ASSAY PRACTICE ON THE WITWATERSRAND

PART I

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William L. Weiss

FOREWORD

In the development of any sphere of mining activity the assayer has always contributed, unobtrusively but in no mean measure, a most important share. The fact is true in the phenomenal growth of the Witwatersrand Gold Mining Industry. The determinations of the assayer, made in keeping with the accuracy established by continuous progress in the technical sciences regarding improved technique and modernisation of equipment, have undoubtedly provided, not only a measure of productive efficiency, but also the basis upon which important decisions are made and new expansive ventures undertaken.

This publication, therefore, which has been arranged and edited by members of the South African Association of Assayers, has come at an opportune moment, particularly in view of present-day rapid development of the Industry both on the Witwatersrand and in the Orange Free State.

Combining technical ability and experience the authors have provided a concise and comprehensive guide to present-day methods of assaying, which are in general use on the Witwatersrand. These methods are not confined to the determination of the value of ores and metallurgical products, but include all those phases of physical and analytical chemistry, which are so necessary for the technical control of every-day operations on a mine. As a result, much useful information is made available to all adherents to the vocation, both locally and elsewhere in the mining world. To students and juniors embarking on assaying as a career the work should prove of inestimable value.

It affords me great pleasure to extend to the Authors, on behalf of the Transvaal Chamber of Mines and on my own behalf, congratulations on a notable achievement.

S. R. FLEISCHER,

President (1951-52)
Transvaal Chamber of Mines.

PREFACE

In assaying, as in all other branches of science, the occurrence of new problems and the development of improved methods and equipment, lead to changes in practice and to improvements in technical skill.

For these reasons the Council of the South African Association of Assayers decided to revise its first text book *Rand Assay Practice*. As this meant that large sections of the book had to be re-written, it was agreed that the name should be altered and at the suggestion of the Transvaal and Orange Free State Chamber of Mines, whose generous financial assistance made this publication possible, the name *Assay Practice on the Witwatersrand* was adopted.

The object of the book is twofold. Firstly to provide a text book for student assayers which will completely cover the syllabus for the assay section of the Assayer's Certificate of Competency; and secondly to give practising assayers a handbook which covers most of the work they may be called upon to perform.

Where possible, references have been included but a really comprehensive reference is impossible as most of the methods used in gold assaying have developed over a period of many years to suit local conditions and very often their origin is lost in antiquity.

The Authors wish to thank the Managements of the Mines concerned, Professor L. Taverner, Director of the Government Metallurgical Laboratory, and Dr. Naude and Dr. Roux of the Council for Scientific and Industrial Research for permission to publish various data and illustrations.

They also wish to thank Dr. D. J. Simpson of the Geological Survey, Dr. S. J. du Toit of the National Physical Laboratory and Mr. C. A. Cousins of the Johannesburg Consolidated Investment Corporation who supplied information on techniques at present being used and who read and criticised Chapter XXIII before it reached its final form.

They also wish to acknowledge their indebtedness to the Metallurgical Committee of the Transvaal and Orange Free State Chamber of Mines for its assistance in producing this book.

V.S.D.

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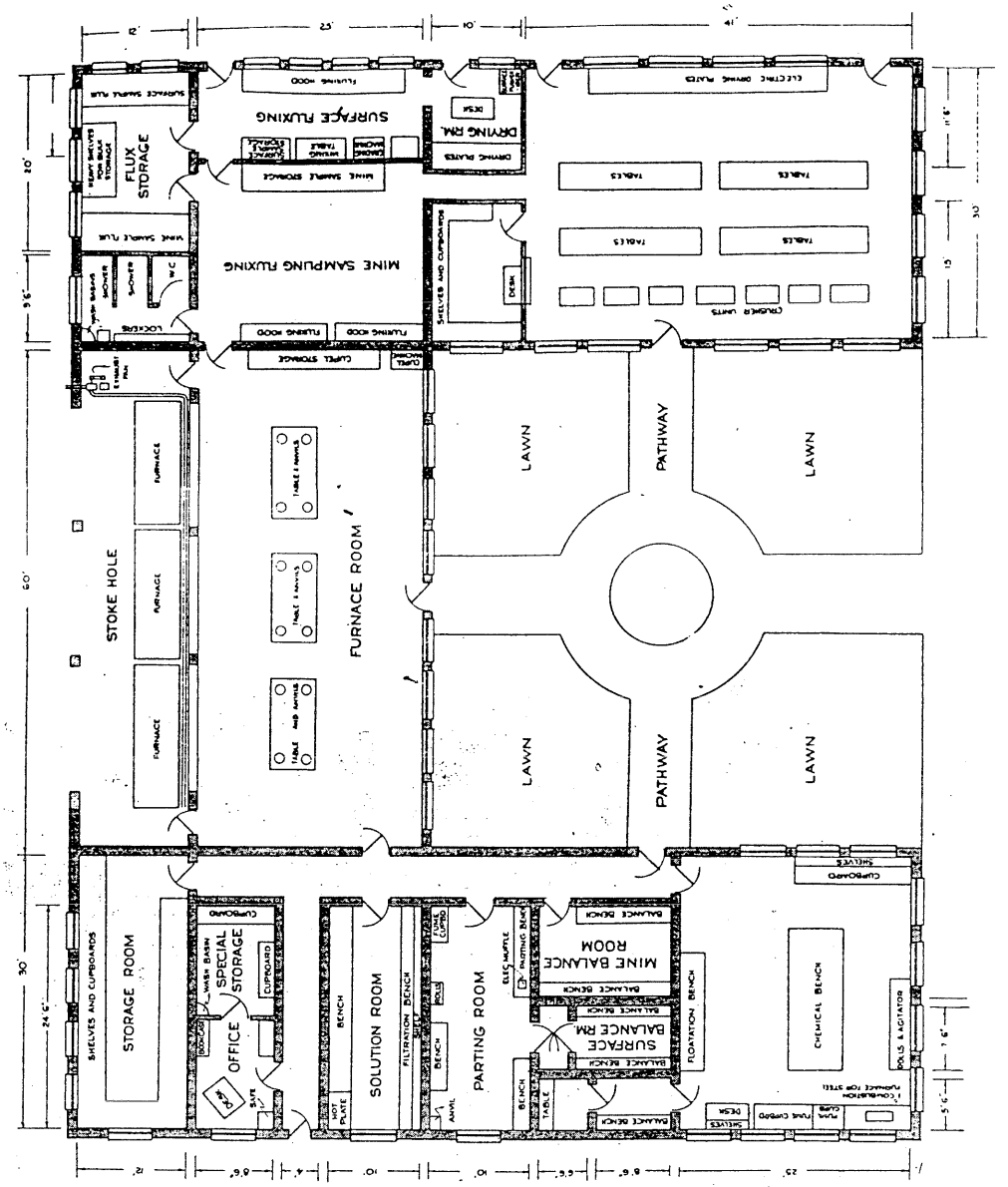
SURFACE FLUXING
DRYING RM.
FLUX STORAGE
MINE SAMPLING FLUXING
TABLES
LAWN
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FURNACE ROOM
LAWN
PATHWAY
LAWN
STORAGE ROOM
SPECIAL STORAGE
OFFICE
SOLUTION ROOM
PARTING ROOM
MINE BALANCE ROOM
SURFACE BALANCE RM.
CHEMICAL BENCH

CHAPTER I.

ASSAY OFFICE DESIGN.

The design of the building plays an important part in the easy handling of the large number of samples which are treated daily in a Rand assay office.

As with any organization which relies on mass production methods, a system should be devised which permits an uninterrupted flow of work from one section to another.

The main considerations underlying the accompanying ground plan of an assay office are to allow for such a flow of work and, in addition, to provide separate rooms for carrying out work which, for reasons of accuracy, prudence or health, should be performed under conditions of isolation.

It will be noted that the furnaces are arranged so that the stoke-holes may be outside the building.

This being accomplished, the other necessary equipment, such as slag and button anvils, tables, etc., may be placed as desired.

On one side of the furnace room and with access to it are the rooms for receiving, drying, crushing, weighing up and "fluxing" of the samples from the reduction works and underground.

It is necessary to ensure that the risk of contamination of surface samples, particularly residues, should be entirely obviated and this can be effected by eliminating all possibility of contact with the richer samples from underground.

In addition to these rooms it will be noted that provision is made for adjacent rooms for storage, drying and also for flux-mixing in bulk.

The balance room, laboratory and office are separated from the furnace room by means of a passage which serves the purpose of excluding, as far as possible, the dust, heat and fumes generated in the other portion of the building.

In the Southern Hemisphere, the balance room should have a southern aspect, light and ventilation being afforded by means of windows placed sufficiently high to prevent disturbing reflections being seen in the glass of the balance cases. This room should not be subject to vibration from any source.

The laboratory, for preference, should be lined with glazed tiles or built of glazed brick and a portion should be partitioned off for coal and air analysis.

The actual equipment of the assay office and the laboratory is described later on in this book.

The building described herein would be suitable for assaying up to 2,000 fusions per day and could be modified as circumstances direct.

Chapter II.

THE CRUSHER HOUSE.

The size of the assay office crusher house must depend on the number of samples which is sent in for assay. In designing the crusher house, however, due consideration should be given to the fact that speedy and efficient handling of the work is essential.

The crusher house should be provided with ample sorting, crushing and quartering equipment and should be spacious, effectively ventilated and well lit. The health of the worker is of paramount importance and an efficient installation for the removal of injurious dust is necessary.

Crusher House Machinery and Lay-out.

In order to facilitate the flow of work in the assay crusher house and to reduce handling to a minimum, the general lay-out of machinery and other installations should be in the following order:—

1. Sorting Tables.
2. Preliminary crushers.
3. Intermediate crushers.
4. Sample dividers.
5. Pulverizers.

Sorting Tables.

Crusher sorting tables can be fixed or movable, and may be built of brick piers with cement tops, or made in the form of sturdy wooden benches, preferably steel-topped to prevent wear. They should be fitted with hoods or cowls connected to the exhaust system for the removal of dust.

Where the transfer of sample to dish takes place outside the crusher house, it is usual to place the sorting tables near windows or hatches through which the dishes may be passed.

Preliminary Crushers.

Several types of jaw crushers suitable for the primary reduction of mine ore samples are available. The work required of these machines calls for robust construction and simplicity of design. The preliminary crushers should be installed close to the sorting tables to obviate unnecessary transport of samples.

Intermediate Crushers.

The types of intermediate crushers generally used on the Witwatersrand are the "Hush", the "Sturtevant" and the "Capelite" jaw crushers. All these crushers are strongly made and are simple in design.

The "Hush" crusher is a small machine and is generally used in conjunction with primary crushers.

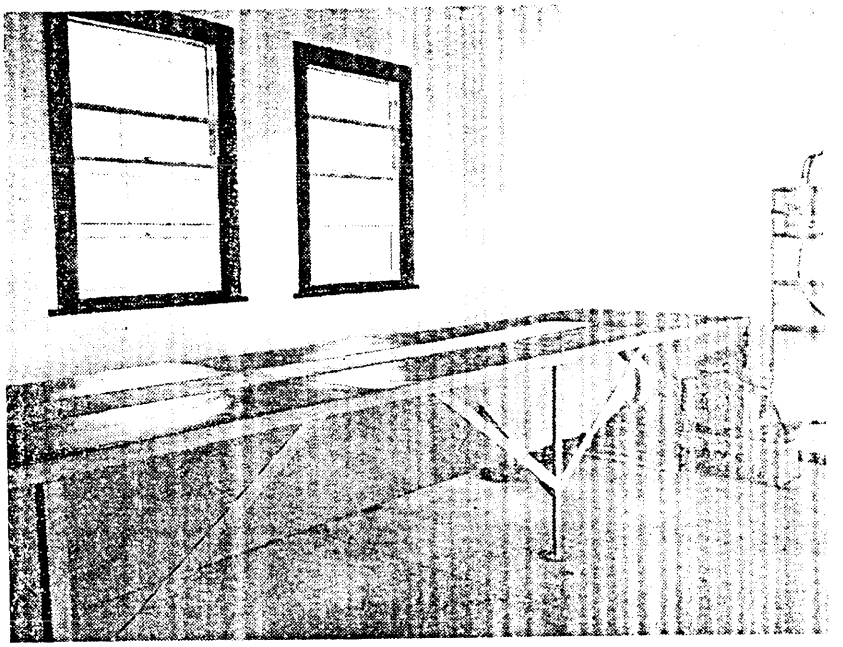


Fig. 1. A Sorting Table for Mine Samples.
The ventilation duct running underneath the table, which is connected to a 6-inch diam. exhaust fan, is covered with perforated plate. The table is 20 feet long by 4 feet and the duct is 1 foot wide.
With acknowledgment to Geduld Prop. Mines Ltd.

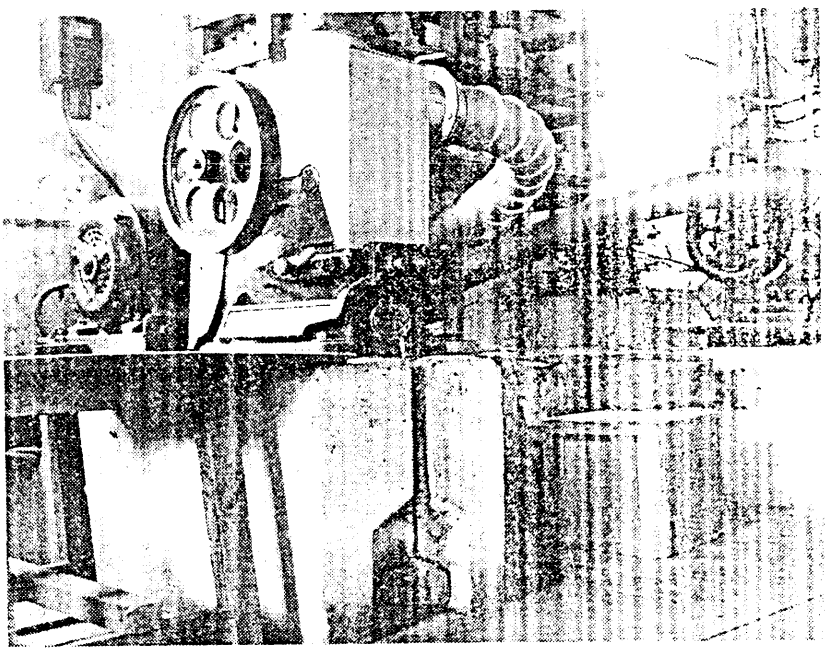


Fig. 2. "Cupolite" Jaw Crusher with Cover Connected to Exhaust System.
(With acknowledgment to Rand Leases (Vogels) G.M. Co.

The "Sturtevant" and the "Cupelite" are larger and the size of the jaw openings permits the crushing of the largest piece of rock that should be found in any underground ore sample, while their efficiency, when properly adjusted, has rendered preliminary crushing unnecessary since they are capable of reducing the sample to a product which is mainly minus $\frac{1}{4}$ inch.

SAMPLE DIVIDERS.

On the Witwatersrand the practice of "coning" and "quartering" a sample, by hand, has been almost entirely superseded by a method of reduction by an automatic divider; nevertheless the process is still termed "quartering". This device consists essentially of a rectangular funnel or hopper, supported on a strong iron stand. The base of the funnel is divided into an even number of adjacent chutes slanting in opposite directions, so that the sample, by dropping down the chutes is divided and falls into a receiving pan on the one side and into a reject bin on the other. The reject bin is placed below the strong iron table on which the apparatus is mounted. The reject chute, in some crusher houses, leads to a bin outside the building itself, and this method of installation is recommended in the interest of the maintenance of a dust-free atmosphere inside the crusher house. For the same reason the quartering apparatus should be enclosed in an efficiently ventilated hood.

The portion of the sample retained in the receiving pan is passed to the pulverizer, where it should be ground to minus 60 mesh. On some mines a portion of the crushed, but not pulverized, sample is retained for reference. This procedure is useful in case contamination in the pulverizer or in the process of assay is suspected, a further sample being then available for check.

