, but it is not recommended for general use. The difficulties incident to weighing bulbs vitiate the application of the method.

Various standard reducing reagents have been used for osmium. Aluminium,[293] hydrazine[294] and formaldehyde[294] have been applied, but none of these is recommended. Hydrogen sulphide has been used frequently, but it also is an unacceptable reagent.

Rhodium

Rhodium is one of the very minor constituents of platinum metal ores. Its analytical isolation has long been a most difficult process. Although the metal resists attack by the usual acid and oxidizing mixtures, it is dissolved under suitable conditions by sulphuric acid and by fusion with certain acid sulphate salts. It was this property that was applied until very recently to the quantitative isolation of rhodium by a procedure that was laborious and inaccurate.

It is unfortunate that this single aqueous dissolution method should introduce an interference into most of the methods for determining rhodium. This interference is frequently accentuated when the sulphate solutions have been subjected to fuming, a process that is sometimes required for the removal of the associated elements ruthenium and osmium. These facts should be recognized by those researchers who seek to find new reagents for the quantitative determination of the platinum metals, particularly when the extent of interference from associated metals is to be determined.

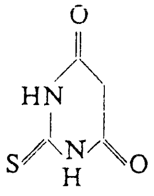
At the present time there are few analytical methods for the determination of rhodium. No gravimetric reagent is specific. In general, these reagents find application to the isolation *en masse* of various groups of associated metals, and are used for the quantitative determination of rhodium only in solutions free of other heavy metal cations.

Limited separations of rhodium may be accomplished by a variety of procedures, however. Certain base metals may be isolated from rhodium by hydrolysis in the presence of nitrite,[143, 144] a method which may become increasingly difficult as the amounts of rhodium relative to the amounts of base metals become smaller. Hydrolysis to the oxide will also separate platinum(IV).[144] Gold may be eliminated by a variety of reducing reagents,[295] and dimethylglyoxime effectively separates palladium. Ruthenium and osmium are usually separated by distillation.

Combinations of iridium and rhodium present the greatest challenge. Selective corrosion by treatment with various acids, acid salts and oxidizing mixtures has, until recently, been the only quantitative method available. This process forms part of long-established wet assay procedures. In some instances its application is futile; in other instances it is laborious and inaccurate. In general, particularly when small amounts of metal are concerned or when good accuracy is required, the process of selective extraction by corrosive reagents should be abandoned. Recently, the accurate separation of μg amounts of rhodium and iridium has been effected by selective reduction,[53, 124] but the reaction products introduce additional difficulties in the subsequent determination of iridium, a problem that is sufficiently onerous in itself. Fortunately, there are now available the processes of separation by chromatography,[190] ion-exchange[126, 129, 174] and solvent extraction.[130] These methods offer the greatest hope for those who must determine accurately the proportions of rhodium and iridium in such complex materials as ores and concentrates.

The reagents used for the quantitative precipitation of rhodium are thiobarbituric acid, 2-mercaptobenzoxazole, thioacetanilide, ammonium p-aminophenyldithiocarbamate, hexammino-cobalt salts, hydrogen sulphide, sodium hydrogen carbonate and reducing reagents such as hydrazine sulphate, formic acid and titanium(III) chloride.

THIOBARBITURIC ACID



Thiobarbituric acid is used successfully to precipitate an impure rhodium complex that requires ignition and reduction to the metallic weighing form. The brown precipitate contains one atomic weight of rhodium and two formula weights of thiobarbituric acid, such a relationship suggesting the unusual valence of two for rhodium. The reagent will similarly precipitate palladium, but whereas copper, nickel and iron do not readily form precipitates under the conditions recommended for the precipitation of rhodium one should not always expect freedom from interference from these metals. Anyway, it is advisable to isolate rhodium. The thiobarbituric acid method produces results comparable in accuracy to determinations using hydrogen sulphide. In both instances the results tend to be a little high when ignitions are not most carefully made. This is a general characteristic of the precipitation of the platinum metals by organic reagents containing sulphur, and these positive errors are not always the result of ineffective ignition.

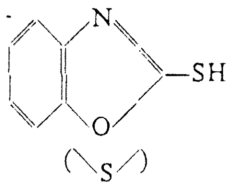
As with the hydrogen sulphide method, the dissolved rhodium constituent should be in the chloride form. Although the reagent has not been used for solutions whose history of preparation includes fuming with sulphuric acid, it is unlikely in these circumstances to be found quantitatively satisfactory. For these solutions the preparation for precipitation outlined for the hydrogen sulphide method, Procedure 87, should be followed.

Frequently, the determination of rhodium is preceded by the destruction of organic matter, and one of the most effective oxidizing reagents for this purpose is a hot mixture of sulphuric and nitric acids. This technique requires some experience when precipitation is adversely affected by small amounts of nitric acid. Even strong fuming sometimes fails to remove the last traces of nitrogen compounds. Intermittent evaporation with water followed by strong fuming is effective, but a more satisfactory procedure involves the oxidation of the organic matter by hot nitric acid containing some 30 per cent hydrogen peroxide solution.

Procedure 82[296]

Add to 200 ml of rhodium solution (in the chloride form) containing 2–25 mg of the metal, 3 ml of hydrochloric acid, 10 ml of a solution of a freshly prepared and filtered 1·4 per cent w/v thiobarbituric acid in 95 per cent ethanol, and heat to boiling. The pink solution of rhodium becomes dark red-brown with a fine red-brown precipitate appearing after 2–3 min boiling. Continue boiling for 2 hr, which should be sufficient for good coagulation. If bumping occurs, add a few cm^2 of ashless paper tablets. Transfer the supernatant liquid to a 7-cm Whatman No. 42 filter paper, wash the precipitate in the beaker with water, allow it to settle, and again transfer the supernatant liquid to the paper. Transfer the precipitate with a fine stream of water, and clean the beaker wall with a small piece of ashless paper moved about by the stirring rod. Place the paper and contents in a porcelain crucible (2-ml crucibles for mg-samples), and ignite at 650–700°C in a muffle. Reduce in hydrogen, cool in the same gas then in nitrogen, and weigh as the metal. The ignition and weighing techniques are as described above for ruthenium in Procedure 72.

2-MERCAPTOBENZOXAZOLE AND 2-MERCAPTOBENZOTHIAZOLE

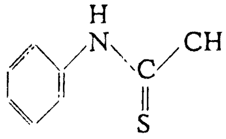


Both 2-mercaptobenzoxazole and the corresponding thiazole were used by Haines and Ryan[297] to precipitate complexes of rhodium from solutions containing ammonium chloride. Complete precipitation in 0·05 M nitric acid occurs with the thiazole but low results are obtained in this medium with the oxazole. The latter forms a complex with rhodium containing three formula weights of precipitant to one atomic weight of rhodium. The accuracy and precision of this method are comparable to that obtained with thiobarbituric acid.

Procedure 83[297]

To the rhodium chloride solution containing 5–20 mg of rhodium, add 5 ml of a 1 per cent aqueous ammonium chloride solution, and make up to about 50 ml with water. Heat to boiling, and add 3–4 ml of the reagent solution containing 1·5 g of 2-mercaptobenzoxazole or 2-mercaptobenzothiazole in 100 ml of glacial acetic acid. Continue the incipient boiling for at least 2 hr, cool, and filter through a 7-cm Whatman No. 42 filter paper. Wash well with 0·1 M acetic acid, ignite in air, reduce in hydrogen, cool in carbon dioxide, and weigh as rhodium metal. The technique of ignition, reduction and weighing is as described in Procedure 72.

THIOACETANILIDE



A number of potentially useful precipitation procedures have been recorded for the separation of rhodium from iridium and the subsequent gravimetric determination of rhodium and/or iridium. These methods involve the reduction of rhodium to the divalent state and the subsequent selective precipitation by the addition of some organic precipitant. The reductants that have been used successfully are chromium(II) chloride, titanium(III) chloride or hypovanadous chloride; the precipitants include a large number of organic thio compounds.

Pollard precipitated rhodium with 2-mercaptobenzothiazole after a reduction with titanium(III) chloride, and then determined iridium in the filtrate. The voluminous rhodium complex precipitate restricted the method to micro amounts, and furthermore the subsequent determination of iridium in the filtrate is an involved process and unsuited to micro amounts.

Jackson[123] preferred to reduce rhodium with chromium(II) chloride and to precipitate rhodium with thioacetanilide. Iridium was determined in the filtrate by a thiourea method (Procedure 91).

The rhodium complex has the composition $Rh(C_6H_5\text{-}NH\cdot CS\cdot CH_3)_4Cl_2$. Precipitation from hydrochloric acid results in contamination by iridium, but a satisfactory separation is accomplished in a solution containing nitric and sulphuric acids together with lithium sulphate that has been taken to fumes and subsequently diluted with water. The ignited and reduced rhodium metal is generally contaminated by a small amount of chromium. This is removed by chlorination and then leaching with *aqua regia*. It is claimed that iron, cobalt and nickel do not precipitate under the prescribed conditions for rhodium, but there is no proof of their non-interference.

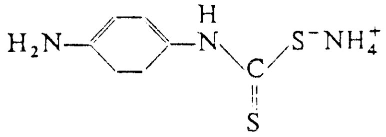
Procedure 84[123]

Evaporate the chloride solution containing about 1–100 mg of rhodium in 10 ml of concentrated nitric acid and 10 ml of the sulphuric acid–lithium sulphate solution (266 g of lithium sulphate in 1 l. of concentrated sulphuric acid warmed to dissolve) until fumes are evolved. Heat strongly, and add 0·5 ml of perchloric acid to ensure complete dissolution. Allow the reaction to subside, and then cool. Dilute, boil, and cool to room temperature.