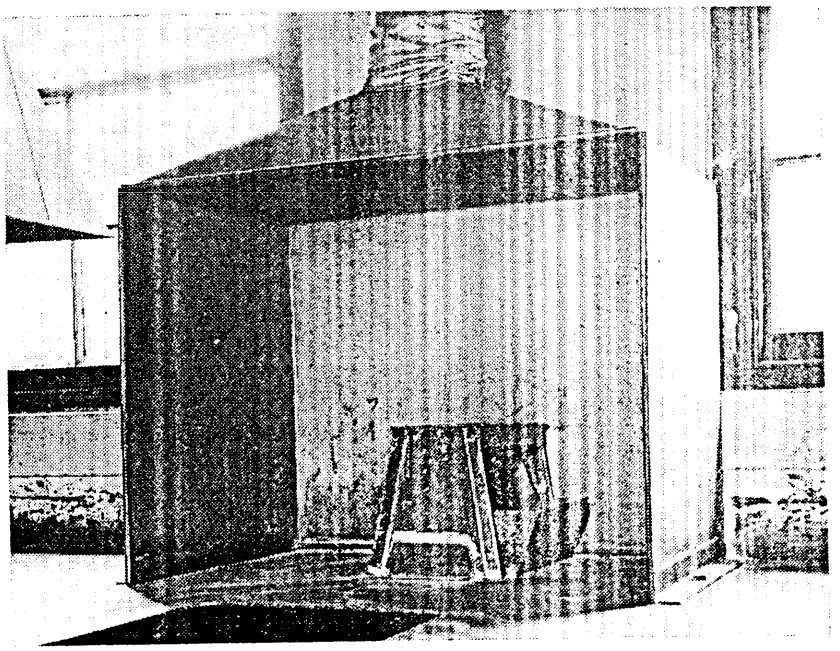
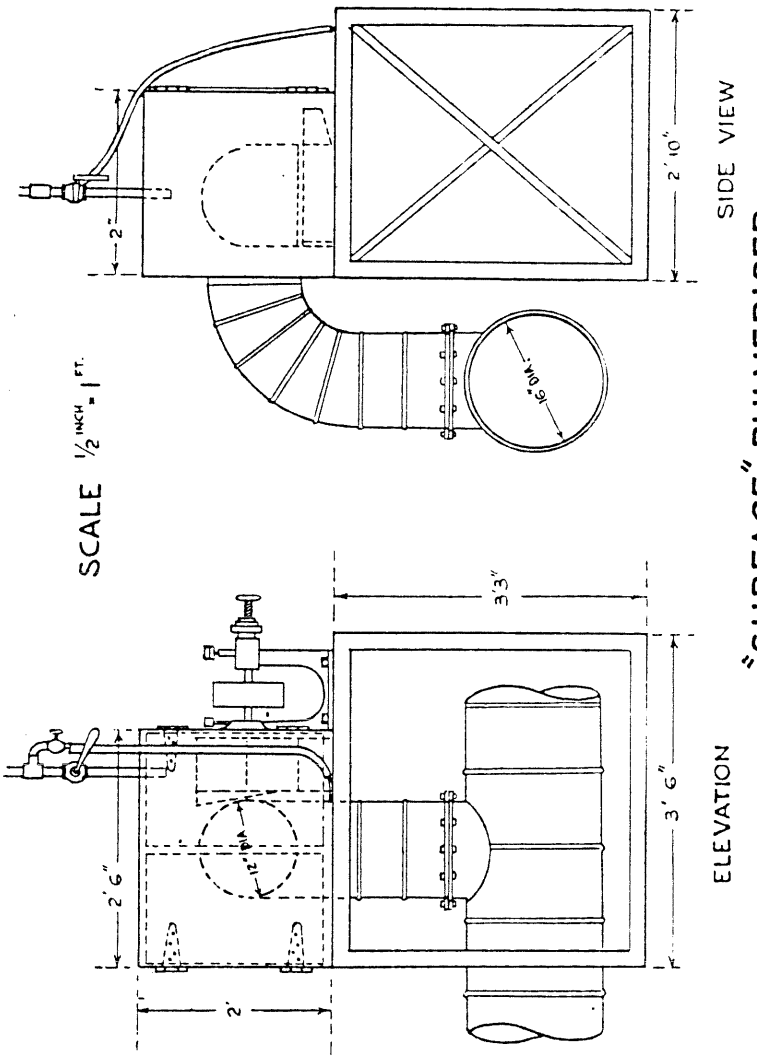


Fig. 3. A Jones Type Riffle Divider.
The reject chute leads to a bin outside the building.
(*With acknowledgment to East Geduld Mines Ltd.*)



"SURFACE" PULVERISER

Fig. 4.

PULVERIZERS.

Pulverizers of the disc type are in general use on the Witwatersrand, the best known being the "Braun", the "Hush", the "Cupelite" and the "Atom".

The Braun Pulverizer.—The main features of this machine are the simplicity of design and the ready accessibility of the grinding discs. The machine is easily opened for cleaning and this fact contributes considerably to its utility. It is not particularly "dust-proof", however, and to maintain a low dust count in crusher houses where it is installed it is necessary to enclose the machine entirely.

The Hush Pulverizer.—This machine is simply constructed and has few wearing parts. Its rate of pulverizing is approximately the same as that of the Braun and the shape of its outer casing simplifies the control of the dust generated while it is in operation.

The Cupelite Pulverizer.—This pulverizer is of similar design to the Braun and the Hush. It is fitted with ball bearings and is capable of dealing with a large number of ore samples over a considerable period with little attention. The dust generated during its operation is inconsiderable.

All three types are fitted with 8″ discs.

The Atom Pulverizer.—This machine is fitted with 10″ grinding discs, and consequently has a faster grinding capacity than the machines previously described. The rotating disc revolves at 800 r.p.m. on an axis which has an eccentric movement.

The stationary plate is attached to a hand-operated lever which causes the grinding surfaces to separate approximately one-sixteenth of an inch and at the same time actuates the compressed air valve allowing the air to travel along special blow-out channels which lead to all points where dust may accumulate. The machine is thus more easily and efficiently cleared of any possible contaminant.

The pulverizer is hinged about the centre and may readily be opened for inspection, or for the changing of discs.

The whole unit is mounted on a hollow cast iron pedestal which contains a 5 h.p. motor connected to the pulverizer by five vee belts, a press

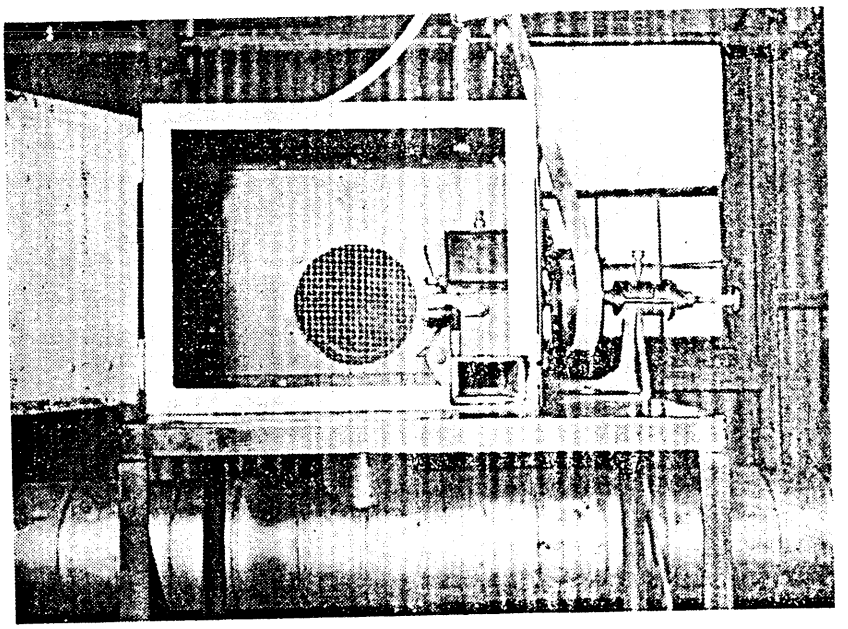


Fig. 5. Surface Pulverizer (See Fig. 4).
(With acknowledgment to Geduld Prop. Mines Ltd.)

button overload switch, and a built-in casting which is attached to the exhaust system. All rotating parts are enclosed making the unit perfectly safe to operate.

A specially designed suction attachment may be fitted to the feed hopper to ensure that no dust escapes into the atmosphere when the sample is introduced.

In modern crusher houses all machines are driven by separate electric motors, and not by belts from a line shaft. This system of separate motors and switches for each machine enables any particular portion of the crushing plant to be operated as required, and is both convenient and economical. Transmission of power from motor to machine is by direct shaft drive or vee belt, the latter being preferable, as, in the event of the jamming of a machine, the shock is not carried direct to the motor with the risk of consequent damage.

The treatment which the samples undergo in the crusher house is as follows:—

The canvas bags are opened and the samples are tipped into steel dishes. The ticket contained in each bag is unfolded and is also placed in the dish. The samples are arranged in numerical order, stacked in piles of a suitable number and carried to the jaw crushers where they are crushed to approximately minus a quarter of an inch mesh. They are then taken to the divider where each one is quartered down until a suitable quantity remains. The samples are then transferred to the pulverizers where they are ground to *at least* minus 60 mesh. After this the samples are placed in trays in numerical sequence and taken to the fluxing room.

A COMBINED CRUSHING, QUARTERING AND PULVERIZING UNIT FOR MINE SAMPLES.

This unit, which was originally designed and installed on the Geduld Proprietary Mines Limited, is now in use on several mines on the Witwatersrand, and has proved successful where a large number of mine samples are handled daily. Considerable saving in time and labour has resulted from its introduction. In addition, the amount of injurious dust generated and dispersed into the atmosphere during the operation of the unit has been reduced to almost negligible proportions. Standard equipment is used in its construction and all desirable features, used in mine sample crushing, are incorporated.

The principle of the Geduld unit is to arrange the separate machines in such a manner that the discharge from the jaw crusher is fed through a divider direct into the pulverizer, thus combining several operations and reducing handling to a minimum. Whereas in the ordinary installation individual operators are required to manipulate the crusher, the divider and the pulverizer, the Geduld unit can be controlled by one attendant whose sole task is to introduce the sample to the crusher hopper and to withdraw it, crushed, quartered and pulverized, from the drawer below.

Precautions against the dissemination of dust are provided, the crushing portion of the unit being fitted with a powerful suction and the pulverizer enclosed in a box connected with the ventilation system. This box, or hood, is open at the front and the operator has complete access to the pulverizer at all times.

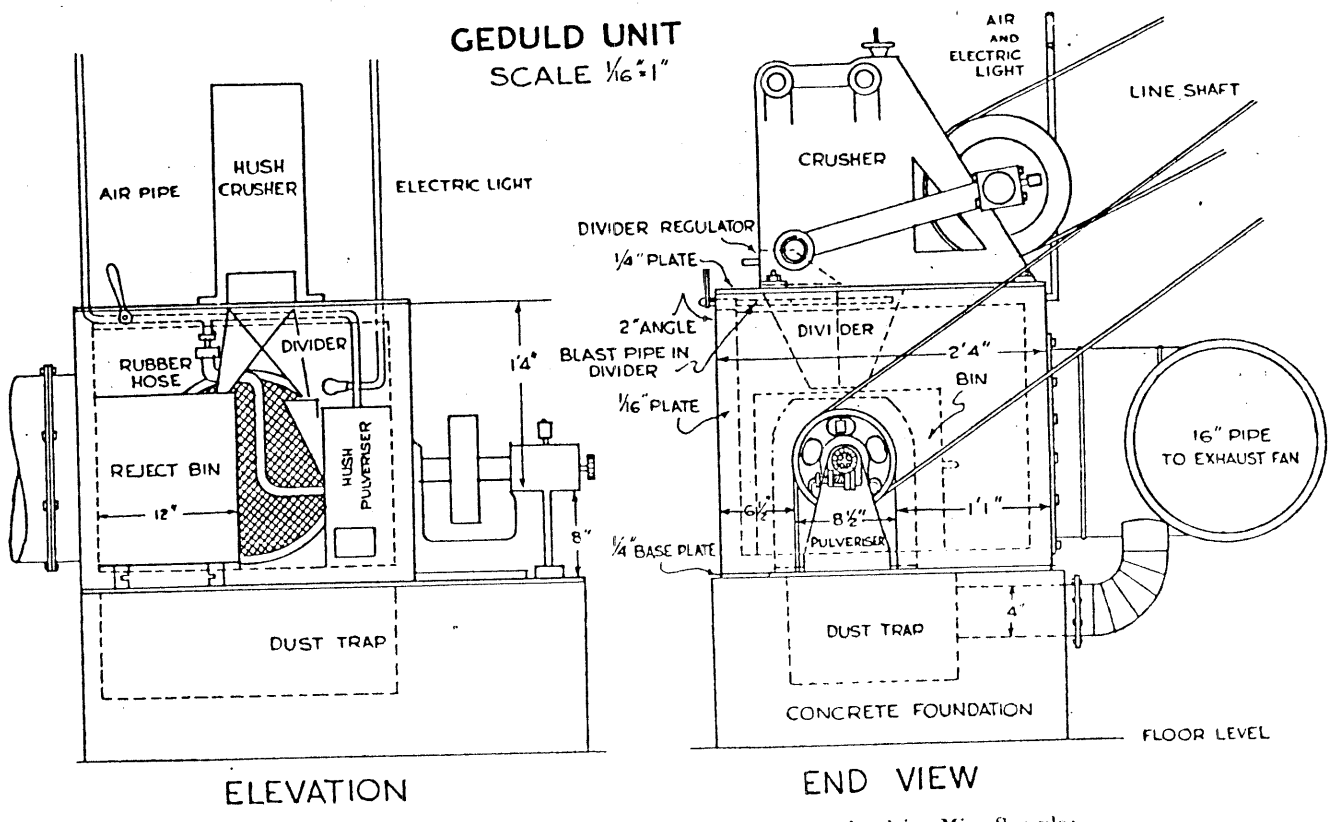


Fig. 6. The "Geduld" Unit, for Crushing, Dividing and Pulverizing Mine Samples.
A single valve controls a series of air jets, which clean the components of the unit after each sample is pulverized. (See also Fig. 7).

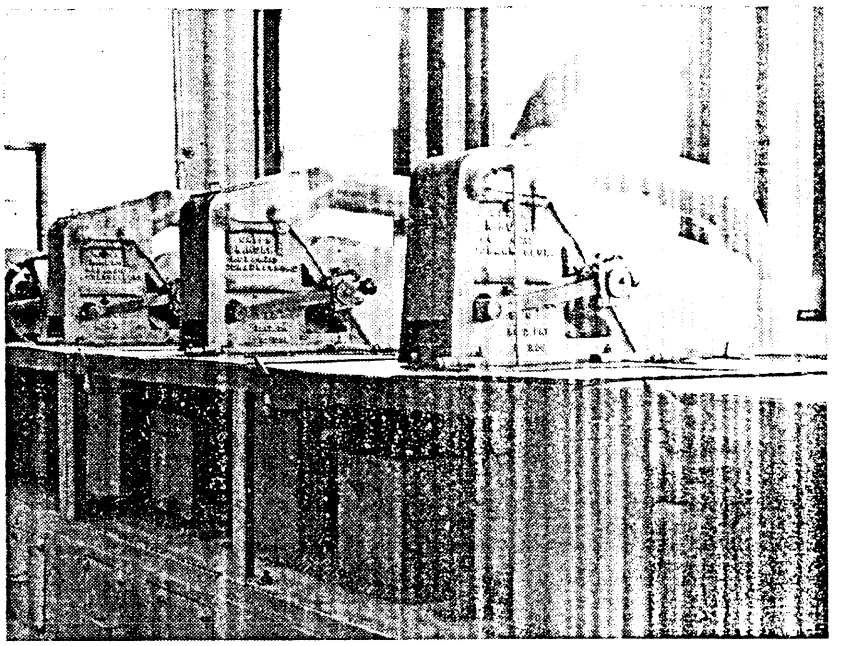


Fig. 7. A Later Version of the Geduld Unit.

Dust is drawn away through the perforated plate on which the pulverizers stand. (See Fig. 6 for original).

(*With acknowledgment to Geduld Prop. Mines Ltd.*)

Description of the Unit.

The Crusher.—The crusher is a standard "Hush" jaw crusher mounted on a steel framework 2′ high. It is driven off the fly-wheel at a speed of 620 r.p.m., which is approximately twice the speed at which a machine of this type is normally driven. The increased speed more than doubles the crushing capacity, and it has been found in practice that the life of the bearings is increased considerably.