Dilute to between 200 and 300 ml with cold distilled water and add about 0·5 ml of a filtered thioacetanilide solution (2 g of thioacetanilide in 100 ml of glacial acetic acid) per mg of rhodium present, followed by 2–5 ml of a 1·0 M chromium(II) chloride solution. During this addition stir the solution, and take care to avoid atmospheric oxidation of the chromium(II). Set aside for 2–3 hr, and stir the solution occasionally. Filter the solution through an 11-cm Whatman No. 44 filter paper, wash the rhodium precipitate thoroughly with (1 + 99) hydrochloric acid and set the filtrate aside for the determination of iridium as described in Procedure 91. Ignite the precipitate gently, heat it in a stream of hydrogen, cool, treat with hydrochloric acid in a platinum dish, and evaporate to dryness. Moisten the residue with (1 + 9) hydrochloric acid, filter through a 9-cm Whatman No. 44 filter paper, wash with hot water, ignite, and reduce. Heat to a temperature of 650–700 C in a current of chlorine, cool, treat with (1 + 4) *aqua regia*, and filter through a 9-cm Whatman No. 44 filter paper. Ignite the rhodium precipitate, reduce to metal, and weigh.

Note. The authors provided no direct evidence to indicate that the chlorination will remove the chromium completely, or that the rhodium is unattacked during chlorination. Data have been recorded,[34] to indicate that the chlorination of rhodium sponge at 600–710 C produces both a soluble rhodium tube deposit and a soluble volatile rhodium salt.

AMMONIUM *p*-AMINOPHENYLDITHIOCARBAMATE



This reagent precipitates both rhodium and iridium. The method involves the evaporation to dryness of the rhodium(III) solution containing about 10 mg of the metal in the presence of 1 g or less of sodium chloride.

Procedure 85[298]

Evaporate the hydrochloric acid solution of rhodium, add water to the evaporated residue, and again evaporate. Repeat to the complete absence of hydrochloric acid. Add 10–20 ml of water, heat on a water bath to incipient boiling, and add, with stirring, a 4-fold excess of a freshly prepared 1 per cent aqueous solution of ammonium *p*-aminophenyldithiocarbamate. The final volume should be 50–100 ml. Continue heating on the water bath for 75 min, add an amount of methyl violet (0·002 g/ml) approximately equal to the weight of rhodium expected, and continue heating for 15 min. Cool, filter, and wash free of sodium chloride. Ignite slowly, reduce in hydrogen, cool in carbon dioxide and weigh.

HEXAMMINO-COBALT(III) CHLORIDE

A direct weighing form for the determination of mg amounts of rhodium was reported by Dema and Voicu.[299] Hexammino-cobalt(III) chloride or nitrate with an excess of sodium nitrite, when added to a warm weakly acidic solution of rhodium(III) produces a yellow crystalline precipitate of $[Co(NH_3)_6]^{3+}[Rh(NO_2)_6]^{3-}$ that can be weighed after washing with ethanol and ether and drying in a vacuum. In the presence of iridium the results are 5–10 per cent high. Gold salts are simultaneously reduced to the metal, and cobalt interferes.

There is no interference from palladium, platinum(IV), osmium(IV), iron, copper or nickel.

Procedure 86[299]

Reagents. Sodium nitrite crystals.

A freshly prepared, saturated hexammino-cobalt(III) chloride solution.

Washing solution: Add 0·05–0·1 g of the hexammino-chloride to 5 ml of a 50 per cent sodium nitrite solution and make up to 100 ml with distilled water.

Absolute ethanol.

Absolute diethyl ether.

Procedure. Add to the neutral or weakly acidic solution containing 0·1–1 g of rhodium (III), sodium nitrite crystals in sufficient excess to change the red colour to yellow. Then add dropwise the warm saturated solution of hexammino-cobalt(III) chloride until the colour changes to orange. A fine, yellow, crystalline precipitate is formed immediately. Allow to cool, and filter through a filtering crucible of suitable porosity (1G4) previously weighed to constant weight after washing with ethanol and ether. Wash the precipitate with the prepared washing solution, then with 45 ml of absolute ethanol, and then wash 2 to 4 times with ether. Allow the crucible and precipitate to stand in the vacuum desiccator for 10–15 min, and weigh to constant weight as $[Co(NH_3)_6][Rh(NO_2)_6]$.

Other organic precipitants of potential value for the gravimetric determination of rhodium are 1-nitroso-2-naphthol, 1,2,3-benzotriazole and thionalide.

Precipitation with 1-nitroso-2-naphthol was proposed by Watanabe,[300] who precipitated $Rh(C_{10}H_6NO_2)_3$ at pH 4·85–5·6. A large excess of reagent is required, and upon ignition Rh_2O_3 is said to be formed. It is unlikely, however, that the latter will prove to be a satisfactory weighing form.

1,2,3-Benzotriazole was used by Wilson and Womack[301] to precipitate quantitatively $Rh(C_6H_4N_3)_3 \cdot 3H_2O$ from slightly acidic solutions. Whereas the authors considered the method potentially useful for gravimetric purposes no procedural data were included.

Thionalide was used by Kienitz and Rombock[302] to determine rhodium titrimetrically (Procedure 118), and the reagent was recommended by Duval *et al.*[303] for gravimetric purposes. These authors include thermolysis curves that indicate organic weighing forms for both the thionalide and the 2-mercaptobenzoxazole complexes of rhodium, the former remaining constant in weight between 79 and 250°C. The analytical chemist is cautioned against interpretations such as this in which the sole evidence for weighing forms is a constant composition level. In this instance and in some others, no data are provided to indicate if the rhodium–organic complex can be washed free of the precipitant, etc. In the absence of these data the present author does not accept either of the above organic complexes as weighing forms.

HYDROGEN SULPHIDE

Precipitation by hydrogen sulphide in acidic solutions remains one of the most useful methods for the determination of rhodium. Unfortunately, sulphuric acid interferes. This effect is said to be eliminated by heat treatment with sufficient hydrochloric acid, resulting in the conversion of the yellow sulphate to the pink chloro complex.[192, 304] The efficiency of this commonly

used method has been disputed,[235] however, and a more satisfactory conversion to the pink solution is obtained by fuming to crystals in the presence of sodium chloride or preferably ammonium chloride.[242] Presumably the sulphuric acid reacts with the added chloride providing sufficient hydrochloric acid to accomplish conversions to the chloride. The sodium salt may contaminate the rhodium metal, and for this reason the more volatile ammonium chloride is recommended. Under suitable conditions precipitation by hydrogen sulphide is a highly satisfactory process. The precipitate has very suitable physical characteristics and is easily coagulated and filtered. The rhodium sulphide thus prepared, however, is not easily purified, and the washed precipitate is generally ignited to the oxide and subsequently reduced to the metal.

Procedure 87[242]

If rhodium is present in a sulphuric acid solution, fume the latter to 5 ml. Add 50 ml of a 20 per cent ammonium chloride solution, and evaporate until crystallization takes place. During this treatment the solution should change from yellow to pink. Add 200 ml of water. The solution should now have a pH of 0·9–1·1. If rhodium chloride is the initial dissolved constituent, adjust the volume to 200 ml, and add 0·5 ml of concentrated hydrochloric acid.

Heat to boiling, and while boiling pass in a rapid stream of hydrogen sulphide until the precipitate is well coagulated and the supernatant liquid is clear. Transfer the precipitate to a Whatman No. 42 filter paper of a size appropriate to the weight of the precipitate. Wash with 0·1 N sulphuric acid, then with 0·1 M hydrochloric acid. Remove any adhering particles of sulphide from the beaker wall with a small piece of ashless paper that is then added to the filter. The ignition, reduction and weighing technique are as described for ruthenium (Procedure 72). When porcelain crucibles of the order of 15–20 ml are used, cool in the constant humidity desiccator for 20 min. with the same period of standing in the balance case before the first weighing. Prepare blanks similarly.

Note. The results from the hydrogen sulphide precipitation are generally slightly high; this error can be reduced somewhat by a very slow initial ignition.

Recently a method has been reported using rhodium sulphide as a weighing form. Taimni and Salaria[281] precipitated $Rh_2S_3 \cdot 3H_2S$ from a solution made alkaline with an ammonia solution then treated with a large excess of sodium sulphide. Subsequently, large excesses of acetic acid and ammonium acetate were added, and the mixture was boiled. The precipitate was said to be purified by washing with organic solvents and drying in a vacuum desiccator. The results obtained indicate errors of less than 0·1 per cent for 18–45 mg of rhodium. The various attempts by the present author to apply the method according to the directions recommended resulted in positive errors of 10–20 per cent. Furthermore, no modification of the method succeeded in effectively improving either the accuracy or the precision.

HYDROLYTIC PRECIPITATION

The hydrolytic precipitation of rhodium is often preferred to the sulphide method because, where re-precipitations are required, the oxide is more readily converted to the soluble chloride. The technique of the precipitation is simple, the physical characteristics of the oxide are advantageous, and the subsequent conversion to the metal is not difficult. For the frequently encountered small quantities of rhodium, however, the method encourages significant contamination. The near neutral solution required for the precipitation allows the simultaneous precipitation of a wide variety of impurities whose weight, although perhaps small, becomes significant in relation to a few mg of recovered rhodium. This positive error can, of course, be reduced somewhat by a reduction of the volume of the solution and the quantity of reagent, but this precaution does not always eliminate a high relative error with small weights of rhodium. With metals of this type, being insoluble in mineral acids, the elimination of these contaminants may appear to be a simple problem of selective dissolution of impurities. These leaching processes in general seldom effectively remove the impurity, and sometimes they remove some of the required precipitate. They are last resort processes, and often do not produce significantly improved accuracy or precision with small amounts of rhodium.