The Divider.—The divider is a specially constructed appliance. It was found that the standard type divider had a tendency to choke and, as the divider is rigidly fixed, difficulty in cleaning was experienced.

The modified type fitted, consists of two chutes running in opposite directions, so arranged that the crushed rock falls directly on the junction of the chutes.

It is necessary, when fitting the divider, to determine its position and setting by experiment, as the moving jaw of the crusher has a tendency to throw the crushed material towards the back of the machine. The correct setting is determined by checking the weights of the separated portions of sample until they are as near as possible to equality. Thorough investigation and checking of both weights and assay values has verified that this method of dividing is efficient for the type of work dealt with by the unit.

The standard receiving tray may be placed under the crusher so that a sample may be crushed and caught before it passes to the divider. Moreover a special divider may be inserted in this space. If inserted one way, all the sample is diverted to the pulverizer and if reversed, only a quarter of the sample is sent to the pulverizer.

The sides and bottom of the divider chutes, which are perfectly smooth, are tapered down from $6\frac{1}{2}''$ to $2\frac{1}{2}''$, the slope being 55° off horizontal, compared with 45° in the case of the locally made "Jones" type divider. This steeper slope prevents the jamming of particles of crushed sample in the chute. A compressed air jet is fitted for blowing out the device after each sample is crushed.

The Pulverizer.—A standard "Hush" pulverizer is used. The discharge from one chute of the divider is fed directly into the throat of the machine and, as the rate of feed is governed by the discharge from the jaw crusher, there is never sufficient ore at any one time to choke the throat.

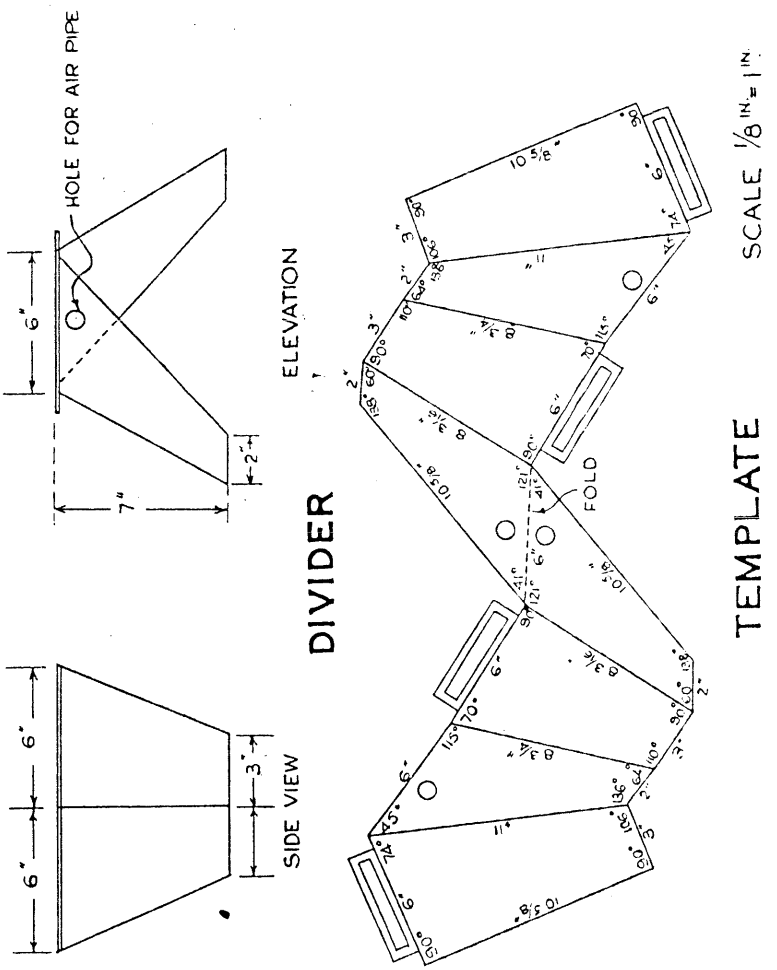


Fig. 8. The sample divider as used in the "Geduld" Unit.

The pulverizer has suction from below, and is fitted with a damper which automatically closes while pulverizing is being performed and opens when the machine is being blown out.

Provision is made for the efficient and rapid cleaning out of the machine in the conventional manner, air jets being fitted to the throat and casing.

The Reject Bin.—The discharge from the reject chute of the divider is fed into a reject bin which stands alongside the pulverizer. The bin is 24″ × 12″ and 14″ in height. The bin must be removed before the pulverizer door can be opened.

Cleaning the Unit.—Compressed air jets are installed at all points in the crusher, divider and pulverizer where dust and particles of sample may collect. These are controlled by a single cock so that the entire unit may be cleaned in one operation.

The Mounting.—The framework holding the jaw crusher is welded to a base plate on which the pulverizer is mounted, and the whole unit stands on a hollow concrete block 14″ high. The space inside the block acts as a trap for the heavier material which is blown out of the pulverizer after crushing.

Each portion of the unit is detachable and can be removed for repairs. Where more than one unit is installed, it is advisable that the same type of components be used throughout, and that a spare crusher and pulverizer be available for replacement of any part of the unit in need of repair.

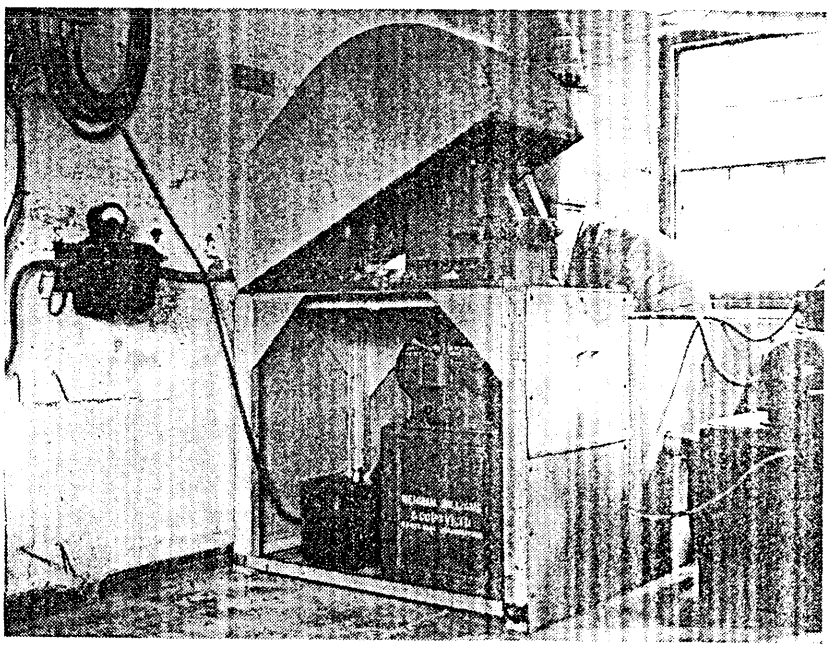


Fig. 9. A "Geduld" type unit made up of a "Cupelite" jaw crusher and a "Cupelite" Atom pulverizer.

PREVENTION OF CONTAMINATION OF SAMPLES DURING CRUSHING.

If a pulverizer is opened and examined after a sample has been pulverized, it will be noticed that all the pulverized material has not found its way into the sample drawer. A small quantity will be found on top of the stationary plate, and on the inside of the casting, particularly if the casting is rough.

These small quantities of sample, if not removed, will contaminate the next sample to be pulverized and in the event of a rich sample preceding one of low value, serious enrichment of the second sample may occur.

For this reason it is necessary to clean out the pulverizer thoroughly after each sample is crushed.

In theory, the machine should be opened and thoroughly brushed out to ensure complete cleanliness; but this procedure is cumbersome and is quite impracticable when a large number of samples is handled daily. Experience has shown that the pulverizer can be efficiently cleaned by the use of compressed air jets directed at those points where the powdered ore is most likely to accumulate.

The suction from the fan should be sufficiently powerful to exhaust all the air and dust produced when the blowers are in operation; otherwise some dust may be dispersed into the atmosphere of the crusher house, and constitute a threat the health of the workers.

Tests MUST *be carried out from time to time to ascertain whether or not the suction from the fan is causing concentration of the sample.* It is generally found, however, that where suction is applied directly to the pulverizer no concentration takes place although the amount of sample drawn off by the fan may be comparatively large.

THE PRINCIPLES OF CRUSHER HOUSE VENTILATION.

In the course of mining operations underground, and in the handling of the ore on the surface, a certain amount of siliceous dust is produced. The finer particles of this dust (those measuring 5 microns and less), if inhaled continuously over long periods, give rise to a chronic disease of the lungs known as silicosis. For this reason every effort is made to limit the formation of this injurious dust and to lay it, as it is formed, by means of water-blasts, atomisers, water sprays, etc., or by passing the dust-laden air through flannel bags or other types of filters.

Although only a small part of the very fine siliceous dust is caught by means of water-sprays, etc., the dust content of the air can be reduced to negligible proportions by large scale dilution.

The rate of fall of the small particles is very slow. In still air, a particle of dust 1 micron in diameter falls at the rate of 0·0075 cm. per second, while a 10 micron particle falls 0·75 cm. per second. Consequently the suction from the fan removes this fine dust from the working place before it has settled.

In the assay office crusher house, however, the removal of dust presents a slightly different problem.

The dust produced during the crushing of the sample is of minor importance and can be removed with comparative ease; but the problem of removing the dust produced during the cleaning-out of the machine is a more serious one.

To prevent contamination, the pulverizer must be thoroughly cleaned after each sample is crushed. It has been found that one of the most rapid and effective means of achieving this end is to employ compressed air at a pressure of from 50 to 80 lb. per square inch. Since up to half an ounce of sample may remain in the pulverizer and this is blown out immediately the air is turned on, it follows that the suction must be capable of coping with this sudden surge of dust-laden, compressed air. For example, if four half-inch pipes, with a pressure of 75 lb. per square inch, are used for blowing out, as much as 1,500 cubic feet per minute may be produced. Therefore the fan must be capable of removing this amount of air and, to ensure efficiency, should have a reserve capacity of 25 to 50 per cent. In such a case a suction of 2,000 cubic feet per minute must be applied to each machine. This is, perhaps an extreme case but even with four quarter-inch pipes a suction of at least 500 cubic feet per minute would be necessary.

It is unusual to have a separate fan for each machine, the usual practice being to have several machines connected to the fan. If these connections are all of the same diameter, it follows that the shortest will draw more air than the longest, since the friction is greater in the longer pipe. In order to apply an equal suction to each machine, the diameter of the shorter pipe should be less than that of the longer.

Similarly, if the suction is induced through a channel running the length of all the machines, the size of the inlet nearest to the fan must be smaller than that of the inlet farthest away, if equal suction is desired.

A third method of ensuring equal draught in each machine is by varying the cross sectional area of the main duct according to the cross sectional area of the sum of the inlets.

The calculation of the variations in the cross sectional area of the duct is based on the following facts:

(*a*) the combined cross sectional area of the inlet pipes shall not be greater than the cross sectional area of the fan inlet.

(*b*) the cross sectional area of the main duct shall vary according to the cross sectional area of the sum of the inlets.

For example, suppose a number of pipes, each of 7 inches diameter, is to join a duct, connected to a fan with a 16-inch diameter inlet. The first portion of the duct, that farthest from the fan, is the same diameter as the inlet pipe, and has a cross sectional area of 38·50 inches until it is joined by the second pipe. The cross sectional area of the duct is now increased to $2 \times 38 \cdot 50 = 77 \cdot 0$ square inches giving it a diameter of 9·9 inches. Where the third pipe joins the duct the cross sectional area is again increased, this time to $3 \times 38 \cdot 50 = 115 \cdot 5$ square inches and a diameter of 12·12 inches.

This procedure is continued until five such pipes have joined the main duct. The cross sectional area of all the pipes is now equal to that of the fan inlet, and no further pipes can be connected without reducing the amount of suction in the pipe farthest from the fan. It follows, therefore, that if a greater number of inlets is required the diameter of each inlet must be reduced.

Alternatively the diameter of the inlet pipes can be calculated if the size of the fan and the number of inlets required is known. Thus, if five machines require suction at the rate of 1,000 cubic feet of air per minute, a fan with a capacity of at least 5,000 cubic feet per minute must be installed. If the diameter of the inlet of the fan is 16 inches, the cross

sectional area of the inlet divided by five gives the cross sectional area of each inlet.

These methods may not give exactly equal distribution of suction, and it may be necessary to fit dampers to accomplish this. For most practical purposes, however, the use of dampers is unnecessary.

The formulae on which the above results are calculated are included below:—

(1) To calculate the number of leads of a particular diameter that may be taken from a main:—

$$\frac{(\text{Diameter of Main Pipe})^2}{(\text{Diameter of Lead Pipes})^2} = \text{Number of Pipes.}$$

(2) In the same way to calculate the diameter of the lead pipes:—

$$\sqrt{\frac{(\text{Diameter of Main Pipe})^2}{\text{Number of Lead Pipes}}} = \text{Diameter of Lead Pipes.}$$

The data given above are intended as a working guide for the assayer. Lay-outs based on these figures will give satisfactory results.

If, for some reason, the machine can only be fitted with a smaller opening, a high-pressure fan will be required. The capacity of the fan is based on the amount of air which it is required to draw through this opening.

Low, medium and high pressure fans are obtainable. The smaller the opening for any given amount of air the higher the pressure must be. Low pressure fans revolve at a slower speed than those of high pressure and consequently this type has a longer mechanical life than the others.

A further problem which is peculiar to the assay office crusher house is the fact that some of the material which is to be drawn off is comparatively coarse. The portion of the crushed sample which remains in the machine is approximately minus 60 mesh, and this is blown out by the pressure of the compressed air. If the suction of the fan is not sufficient to draw it along the pipe, the material settles and, in a comparatively short space of time, considerably reduces the effective diameter of the pipe.

For this reason a dust trap should be fitted under each machine. A dust trap is an expansion box which reduces the velocity of the air and allows the coarse dust to settle. Easy access to these traps is recommended so that they can be cleaned out at regular intervals.

DUST COLLECTION AND DISPOSAL.

The problem of collecting and disposing of the dust withdrawn from the assay office crusher house is one which receives continual attention, and various methods of collection and disposal are in use throughout the Witwatersrand.

In most of these systems the dust-laden air is passed through expansion chambers in which the coarser particles are collected and thence through stacks or towers in which the fine dust is settled by means of water sprays.

Although most installations collect a large proportion of the dust, few give completely satisfactory results and a cloud of fine dust can usually be seen issuing from the final exit.

Good results have been obtained from flannel bag filters, from filter cabinets filled with wood shavings and from Multi-cyclones and it is suggested that complete efficiency may be attained by the development of such devices.

The whole purpose of the dust filtration plant is to separate and collect the harmful dust, so that the air being discharged into the atmosphere, causes neither injury nor inconvenience.

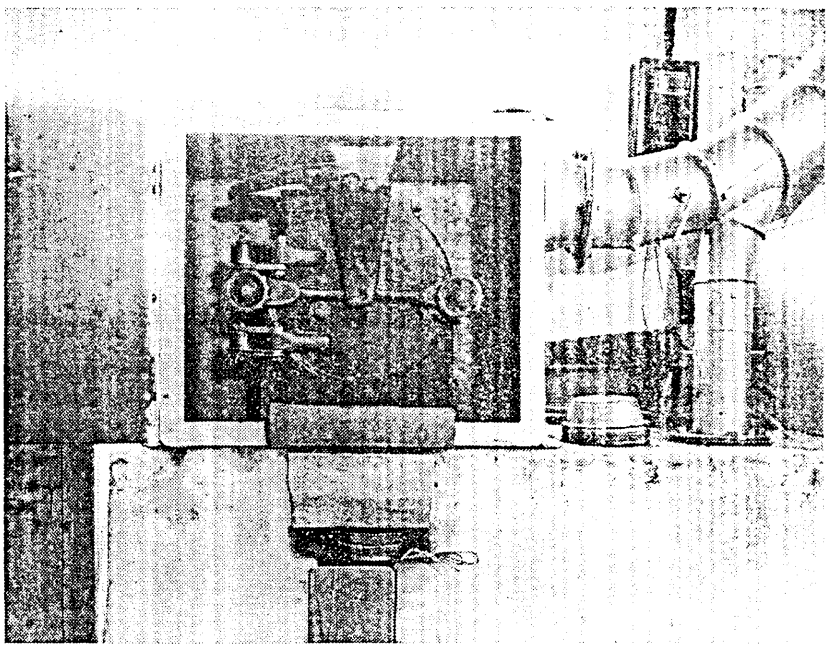


Fig. 10. A Completely Enclosed Pulverizer.
During crushing and blowing out the door is kept closed. The branch draws dust from underneath the machine.
(*With acknowledgment to Rand Leases (Vogels) G.M. Co.*)

METHODS OF REMOVING DUST FROM THE CRUSHER HOUSE.