Several procedures involving the principle of leaching have been proposed. To determine rhodium in the presence of copper, Moser and Graber[305] precipitated both metals as their sulphides, oxidized then reduced them, and then removed copper with nitric acid. None of these methods is recommended except for approximate determinations.

The existing hydrolytic methods are the products of a large number of techniques. The early methods involved the use of both tervalent and quadrivalent rhodium. Moser and Graber[305] used an oxidizing hydrolysis using potassium bromate and potassium bromide. Reagents such as solutions of sodium hydrogen carbonate in bromine water probably resulted in the precipitation of the hydrated rhodium dioxide.[306] A variety of carbonates would produce rhodium(III) oxide at the favourable pH of about 7.[307] There is evidence to suggest that basic media, in the absence of oxidizing constituents, encourage the formation of rhodium(III) even in the initial presence of quadrivalent rhodium. Anyway, from the analytical point of view, the green, hydrated rhodium dioxide has the more desirable physical properties, and all acceptable modifications of the hydrolytic method involve the use of an oxidant during the neutralization of the rhodium solution. Sodium bromate has become the accepted oxidant, and the technique for its addition and of the method of neutralization are somewhat critical. In the method by Moser and Graber,[305] which uses potassium bromate in a nearly neutral solution containing bromide, the completeness of precipitation could be indicated by the absence of a bromine odour. The following method, a modification of that recorded by Gilchrist,[119] has been used successfully for the determination of 10–25 mg of either rhodium or iridium.

Procedure 88[119]

Heat the 150–200 ml of rhodium chloride solution to boiling, and add 10 ml of a 10 per cent solution of sodium bromate. Add dropwise to the gently boiling solution a filtered 10 per cent solution of sodium hydrogen carbonate until the pH is about 6, as indicated by bromocresol purple applied as an external indicator. This technique can be managed by dipping a slender stirring rod, drawn to a small glass bulb, into the solution to obtain a drop of the precipitating medium, then adding to this drop by means of a capillary a drop of the indicator. The colour change can be observed easily around the glass bulb. Alternatively, if a pH meter is used, cool the solution before immersing the electrodes (Note 1). At about pH 6 add another 5 ml of the bromate solution, and boil for 5 min while the dark suspension is coagulating. If necessary add the required amount of sodium hydrogen carbonate solution to reach a pH of about 7·5 as indicated by a pH meter or by using cresol red as an external indicator added to the stirring rod.

Filter hot through a 7-cm Whatman No. 42 paper, and wash with 200 ml of a 1 per cent ammonium chloride solution. Unless this washing is thoroughly carried out, the results will be excessively high and inconsistent. Clean the beaker with one or two small pieces of filter paper; use a third small piece of paper to clean the funnel area adjacent to the upper rim of the filter paper, because there is some tendency for the dioxide to creep (Note 2).

Notes—1. With considerable experience the operator should be able to arrive at the required end-point through the physical appearance of the green rhodium dioxide assisted by the odour of bromine that is evolved as the solution becomes basic. Anyway, the optimum pH lies between 6 and 8. Thus 2 or 3 ml excess of the bicarbonate solution seems to have no adverse effects such as peptizing the precipitate.

2. Tear the three scraps of paper from the same filter paper to maintain a consistent blank. This method of cleaning is preferred to the use of the feather.

For the determination of small amounts of rhodium that have been isolated from a lead button and thus contaminated with boron, silica, aluminium, etc., the modified hydrolytic procedure described for iridium in Procedure 90 may also be used for rhodium.

REDUCTANTS

Few of the reductants for rhodium have been used gravimetrically. In general these procedures are only designed to accomplish the isolation of rhodium prior to a determination.

For gravimetric purposes hydrazine sulphate or hydrate was used by Gutbier and von Muller,[308] and various text-books record procedures for the reduction by formic acid and the subsequent purification by leaching the ignited residue with *aqua regia*. Treatments such as the latter are often ineffective and are not recommended for accurate analytical work.

Reductions by zinc or magnesium formed a part of many of the earlier procedures for the analytical treatment of assay beads or buttons. Brief procedures for the application of these metallic reductants to solutions of rhodium are described by Scott.[304] There are no data, however, known to the present author, that describe the accuracy and precision of these reduction methods. Factors which militate against efficient recoveries are the tendency toward redissolution of rhodium in the absence of excess of reductant and, with an excess of metallic reductant, the inevitable contamination. Removal of the latter by the usual process of selective dissolution by the addition of excess of acid may be ineffective because of the susceptibility of finely divided rhodium to acidic oxidants.

Titanium(III) chloride has been used for the separation of rhodium from iridium, followed by a precipitation of rhodium sulphide.[119] In a similar way chromium(II) chloride[125] will separate rhodium from iridium. Of these two separation methods the present author prefers the titanium(III) reduction because the chromium(II) salt is particularly sensitive to air oxidation. It is not improbable, however, that the excess of chromium(II) salt in a filtrate containing iridium will be more readily removed than titanium by cation-exchange.

Antimony as a Reductant

For the precipitation of μg amounts of rhodium and the separation of the latter from iridium, selective reduction by finely dispersed antimony powder gives an accurately quantitative recovery.[124] Iridium is merely reduced to the tervalent state. Either sulphuric or hydrochloric acid solutions may be used. Antimony in the filtrate can be separated from iridium by the distillation of antimony from fuming sulphuric acid. This reduction method, however, has been proven only for quantities of rhodium and iridium below the range to which gravimetric methods should be applied. The details are described in Procedure 11.

Copper as a Reductant

Finely divided copper can be used for the quantitative collection of rhodium metal from solutions containing either μg or mg amounts of metal. Although an upper limit of concentration has not been determined one may expect applications of the method to gramme quantities of rhodium. The method was devised[122] to provide a simultaneous separation from iridium. The removal of excess of copper salt from the iridium solution is readily accomplished by ion-exchange, because copper is present as the cation and iridium as an anionic complex. The method of separation is described in Procedure 8.

Iridium

The analytical difficulties associated with the determination of rhodium apply also to iridium. In addition there is the fact that, unless it is very finely divided, iridium is inert to all mineral acids or mixtures of these acids. The susceptibility to attack of very finely divided iridium by concentrated mixtures of hydrochloric and nitric acids has been grossly misapplied. For example, procedures that involve the quantitative dissolution of iridium contained in silver bead residues by the addition of strong *aqua regia* are quite unacceptable.[236]

Conversion of the metal or its oxides to soluble iridium salts may be accomplished by a variety of procedures: molten fluxes containing sodium

peroxide may be used, with the relative disadvantage that crucible material and relatively high proportions of salt are added to the solution of iridium. The inactivity of iridium is well illustrated by the very useful procedure[198] for its determination in the presence of platinum by fluxing to form a lead button and subsequently recovering the iridium by the selective dissolution of lead by nitric acid and of platinum by *aqua regia* (see Procedure 38).

A further difficulty in the gravimetric determination of iridium is associated with the loss of iridium metal when it is heated in air. The chemical literature fails to suggest the fact that such losses may be a source of considerable error, particularly with micro quantities of metal. In this connection the following study was made by the author[34] to determine the significance of these weight losses.

A set of crucibles was selected whose weights proved to be constant over the range of conditions tested. Reduction residues from the hydrolytic determination of iridium were heated at 650–675°C in the crucibles for 4 hr without appreciable decreases in weight. Above 800°C, however, significant losses occurred, as indicated in Table 40. The ignitions were made in a muffle furnace, with the door slightly ajar to admit air, and the residues were reduced in hydrogen before each weighing.

TABLE 40. IRIDIUM LOSSES ON HEATING IN AIR[34]

		1		2		3		4	
Time (hr)	Temp. (°C)	Sample wt. (mg)	Wt. loss* (mg)	Sample wt. (mg)	Wt. loss* (mg)	Sample wt. (mg)	Wt. loss* (mg)	Sample wt. (mg)	Wt. loss* (mg)
0	—	12·310	—	13·124	—	16·283	—	15·864	—
1·5	800–925	11·883	0·427	12·929	0·195	16·087	0·196	15·681	0·183
1·0	850–950	11·689	0·194	12·774	0·155	15·981	0·106	15·525	0·156
1·0	850–950	11·504	0·185	12·625	0·149	15·833	0·148	15·405	0·120
1·0	850–950	11·316	0·188	12·462	0·163	15·698	0·185	15·308	0·097

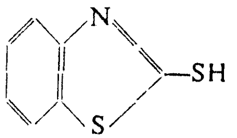
* Loss in weight after each ignition.

It was concluded that excessively high temperatures during ignition must be avoided in the gravimetric microdetermination of iridium. Temperatures below 650°C may be used safely for the usual periods of heating.

During the ignition in air, the iridium always changed from grey to black and increased in weight. If one attributed this gain to combination with oxygen, the composition of the black material corresponded approximately to the formula Ir_2O_3. The composition of the oxide resulting from the air oxidation of iridium is usually accepted as IrO_2. The explanation for the losses of iridium when heated in oxygen is discussed in Chapter 1, and is attributed to the formation of IrO_3 above 1000°C.

As for rhodium, there are few suitable gravimetric reagents, and none is specific. Those which merit attention are: 2-mercaptobenzothiazole, sodium hydrogen carbonate, thiourea, *p*-aminophenyldithiocarbamate and tetraphenylarsonium chloride.

2-MERCAPTOBENZOTHIAZOLE[197]



Although a number of organic reagents will form precipitates with iridium none of the resulting complexes is recommended as a weighing form and only one has been used for quantitative purposes.