Removing Dust Caused During Crushing and Blowing Out.

The methods adopted to deal with the problem of dust removal vary from mine to mine but may be classified into three main groups, all of which depend upon the suction provided by an exhaust fan.

1. *By entirely enclosing the machine.*—In this method the machine is placed inside a box or cover which encloses it completely.

The sample is fed into the machine through a chute. This chute has a lid on the outside which is closed during crushing and blowing out. After the sample has been crushed or pulverized it is withdrawn through another opening which is also fitted with a lid.

The box is connected to the exhaust fan and the dust which escapes from the machine during crushing is trapped by the box and removed by the fan. The compressed air, used for cleaning, blows that portion of the sample which remains inside the machine after crushing, into the box where it is also trapped and removed. In addition the box should be provided with a large door, preferably occupying a complete side of the

box. This door should be easy to open and should allow complete access to the machine for cleaning and servicing.

Considerable ingenuity has been displayed in the design of this type of cover and in satisfactory types it is possible to adjust the setting of crusher jaws and pulverizer discs from outside the cover, and also to observe the operation of the machine through glass covered observation windows.

2. *By partly enclosing the machine.*—In this case a hood partly covers the machine and both the hood and the body of the machine are connected to the exhaust fan.

These hoods or cowls may take the form of a box, in which the machine stands and which is open in the front or they may be bell-shaped cowls which are suspended over the machine.

The machine itself is connected to the fan by means of a pipe.

The suction from the hood must be very much stronger than that from the machine for, while a comparatively gentle suction may be sufficient to remove the dusty air from the cover in the previous type, in this instance the draught must be strong enough to draw in the air immediately surrounding the machine and so prevent the escape of the dust into the atmosphere. Consequently this surrounding air must be made to flow away from the operator and towards the cowl.

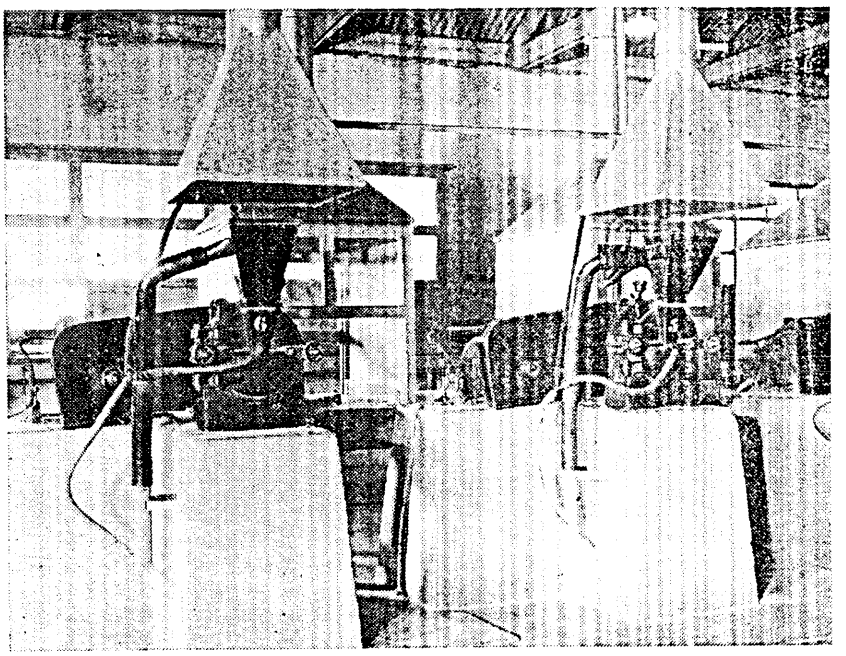


Fig. 11. Pulverizers mounted on hollow concrete blocks connected to an exhaust fan. Overhead cowls, also connected to the exhaust fan, remove any dust which may escape from the pulverizers.

The suction from the inlet chute is boosted by means of the "Venturi" during "blowing out".

(With acknowledgment to Modder East Ltd.)

3. *By making the machine itself dust-proof.*—In the methods previously described the principle is to blow the dust out of the machine and then remove it before it is dispersed. In this method, the machine itself is made dust-proof by fitting spring lids to all openings except special openings which are connected directly to the suction fan and through which the dust is drawn off. Since a certain amount of dust will tend to escape when the lids are opened to introduce or withdraw the sample, it is necessary to have a slight suction at these points at all times. When the machine is blown out the main suction pipe is fully opened thus providing a large outlet for the compressed air and dust.

The spring lids used to make the machine dust-proof are lined with felt or rubber. The springs should be strong enough to resist the pressure of the compressed air, but too strong a spring should be avoided as it makes the lid difficult to open.

The above three methods give excellent results if properly installed.

The chief causes of inefficient ventilation are:—

1. Badly fitting lids or covers.
2. Insufficient suction.
3. Too short a stack at the outlet end of the fan.

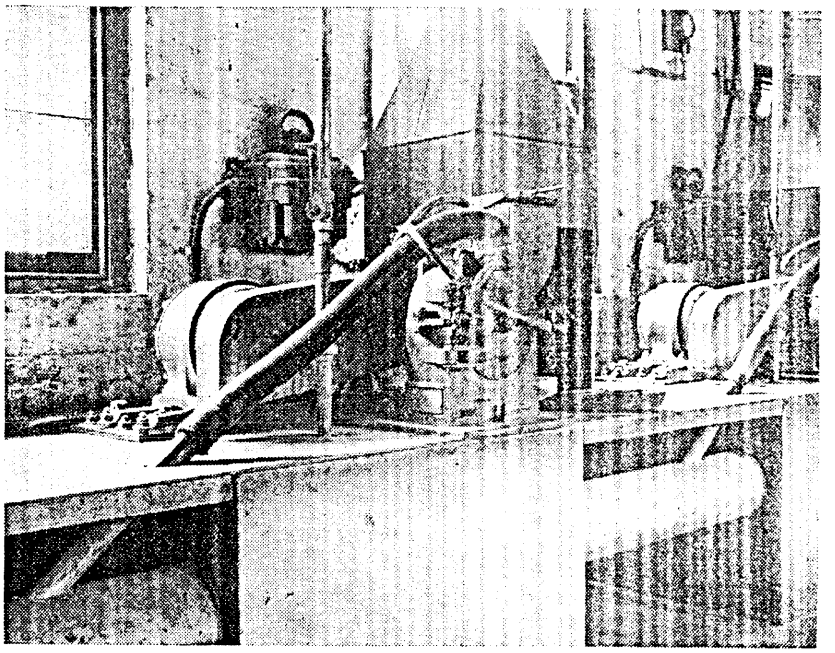


Fig. 12. A "Cupelite" Pulverizer Mounted on a Concrete Block with the Suction Duct Below.

The compressed air pipes for "blowing out" the pulverizer can be seen, as well as the pipe connecting the throat of the machine to the suction duct below. This pipe applies a continuous suction at the throat and provides an outlet for any blow back during the "blowing out" with compressed air.

The hood in the background removes dust during the transfer of the sample from the pulverizer receiving tray to the paper packet.

(With acknowledgment to East Geduld Mines Ltd.)

The ventilation system of the crusher house may be considered satisfactory if Konimeter counts show that the dust content does not exceed that of the outside air by more than 50 particles per cubic centimetre but it is possible, by using any of the three methods described, to reduce the dust content to within ten particles per cubic centimetre of that of the air being drawn into the building.

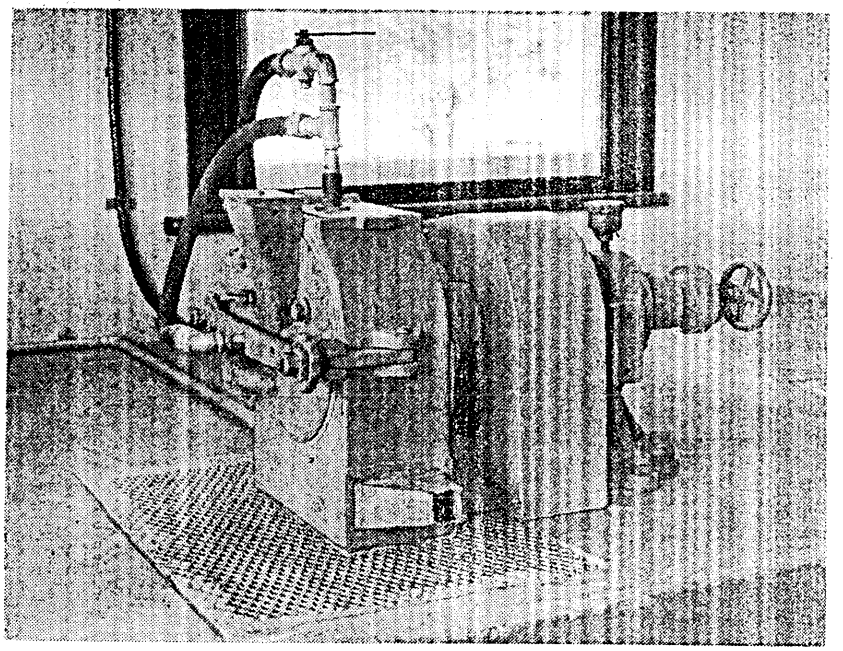


Fig. 13. A pulverizer mounted upon a concrete expansion box, which is connected to an exhaust fan.

The down draught through the perforated plate draws away the dust.

(Acknowledgment to Geduld Prop. Mines Ltd.)

Air Ducts.

In the case of the overhead cowl the connection to the fan is usually an overhead ventilation pipe and this is also used for certain completely enclosed machines.

In most other cases the main dust exhaust system consists of an underground channel, running the whole length of the crushing plant. It is usually situated below the concrete blocks on which the machines stand and is connected to the exhaust fan. The opening in the base of each machine is connected to the channel by a steel pipe running down through the block. Some assayers prefer to use a large diameter ventilation pipe in place of the underground channel. Whichever system is used, however, it is important that the channel or the main pipe be fitted with air-tight doors at intervals to admit of easy access for periodical cleaning.

Removal of Dust caused by the Transfer of Samples from Bags to Dishes.

The samples are received in canvas bags and, before crushing, are generally transferred to steel dishes.

This operation should be performed under a hood which is connected to an exhaust fan or on a table which has a perforated top with a suction from below.

The practice of transferring the samples to their dishes outside the crusher house is one that has much to commend it since it reduces the amount of dust produced inside the crusher house. A lean-to roof to give protection from the weather should be provided and a window or hatch through which the dishes can be passed to hooded tables inside.

Removal of Dust Caused by Transfer of Pulverized Samples.

The transfer of pulverized samples from one container to another gives rise to considerable dust and should be carried out as seldom, and with as much care, as possible. All transferring, such as from pulverizer drawer to sample dish or paper packet should be done under a hood or near a ventilator cowl connected to the exhaust. The use of metal liners for pulverizer drawers abolishes one stage of transfer of sample. These liners are shaped to fit, in all dimensions except length, the pulverizer drawer. The liner is approximately three inches shorter than the drawer so that it can be easily grasped for removal, and in order that the pulverized sample shall be directed into the liner and not over its ends into the drawer, it is necessary to fit two small baffle plates to the pulverizer. The liner replaces the receiving pan under the quartering machine, and carries the sample to the pulverizer. The sample is tipped into the pulverizer hopper and is received into another liner in the drawer. This second liner is removed and is replaced by the one from whence the sample was tipped, and is ready to receive the next sample to pass through the machine. This method abolishes the necessity of transferring from the drawer to the sample dish, and the liners form neat containers from which portions may be taken for assay. They are also convenient for the filing of mine samples on shelves for reference.

Where paper bags are preferred as containers, a funnel drawer is used to receive the sample. This is an oblong drawer which fits under the pulverizer and has one end drawn out in the shape of a funnel. The paper bag is placed over this funnel during crushing, after which the drawer is withdrawn and tilted so that the sample runs into the paper bag.

Each method has its advantages and disadvantages, and opinion as to the best method is fairly evenly divided.

Chapter III.

THE FURNACE ROOM.

In most Rand assay offices the furnace room is the largest room in the building. It should be bright and well ventilated and, if possible, no work other than that incidental to the fusion and cupellation of samples should be done in this section.

THE ASSAY FURNACE.

Assay furnaces are divided into two types, the crucible furnace used for the fusion of samples and the muffle furnace used for the cupellation of lead buttons.

In the construction of these furnaces brick arches are commonly used, and in order to prevent excessive expansion and contraction, with consequent loosening of the brickwork, it is necessary to encase the furnace block in mild steel plates, braced with tie rods.

For "free milling" ores a temperature of 950° Centigrade may be sufficient for fusion but, as the percentage of pyrite increases, greater heat is required to produce satisfactory fusions. When dealing with ores con-

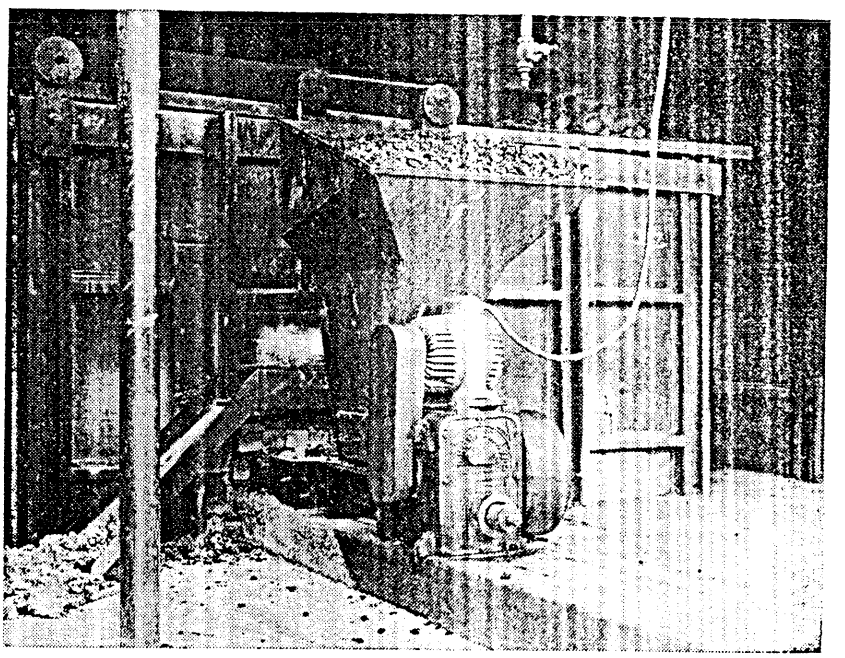


Fig. 14. An Assay Furnace fitted with an automatic stoker.
(With acknowledgment to East Geduld Mines Ltd.)

taining over 50 per cent pyrites a temperature of 1,100° Centigrade may be necessary and all assay furnaces should be capable of exceeding this figure. A furnace of this type should be capable of fusing a "crucible charge", usually 40 to 80 No. 1 crucibles, within 30 minutes.

Owing to the comparative cheapness of coal on the Rand most assay furnaces are coal-fired and until recently, were hand-stoked. However, a considerable saving in the cost of labour and fuel can be effected by the use of automatic underfeed stokers and these are becoming increasingly popular.

In some cases the stoker has been successfully fitted to an existing furnace but, in others, new furnaces have been designed and built.

A most important point in connection with an automatic stoker is that it can be controlled by means of a thermostat. Thus a pre-determined temperature can be maintained to within a few degrees. This is particularly important in the case of muffle furnaces.

Coal consumption, comparable with that obtained from automatic stoking, has been attained by means of a modified method of hand-firing. In this type of stoking the fire-box is sealed, air being supplied by means of a fan-duct under the fire-bars. The coal, in the form of nuts, is fed in from the top of the fire-box through a chute which can be closed by means of a cast iron plug. The fire-box is comparatively large and the draught is strong enough to force its way through the ash, coal-bed and clinker. No ash or clinker need, therefore, be removed until the end of the shift.

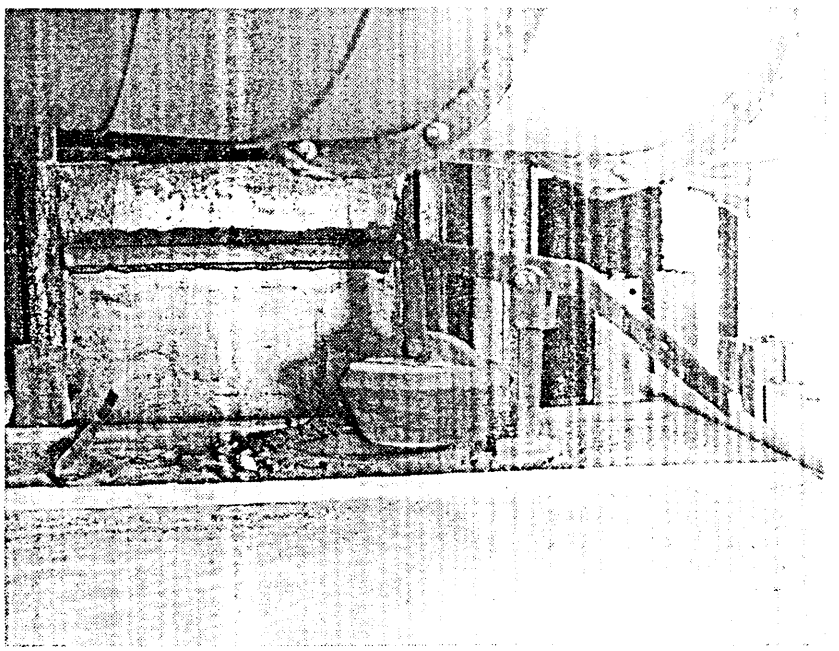
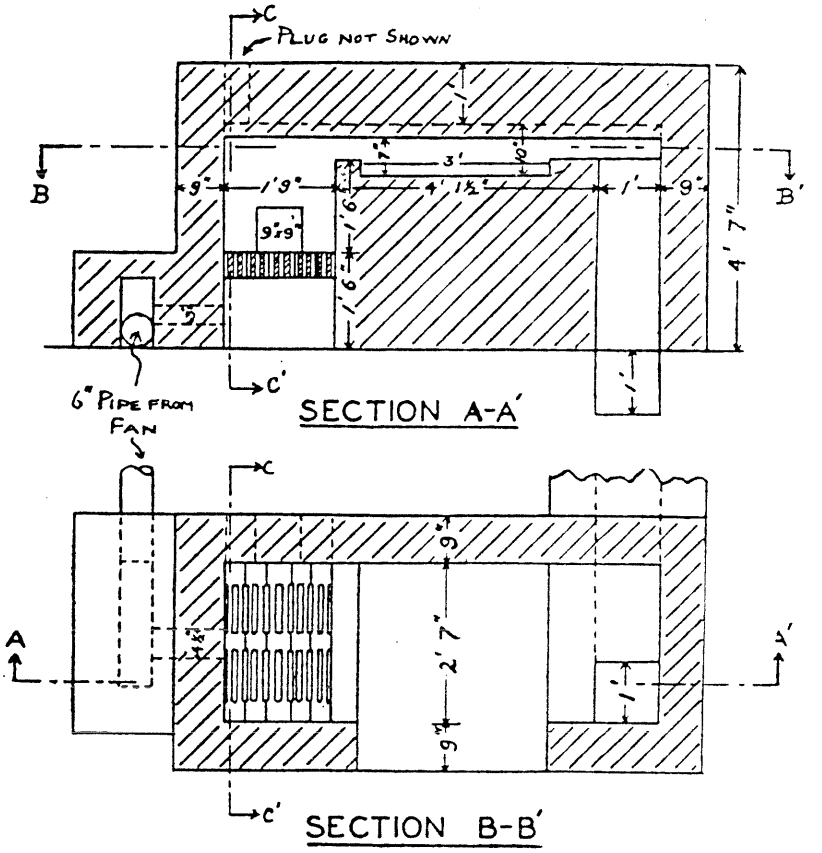
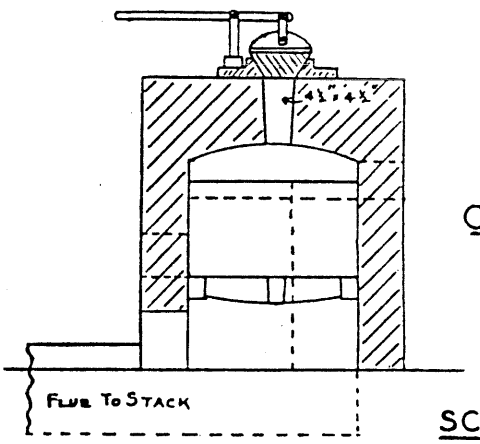


Fig. 15. Loading chute on Geduld crucible furnace, showing lever-operated conical plug.

(With acknowledgment to Geduld Prop. Mines Ltd.)





GEDULD CRUCIBLE FURNACE

SCALE ⅓" = 1'

SECTION C-C'

Fig. 16.

TYPES OF FURNACES.

Although the general principle of most assay furnaces on the Rand is the same, there are, nevertheless, various types. These may be divided into two main groups.

(*a*) Those having separate fire-boxes for the hearth and for the muffles.

(*b*) Those having one fire-box to serve both hearth and muffles.

In the first group the muffle furnace and the hearth furnace may be separate units or they may be built into one block. In the second group there are three types, depending on the sequence of the muffles and the hearth. The muffles may be heated either before or after the hearth, or the flame may be split and both heated simultaneously.

The Crucible Furnace.—In its simplest form this consists of a fire-box, a hearth and a flue leading to the stack. The flame from the fire-box passes over the hearth and thence through a flue to the stack. The simplicity of design makes this a very inexpensive furnace to build.

Various flue arrangements have been incorporated in order to conserve the heat. The more complicated these become the greater the cost of building and the greater the need for flue cleaning to maintain satisfactory working conditions.

The Muffle Furnace.—The muffle furnace differs from the hearth furnace only in its dimensions. The fire-box is usually smaller and the hearth is replaced by a flue with openings in the front through which the muffles are sealed into position so that the flame passes over, under and behind each muffle.

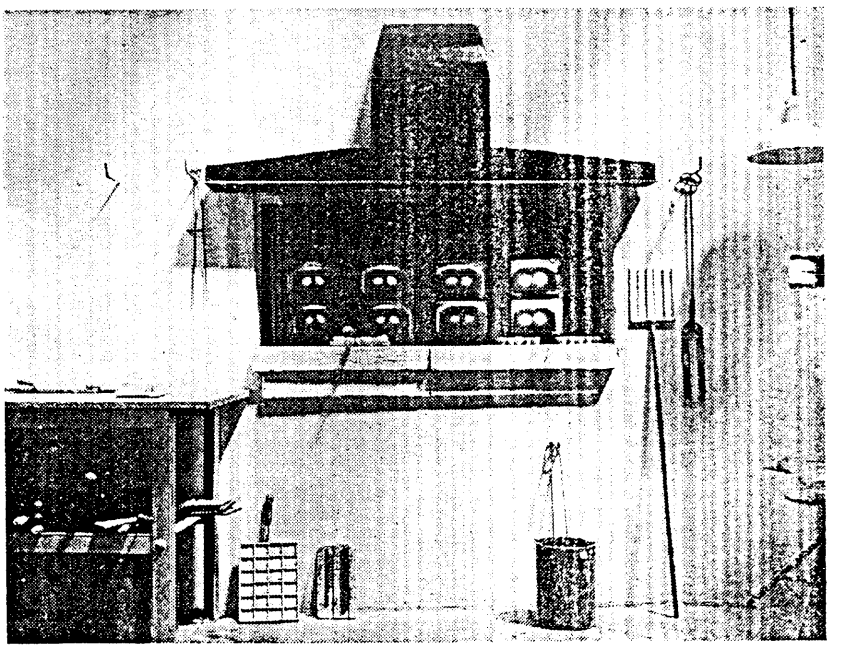


Fig. 17. "Geduld" Muffle Furnace.
(*With acknowledgment to Geduld Prop. Mines Ltd.*)

Another type has the muffles directly above the fire-box. The flame passes from the bottom of the muffles, by way of a flue, back over the top of the muffles and then on to the stack.

The Rival Furnace.—The Rival furnace is a combined hearth and muffle furnace. The main advantage is that it saves space. Apart from this the furnace has the advantages and disadvantages of the separate units but it has the added disadvantage of being more costly to rebuild since the hearth section cannot be rebuilt without demolishing the muffle

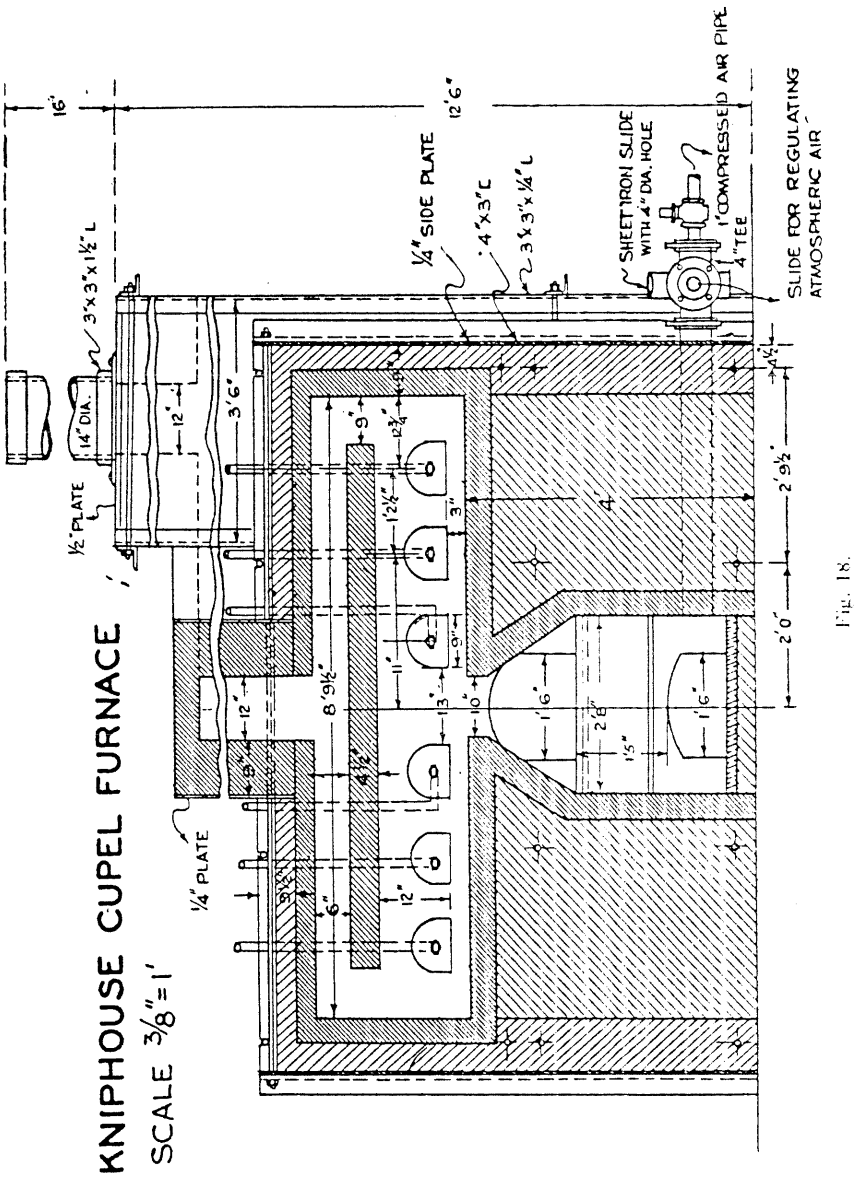
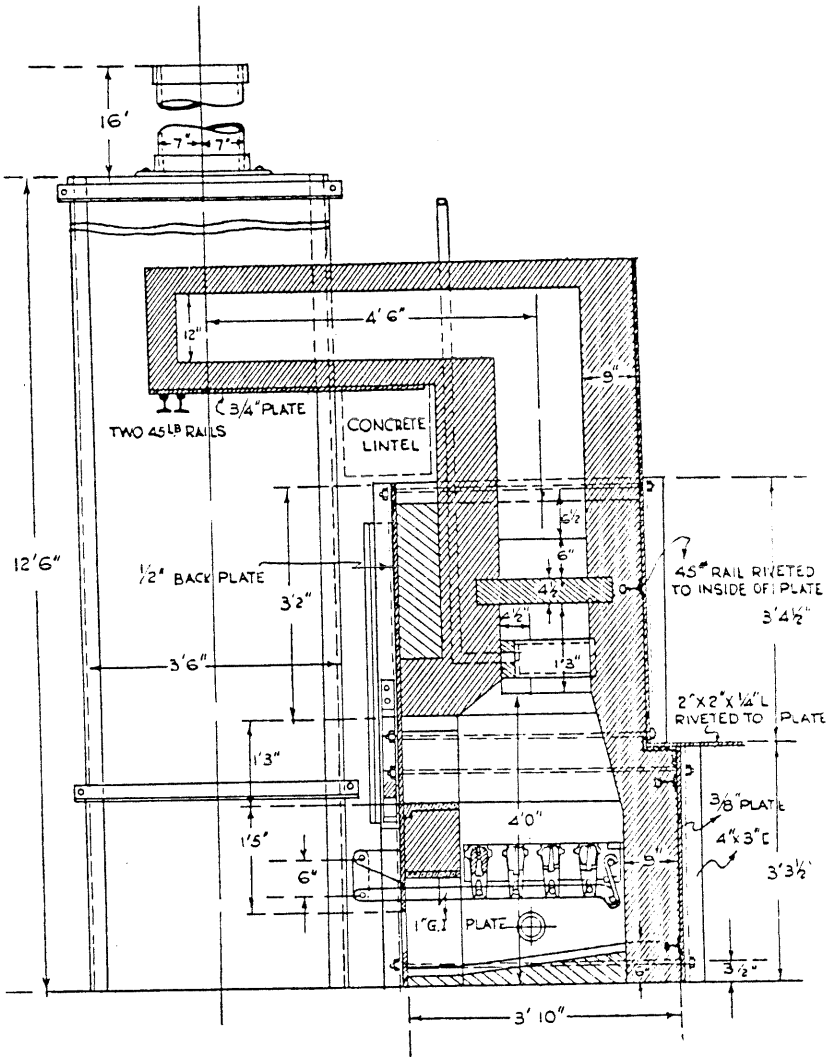


Fig. 18.

section. This is not a serious matter however and the Rival furnace is a popular one on the Rand.