2-Mercaptobenzothiazole forms a bulky orange precipitate from solutions containing acetic acid and ammonium acetate. A 15-hr digestion period is required for its precipitation, and high concentrations of mineral acids must be avoided; their optimum concentration is 0·005–0·01 M. The method is suitable for small amounts of iridium, but amounts in excess of about 20 mg produce unmanageable quantities of precipitate. With these large quantities the hydrolytic precipitation described later is advantageous.

Procedure 89[197]

To a 5-ml sample of a sodium chloroiridate solution containing approximately 1 mg of iridium per ml add 10 ml of glacial acetic acid, 1 ml of a 20 per cent ammonium acetate solution and 25 ml of water. Heat to incipient boiling, and add 10 ml of a freshly prepared 1 per cent solution of 2-mercaptobenzothiazole in 95 per cent ethanol, together with 2 small glass beads to minimize bumping. (The precipitant is purified by crystallization from ethanol and has a m.p. of 180·5–181·0°C.) Boil the mixture vigorously for 1 hr, during which time the iridium separates as a bulky orange precipitate. At the end of the hr (or before if the volume of the liquid becomes less than 20 ml) wash the cover glass and beaker wall with a hot solution that is 2 per cent in ammonium acetate and 2 per cent in acetic acid. The final volume of the liquid should be 50–70 ml.

Allow the mixture to stand at least 24 hr on a steam bath, filter through a 7-cm Whatman No. 42 filter paper, and wash with 100 ml or more of the hot solution that is 2 per cent in ammonium acetate and 2 per cent in acetic acid. Partially dry the paper (a heat lamp is suitable), and transfer to a tared crucible. Char the paper in a muffle at 350°C, heat for 45 min at 650–700°C, cool, reduce in hydrogen, cool in nitrogen, and weigh. An increase in precision is obtained by cooling in a desiccator containing saturated calcium nitrate. Determine a blank with the full procedure. This should not exceed 0·1–0·2 mg.

During the analytical recovery of iridium from natural sources by fire assay, etc., appreciable amounts of impurities such as silica, aluminium, boron, etc. may be introduced. Under these circumstances the following procedure is recommended.

Procedure 90

After the preparation of an iridium solution as the effluent from an cation-exchanger (see Procedure 8), evaporate to dryness. To eliminate boron, add a few drops of hydrochloric acid and 10 ml of pure methanol, and evaporate slowly to dryness. Add a few drops of strong hydrochloric acid and 50 ml of water. Precipitate hydrolytically as described for rhodium in Procedure 88 (Note 1).

Filter the hydrated iridium dioxide onto a 2-ml filter crucible, ignite and reduce as described for rhodium. Chlorinate at 700°C, dissolve the residue in the crucible and in the tube with about 100 ml of 0·1 M hydrochloric acid, and filter. Evaporate the filtrate to dryness, add 5 ml of water, then 2 ml of a solution containing 70 mg of tartaric acid, and proceed as described for 2-mercaptobenzothiazole (Procedure 89) (Note 2).

Notes—1. Precipitation at this stage by 2-mercaptobenzothiazole has been found to be incomplete. The hydrolytic precipitation is made here only as an intermediate step because the accumulated blank may amount to 5 mg or more. Here, particularly, some difficulty may be experienced in achieving a good hydrolytic precipitation.

2. After a fire assay separation, the silica, boron and aluminium are derived from an admixture of slag in the collection button.

TABLE 41. THE DETERMINATION OF IRIDIUM IN THE PRESENCE OF LEAD WITH 2-MERCAPTOBENZOTHIAZOLE[197]

Set No.	Iridium taken (mg)	Lead taken (mg)	No. of detns.	Average iridium recovery (mg)	Average deviation (mg)	Error of average (%)	Test of filtrates
1	5·02	—	4	5·02	−0·01	—	No colour
2	10·03	—	3	10·03	−0·01	—	No colour
3	15·05	—	4	15·03	−0·01	−0·1	No colour
4	20·06	—	2	20·05	—	—	No colour
5	25·08	—	1	25·04	—	−0·2	Faint colour
6	—	1	.	−0·01	—	—	
7	4·95	—	2	4·95	—	—	No colour
8	4·95	1	3	4·98	−0·02	+0·6	Faint colour
9	4·95	2	2	4·96	—	+0·2	No colour
10	4·95	3	4	4·93	−0·02	−0·4	
11	4·95	7	3	4·95	−0·04	—	Faint colour

Because the analytical recovery of iridium frequently involves an association with lead it should be noted that the 2-mercaptobenzothiazole method can be applied in the presence of limited amounts of lead. The efficiency with which this precipitation is accomplished is indicated by Table 41. The details of the separation are given in Procedures 89 and 90.