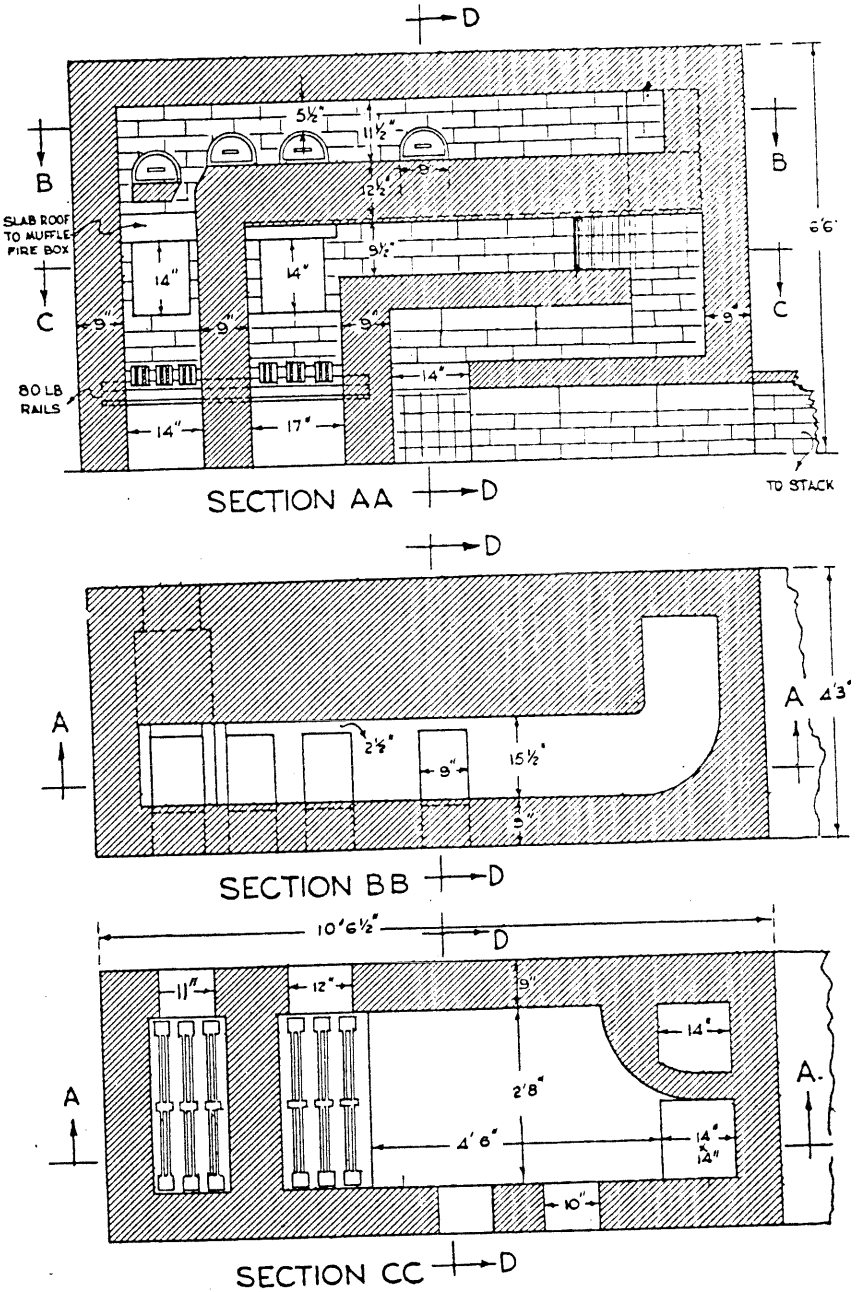
The Hearth to Muffle Furnace.—This is a modified Rival furnace. The muffle fire-box has been dispensed with and the flame from the hearth, instead of passing underneath, is diverted upwards and along the muffle flue before going to the stack.



KNIPHOUSE CUPEL FURNACE

SCALE 3/8"=1'

Fig. 19.



THE RIVAL FURNACE

SCALE ⅓" = 1'

Fig. 20.

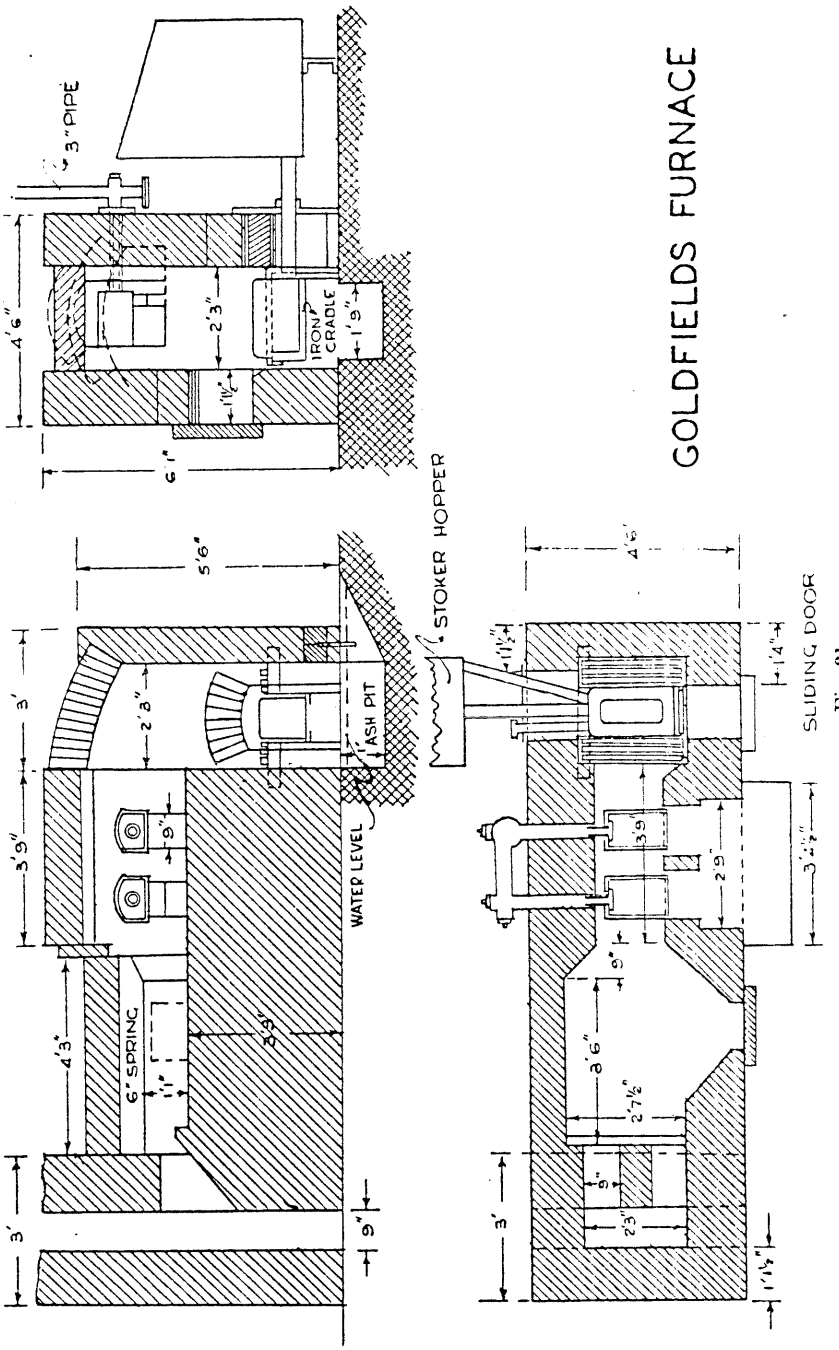

GOLDFIELDS FURNACE
3" PIPE
4'6"
2'3"
IRON CRADLE
1'9"
1½"
6'1"
5'6"
STOKER HOPPER
3'
2'8"
ASH PIT
3'9"
9"
WATER LEVEL
6" SPRING
4'3"
2'9"
3'
9"
4'6"
1½"
1'4"
SLIDING DOOR
3'9"
2'9"
3'2½"
9"
3'6"
2'7½"
3'
9"
2'3"
1'1½"

Fig. 21.

If a good, long-flame coal is used the muffles are adequately heated, but it has the serious disadvantage that cold air is drawn in every time the hearth door is opened, with consequent cooling of the muffles.

The Split-Flame Furnace.—This is a modified Rival furnace. It has only one fire-box and the arch above the fire has an opening through which a portion of the flame passes to the muffles. The remainder of the flame passes over the hearth. This furnace gives excellent results, but great care has to be taken in the splitting of the flame to ensure the even and adequate heating of the muffles.

The Muffle to Hearth Furnace.—A typical example of a single fire-box furnace which heats first the muffles and then the hearth is the Goldfields furnace, which is an elaboration of the older Duplex furnace.

The furnace is similar to a crucible furnace in principle except that the hearth is much longer and the height of the interior is greater at the fire-box end.

The fire-box is supplied with insufficient air to enable complete combustion to take place at this point, but pre-heated air is introduced beyond the fire-box, causing complete combustion of the gases from the coal only as they pass the muffles.

The muffles are fitted into the first section of this hearth where they split the flame. The space between the first muffle and the fire-box acts as a mixing chamber for the hot gases and the pre-heated air, and complete combustion only takes place over the hearth. It follows, therefore, that the greatest heat is at this point. The partial combustion in the muffle

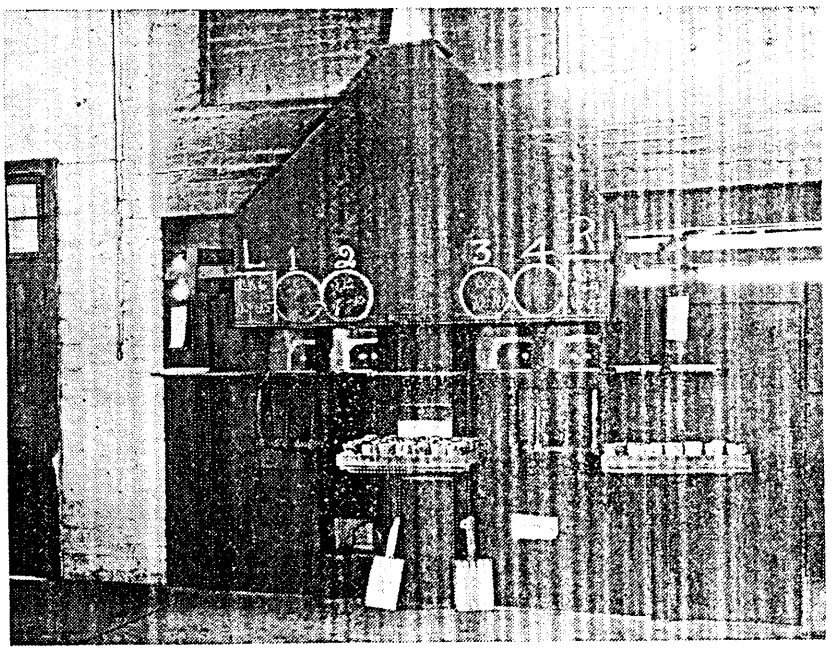


Fig. 22. Rand Leases Furnace.
(With acknowledgment to Rand Leases (Vogels) G.M. Co.)

section is sufficient to maintain the temperature of the muffles which are not cooled down by the entry of the extra pre-heated air. This air is introduced by blowers through flues which run alongside the exit flues of the furnaces, thus heating the air and, incidentally, returning to the furnace, heat which would otherwise be lost.

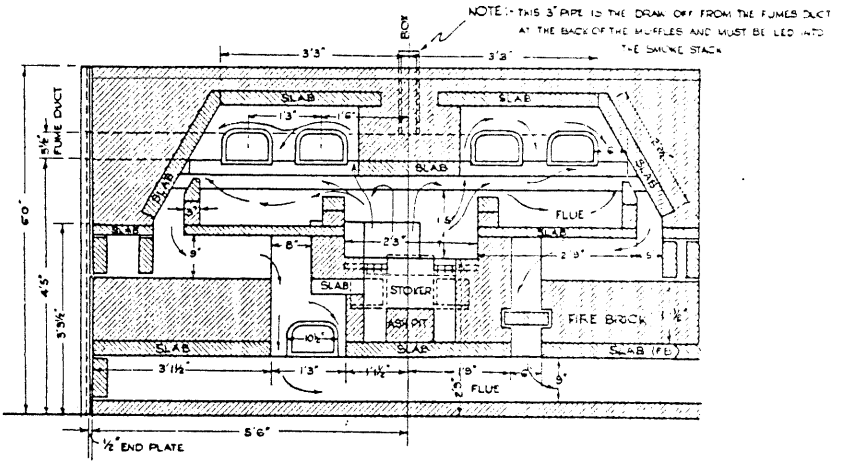
The Rand Leases Furnace.—This is a mechanically stoked, split-flame, furnace having two muffles and a hearth on either side of the fire-box. This design ensures that the two crucible hearths, with their muffles, are equidistant from the source of heat and, as the flame is split into two sections, each travels a shorter distance than is the case with the more usual arrangement.

The fire-box is small and complete combustion does not take place at this point. The burning and unburnt gases fill the heating chambers on either side of the fire-box. These chambers, being comparatively large, permit continued combustion of the unburnt gases to take place.

The muffles are situated near the top of these chambers, virtually dividing each flue into two, one being the section above the muffles and the other being the section between the muffles and the crucible hearth. As combustion takes place throughout the chamber it is heated at all points.

After passing out of the chambers the burning gases travel underneath the thin hearth and thence to a flue which heats a drying oven.

Very little heat is wasted in this furnace, but the somewhat involved flue system makes regular cleaning essential. This cleaning is done through ports which are situated at all the necessary points.



RAND LEASES FURNACE

Fig. 23. Plan of Rand Leases Furnace.

Furnace Room Equipment.

Cupel Tongs and Forks.—For a small number of samples the cupels and lead buttons may be handled with tongs, but where large numbers are handled daily the Monckton Fork and the Monckton Transferrer save time and lessen the possibility of mistakes.

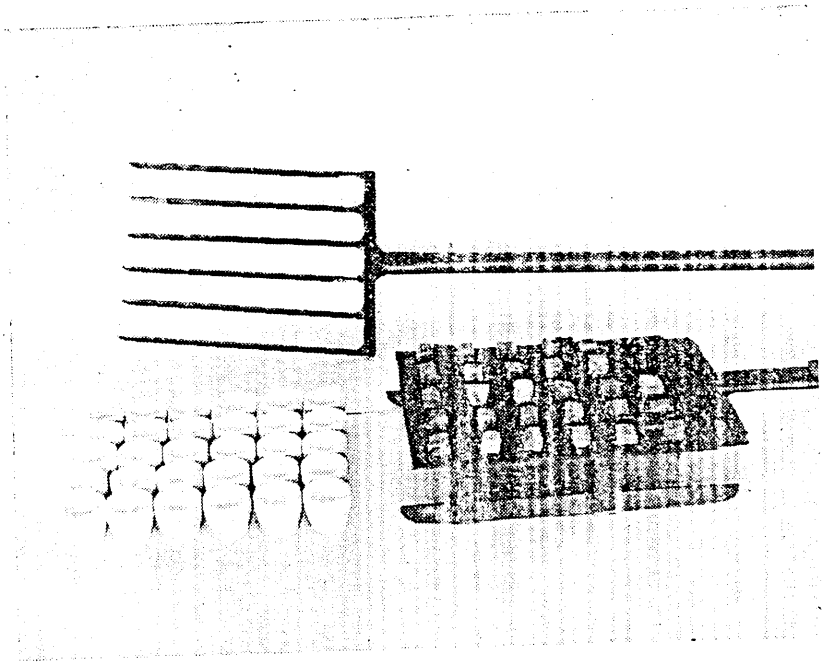


Fig. 24. Cupel Fork and Sleigh Transferrer for loading cupels and lead buttons respectively.

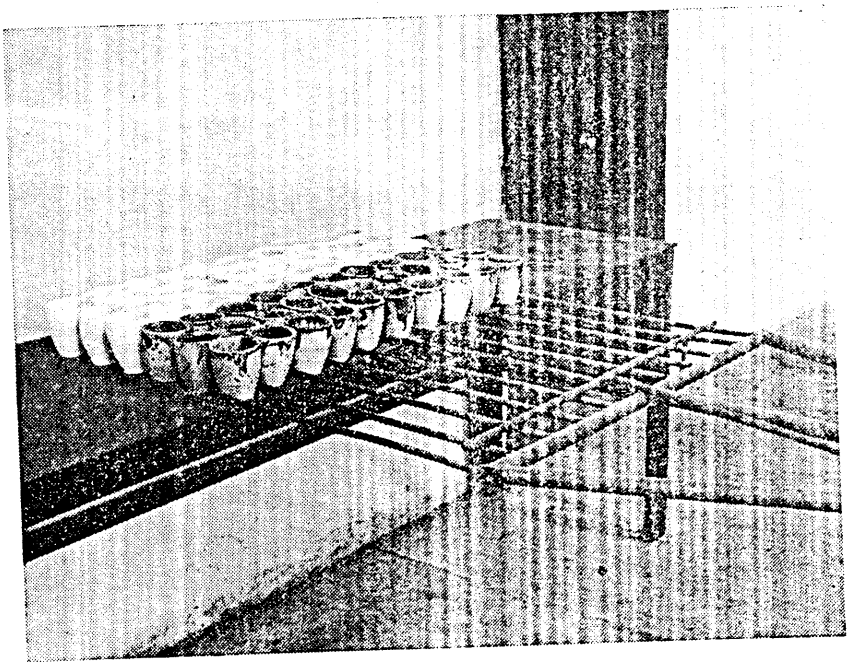


Fig. 25. Crucible Loading Fork.
(With acknowledgment to Geduld Prop. Mines Ltd.)

The Monckton Fork is an implement shaped very like a garden fork with straight prongs. The rows of cupels fit between the prongs and the whole batch is lifted and placed in the muffle at one time. The fork can be designed to handle any number of cupels.

The Monckton Transferrer consists of a tray with a false bottom; the apertures in the tray coincide with the cupels. The tray, loaded with the lead buttons, is placed over the hot cupels, the false bottom is withdrawn and the lead buttons fall into the corresponding cupels.

Scorifier Tongs.—These are similar to cupel tongs, but the end of one prong is U-shaped. This U fits underneath the scorifying dish, while the other prong clamps the dish in position from the top.

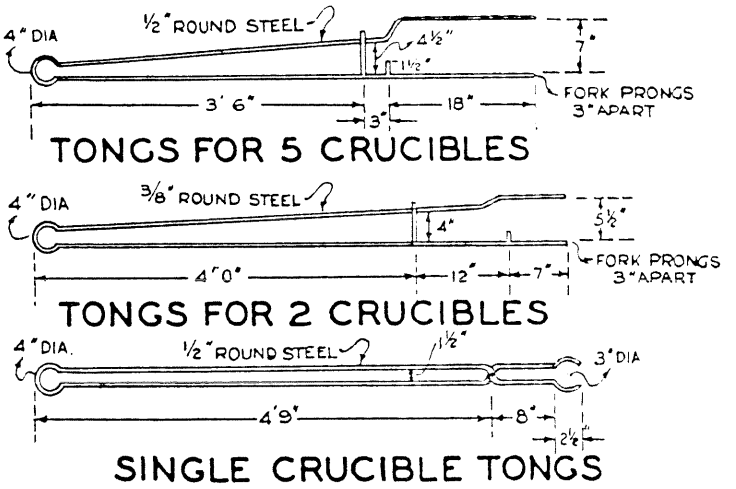


Fig. 26.

Crucible Tongs and Forks.—Crucibles may be loaded one at a time and this, indeed, is the common practice. Recently, however, an adaptation of the Monckton Fork has been designed which loads the required number of crucibles at one time. Owing to the extra weight of the crucibles the fork must be either suspended from a running block or it must be supported by a wheeled framework. To load crucibles in this manner, the door of the furnace must extend the full length of the hearth.

Tongs are used for pouring. These may be of the single or multiple type.

The single type is merely a straightforward pair of tongs which grips one crucible at a time. The multiple type is similar in construction to scorifier tongs, but is larger and longer and has a deeper U. They are used in the same way as scorifier tongs. A line of crucibles is firmly gripped by sliding the tongs forward with one arm of the elongated U on either side of the crucibles and by clamping them in that position with the other prong. The U can be made to hold any number of crucibles, but the tongs become cumbersome when an attempt is made to pour too many crucibles at one time.

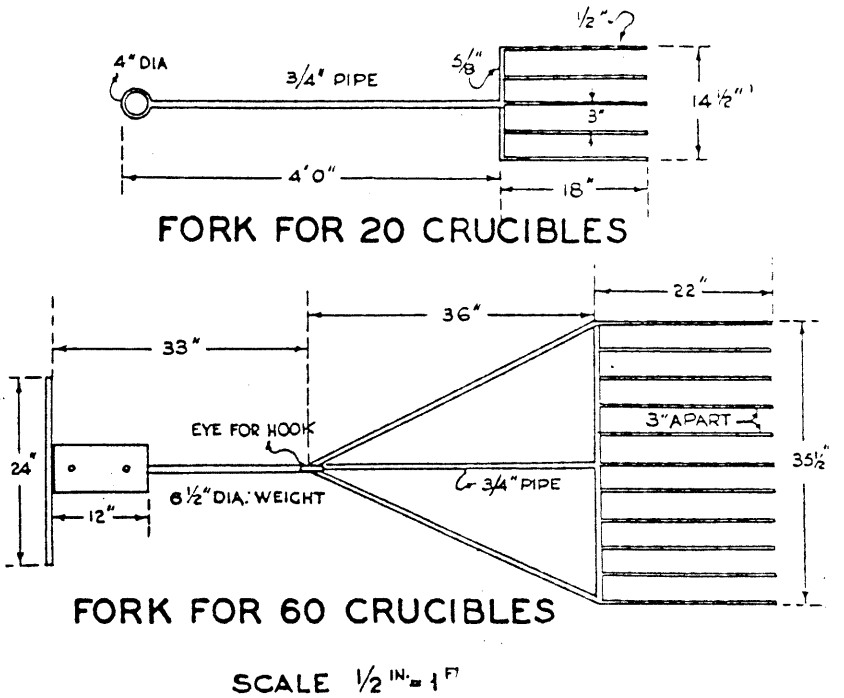


Fig. 27.

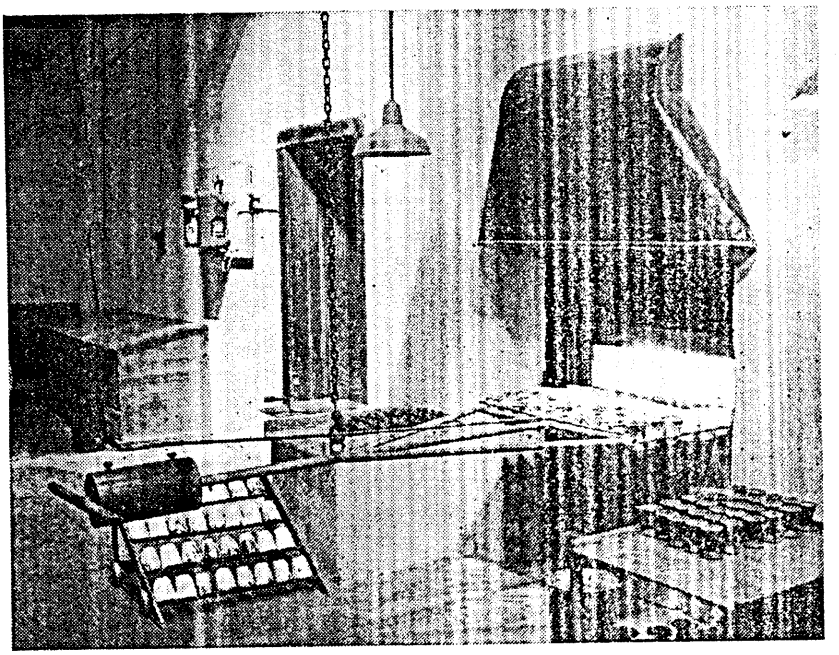


Fig. 28. Crucible Loading Fork.
(With acknowledgment to Geduld Prop. Mines Ltd.)

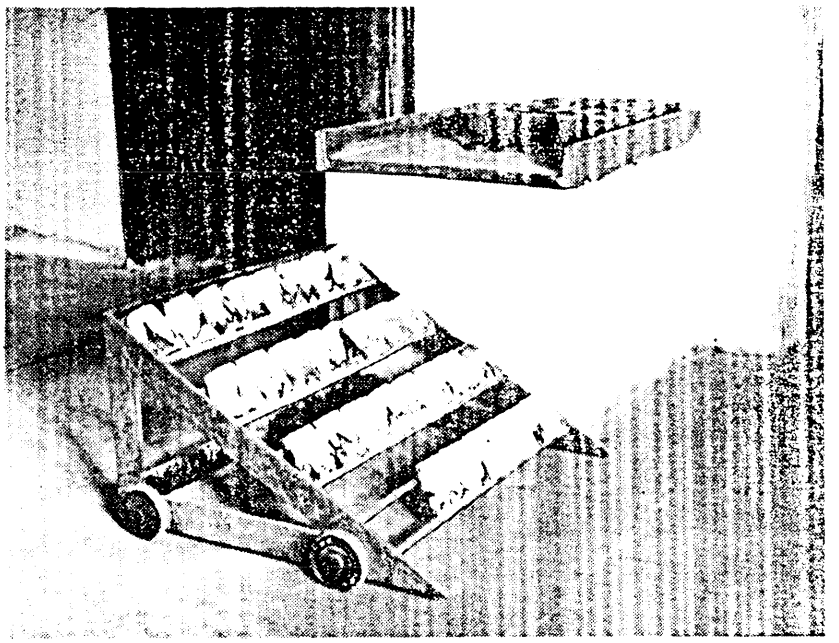


Fig. 29. Draining Rack for Crucibles

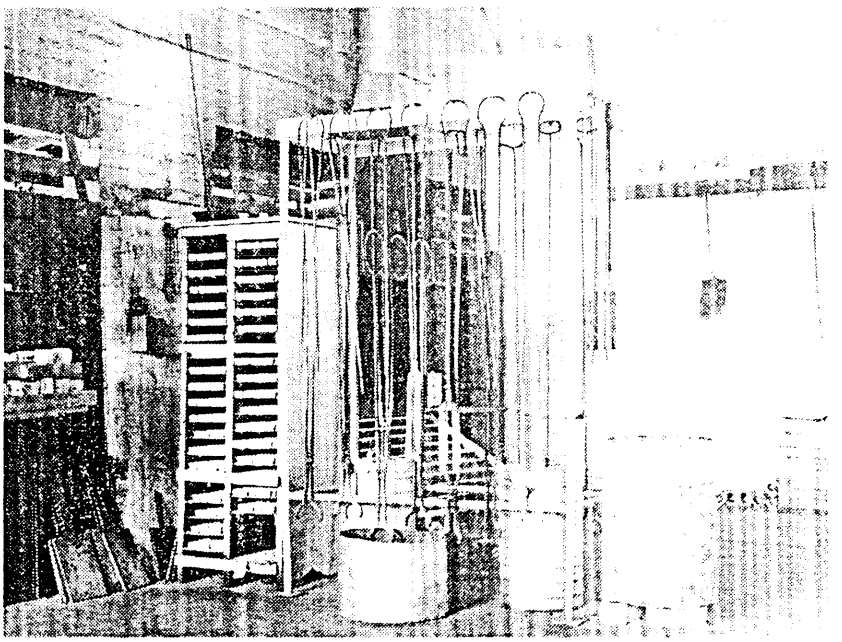


Fig. 30. Rack for Crucible Tongs
With acknowledgment to Baker Perkins (Vogel-Cox) Ltd.

Tables.—Tables in the furnace room should be capable of withstanding the effect of having hot articles placed upon them. Steel tables with heavy cast iron tops have been used with success but tables with flat iron tops tend to warp in time.

The most satisfactory table tops are made of flat strips of mild steel placed on edge. The strips are about $\frac{3}{8}$" wide by $1\frac{1}{2}$" deep and have spaces of about $\frac{1}{2}$" between them. Distance pieces placed at regular intervals help maintain rigidity and the whole is welded to a stout iron framework.

Anvils.—A cheap and very satisfactory anvil can be made by sinking a piece of steel shafting into a concrete block. The end of the shafting should not project more than $\frac{1}{2}$" above the top of the block.

Such an anvil withstands wear and tear and cuts down the noise of hammering to a minimum.

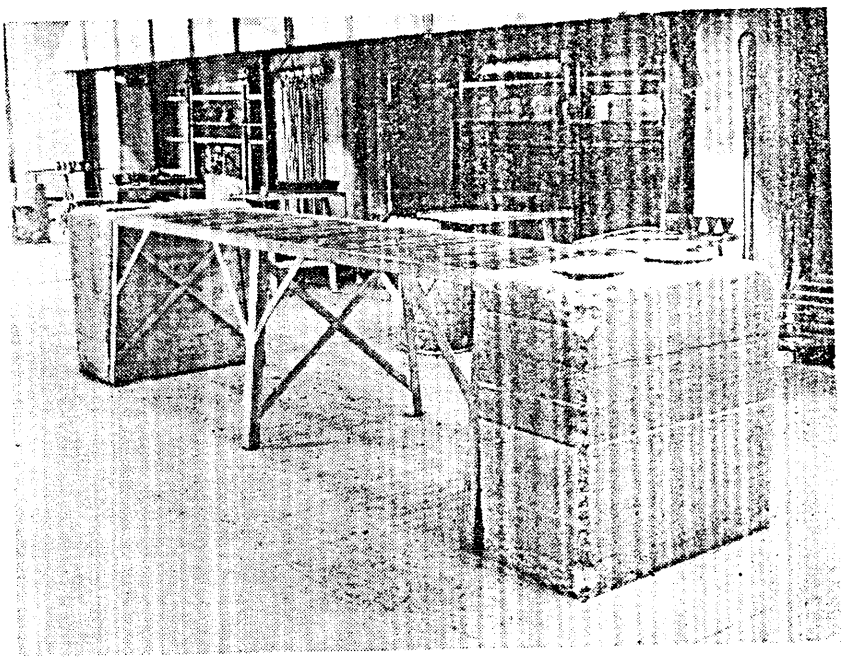


Fig. 31. Anvils and Table for Hot Cupel Trays.

(With acknowledgment to East Geduld Mines Ltd.)

Fume Vents and Fans.—All muffle furnaces should have a cowl fitted above the front of the muffles to take away the lead fumes which are given off as the cupels are withdrawn. A fan should be fitted to ensure positive suction.

Some furnaces are fitted with small shelves above or below the muffles, and the cupels are placed on these shelves until they have cooled below the temperature at which litharge volatilizes.

The action of the fan, being continuous, also assists materially in cooling the atmosphere of the furnace room. Ventilators placed in the roof help to keep the temperature normal.

Another aid is to have the furnace itself outside the furnace room, the front of the furnace being flush with the wall or even recessed slightly. The latter method enables the cowls to be fastened to the outside of the furnace room, with consequent improvement to the appearance of the room.

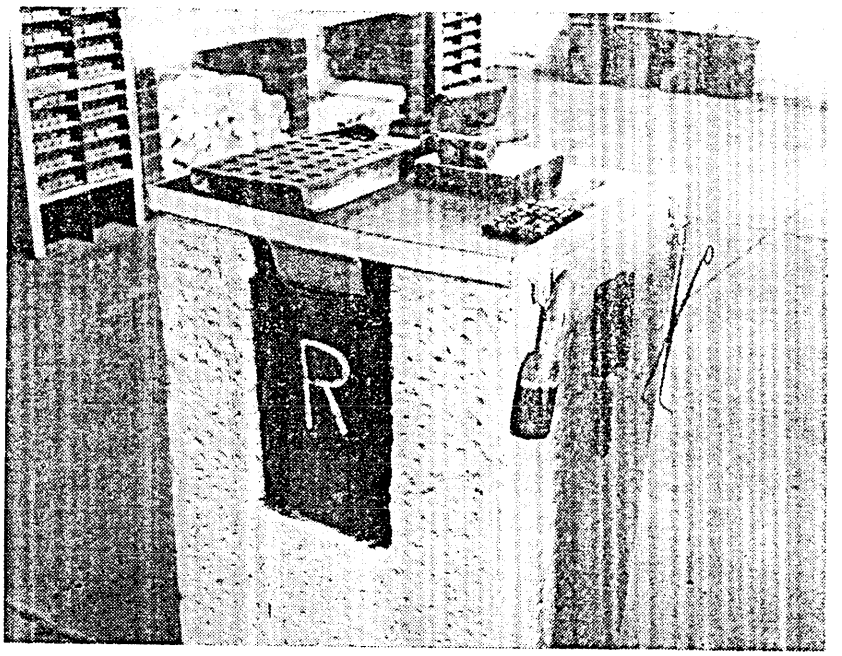


Fig. 32. Anvil with Chute and Receptacle for Slag.
(With acknowledgment to Rand Leases (Vogels) G.M. Co.)

CUPEL MAKING.

On the Rand two types of machines are used for making cupels. The piston press, actuated by compressed air, and the "fly-screw" press.

The following is a description of a compressed-air cupel press which has been used with success on the Witwatersrand.

The machine stands on a table of solid construction, having a surface 24″ × 24″, on which lies a ¾″ base-plate of polished steel of the same dimensions.