HYDROLYTIC PRECIPITATION[119, 34]

For general applications no procedure for the gravimetric precipitation of iridium is comparable to the hydrolytic method. The most effective modification of this method involves an oxidation to iridium(IV) and a carefully regulated adjustment to pH 6 to form the hydrated iridum dioxide. The latter is then converted to the metallic weighing form by conventional methods. As for other platinum metals, the method, when applied to very small amounts of metal, produces high values that, as one would expect, are only partially corrected by any direct leaching process. The procedure for the hydrolytic precipitation of iridium is identical to that described above for rhodium (Procedure 88). Table No. 42 indicates the accuracy that can be attained with mg samples of iridium.

TABLE 42. THE HYDROLYTIC PRECIPITATION OF IRIDIUM[197]

Sample No.	Metal taken, as sodium chloroiridate (mg)	Metal recovered (mg)	Test of filtrates
A1	10·07	10·29	No colour
A2		10·28	No colour
A3		10·26	No colour
B1	2·48	2·50	No colour
B2		2·51	Trace
B3	4·96	5·00	No colour
B4		5·00	No colour

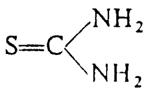
HYDROGEN SULPHIDE

For accurate quantitative work hydrogen sulphide is not recommended. It is generally recognized that complete precipitation is difficult to attain. In this connection it must be admitted that there is no unanimity of opinion, and some analytical chemists do use this precipitation method. Various methods of overcoming the resistance to the complete conversion to sulphide have been advocated. Of these the use of pressure and repeated treatments with hydrogen sulphide are frequently recommended. The present author has yet to succeed in obtaining quantitative sulphide precipitation by any of the procedures recorded prior to 1959. This is an experience very much at variance with the recently recorded statement that "the most reliable method for the estimation of iridium depends upon its precipitation as sulphide from a hot solution containing 20 per cent hydrochloric acid by volume".[281] This proposed sulphide method involves the precipitation of $Ir_2S_3 \cdot 10H_2O$ obtained by the addition of a large excess of sodium or ammonium sulphide followed by similar excesses of acetic acid and ammonium acetate. Purification is carried out by washing successively with aqueous ethanol and ether and drying *in vacuo*.

Whereas the data reported for the method showed errors of less than 0·5 per cent over the range of 1–38 mg of iridium, the present author found positive errors of 6–14 per cent. Taimni and Salaria claimed that the iridium sulphide ($Ir_2S_3 \cdot 10H_2O$) so obtained was stable up to 85°C. A thermogravimetric study by Duval *et al.*[309] failed to reveal the above compound or any other weighing form of iridium sulphide.

The recognition of difficulties inherent in the quantitative precipitation of iridium by hydrogen sulphide has resulted in the use of sulphide precipitants other than H_2S. Gagliardi and Pietsch[310] used thioformamide, and claimed that with this reagent the platinum metals are precipitated in the order: Pd, Ru, Pt, Rh, Os, Ir. Presumably one may thus separate palladium from iridium, etc. These methods have little to recommend them.

THIOUREA



Pshenitsyn and Prokof'eva[311] used thiourea in a sulphuric acid solution of the platinum metals to precipitate sulphides at elevated temperatures. The authors recorded procedures and stated that there were no interferences from copper, lead or low concentrations of iron and nickel. Thiourea was also used by Jackson[123] to precipitate iridium after the thioacetanilide separation of rhodium. This method produced acceptable results for 0·5–100 mg of iridium. For very small amounts of iridium the latter is determined titrimetrically. In general, both rhodium and iridium should be isolated from associated base and noble metals. The method is capable of useful extensions.

Procedure 91[123]

Add 25 ml each of concentrated nitric and sulphuric acids to the solution of iridium containing the thioacetanilide used for the rhodium precipitation (see Procedure 84). Heat on a hot plate to 250°C (indicated by a 360°C-thermometer in the solution), and without delay oxidize by adding a few drops of concentrated nitric acid and then perchloric acid. When the reaction has subsided, add 2–4 g of thiourea, and remove from the hot plate when the iridium sulphide has flocculated (after a few sec). Cool, dilute to 250 ml, and separate the precipitate on an 11-cm Whatman No. 41 filter paper. If there is no evidence of any iridium sulphide, dilute, boil (as it is precipitated, sulphur collects any small amounts of iridium sulphide), and then filter the solution. Wash the precipitate thoroughly with hot water, and ignite carefully.

Treat with hydrofluoric acid in a platinum dish, and evaporate to dryness. Moisten with dilute hydrochloric acid, and wash the residue into a small beaker. Add an equal amount of concentrated hydrochloric acid, and boil. Filter the solution through a 9-cm Whatman No. 44 paper, ignite the precipitate, reduce to metal, and weigh.

When the amount of iridium sulphide is extremely small, return the thiourea precipitate to the beaker, and decompose it with 20 ml of concentrated nitric acid and 2–3 ml of a sulphuric acid–lithium sulphate solution (see Procedure 84). Evaporate until fumes are evolved, oxidize any remaining carbon with nitric acid then finally with perchloric acid.