A bridge, made of ⅞″ iron plate, 12″ × 20″ in surface and 12″ in height, is fixed on to the base-plate by bolts, passing right down through the table-top. It should be placed somewhat to the rear, in order to leave working room at the front of the base-plate.

A steel cylinder, 6″ in diameter, 14″ in height, is set vertically on the bridge.

Two classes of cupel are made on the mines of the Witwatersrand, viz: (1) A cupel made entirely of calcined magnesite, and (2) a combination of a magnesite surface, with either a cement body or a body made from the unused portion of old cupels. In the latter case the unused portion is knocked off with a hammer and is crushed and ground to pass a 90 mesh screen.

The method of operation is as follows:—

The mixture from which the cupels are to be made should be fine enough to pass a 90 mesh sieve, and the amount of water usually employed is about 10 per cent by weight of the material taken.

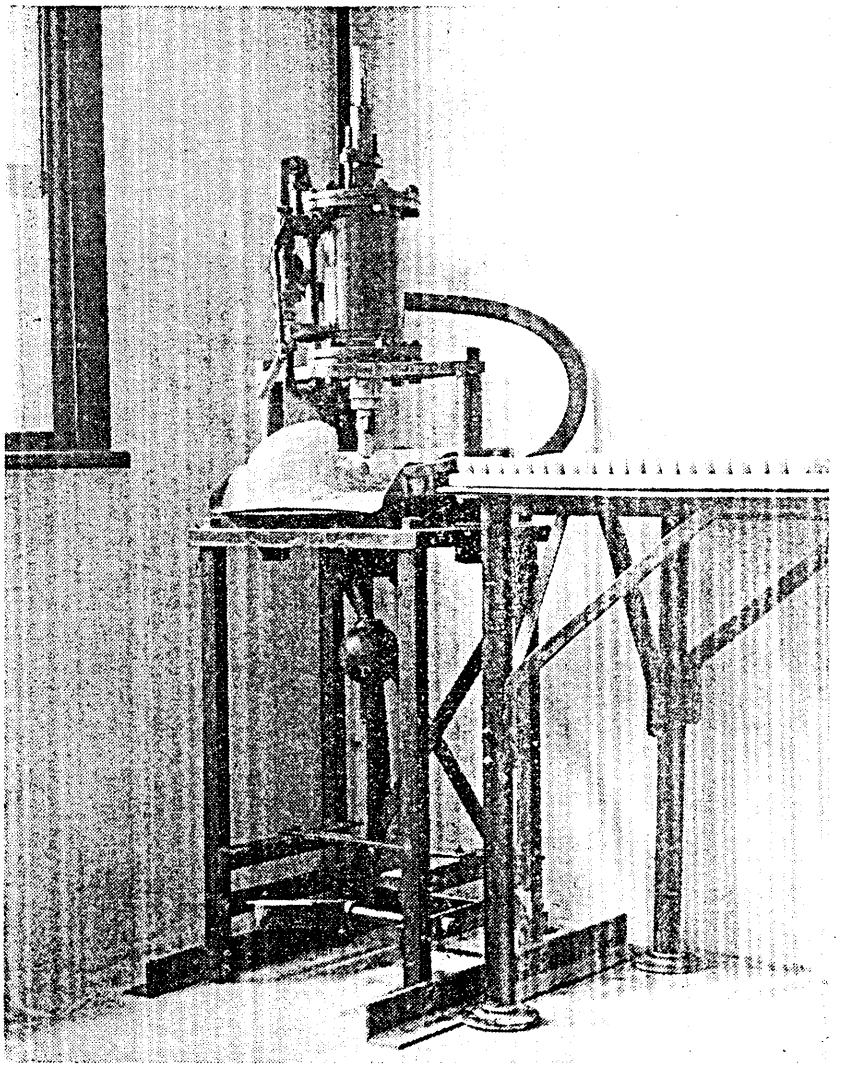


Fig. 34. A Compressed Air Cupel Press.
(With acknowledgment to Geduld Prop. Mines Ltd.)

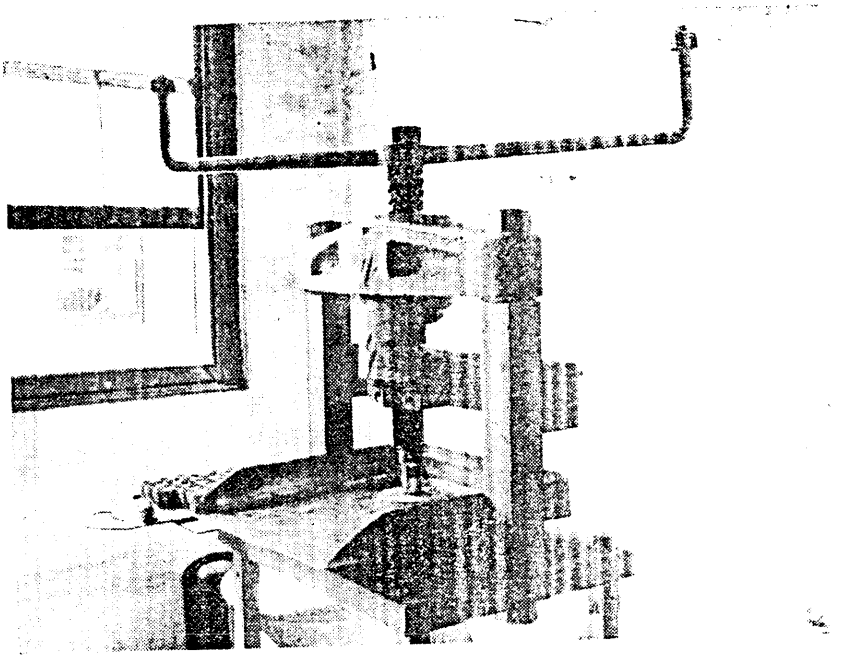


Fig. 35. A "Fly Screw" Cupel Press.
(With acknowledgment to East Geduld Mines Ltd.)

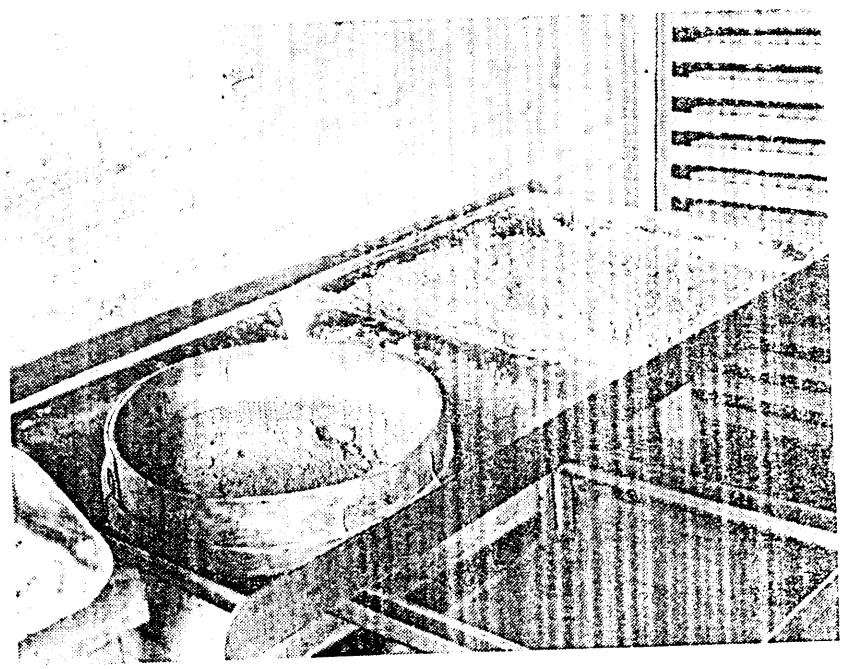


Fig. 36. Trough for Mixing and Sieving Cupel Powder.
(With acknowledgment to East Geduld Mines Ltd.)

The material is thoroughly mixed with the water until the mass is perfectly homogeneous. The mixture is then rubbed through a sieve, having $\frac{1}{8}$" apertures, in order to break up any lumps.

The mould is filled up level with the base-plate, and the scraper attached to the latter is drawn across to remove the surplus material.

The air valve is opened, the piston descends and firmly presses the plunger on to the mixture inside the mould.

When the required pressure is registered on the gauge, the valve lever is reversed, the air escapes, and the piston ascends to its original position.

A gentle pressure on the foot lever raises the false bottom in the mould and lifts the finished cupel from the mould.

The pressure exerted by the piston is generally between 1,000 and 1,200 lb. per square inch.

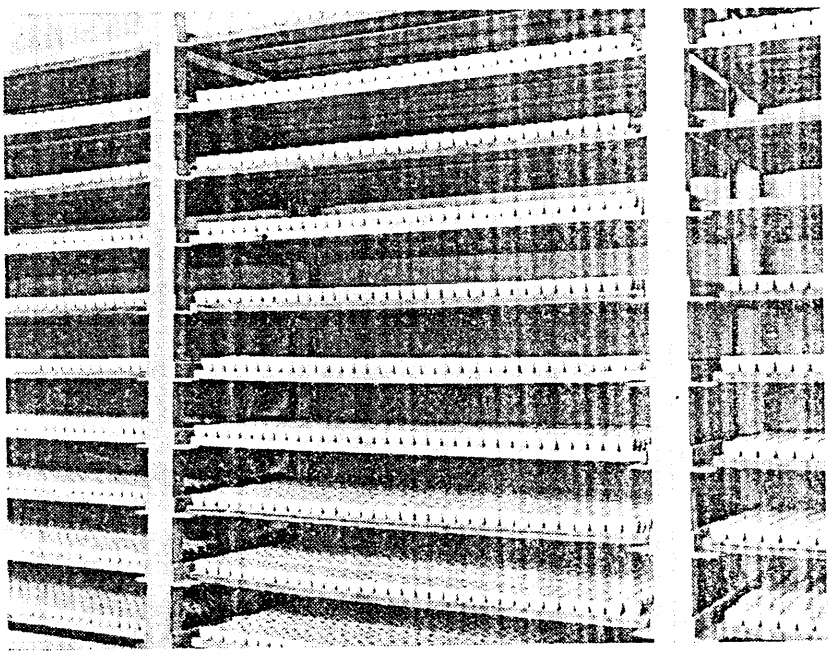


Fig. 37. Cupel Drying and Storage Rack.

(With acknowledgment to Geduld Prop. Mines Ltd.)

(2) The cement used in this class of cupel is passed through a 60 mesh sieve and then mixed with 10 per cent, by weight, of water.

It is advisable to have a small tin of the required capacity with which to measure the moistened cement; the latter should constitute about seven-eighths of the whole cupel.

The cement is placed in the mould and the final layer of magnesite placed on top and levelled down with the scraper; the air is turned on and the operation completed as with the first method. The cupels must be

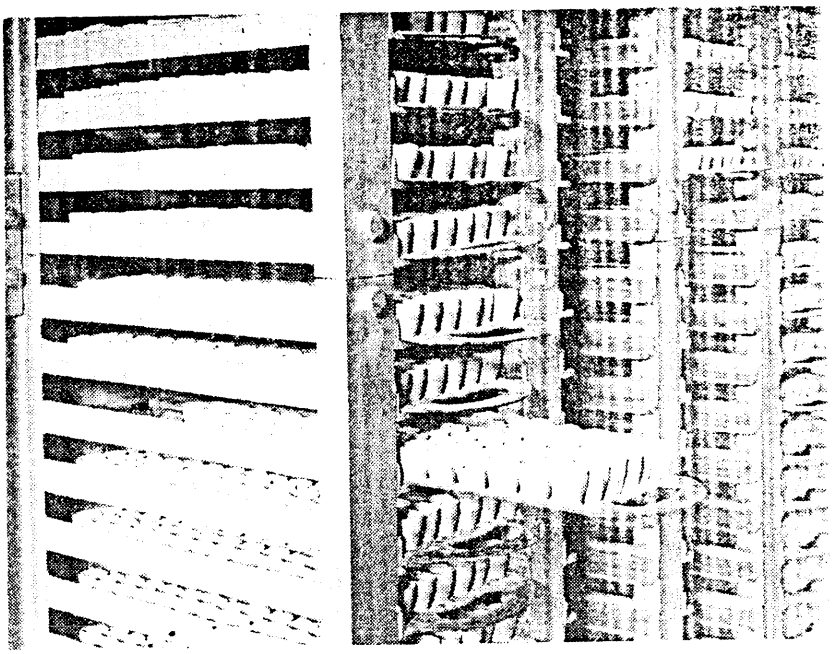


Fig. 38. Cupel Drying and Storage Racks.
With acknowledgment to East Geduld Mines, Ltd.

slowly but thoroughly dried before using. A well-made cupel should absorb practically its own weight of lead oxide.

The other type of machine is an ordinary "fly-screw" press having a three-lead screw (3" pitch) which actuates the punch tool.

The mould block is attached to the foot of the machine swing. Ample pressure (800 to 1,000 lb.) is obtained for the making of the largest-sized cupels used in assaying, the downward impetus of the plunger being considerably augmented by the heavy horizontal arms.

The blocks and dies are identical with those of the air-pressure machine

Chapter IV.

THE BALANCE ROOM.

The determination of mass, or weighing as it is commonly called, is a fundamental step in all analyses and it need hardly be stressed that accuracy in weighing is an essential in assaying. In a mine assay office a large number of weighings has to be carried out daily and, as the operation calls for extreme concentration and care on the part of the operator, conditions in the balance room should be such that efficiency is in no way impaired.

While it is obvious that the assay balance should be set up in such a manner that it may be operated to the maximum of its specified efficiency, it is just as necessary to ensure that the assayer himself works under such conditions that he is able to obtain the utmost from the delicate instrument upon which the accuracy of his work depends.

Fatigue due to concentration for considerable periods, as well as eye-strain, are matters which should be carefully guarded against, and it will be seen, therefore, that comfortable seating, correct height of the balance table, restful efficient lighting and provision against shadow on the instrument are essential. Draughts and variation in temperature and humidity

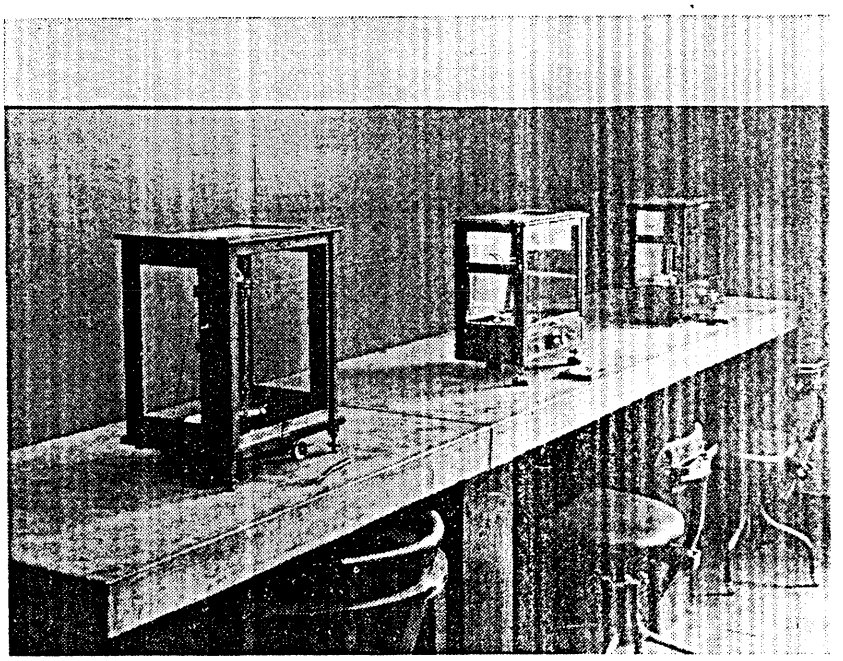


Fig. 39. Balance Bench with Concrete Top.
(With acknowledgment to Geduld Prop. Mines Ltd.)

should be provided against, and noise is a disturbing factor. It might be stated that under ideal conditions no other work than weighing should be carried out in the balance room.

It is common practice on the Witwatersrand to set balances up on slate-topped tables, standing on concrete foundations, separate from those of the building itself. A solidly-built heavy-topped wooden table, its supports resting on concrete piers, has also proved satisfactory, and it is claimed that this type of table or bench is more comfortable from the point of view of the operator. The separate foundations are designed to insulate the balance table from floor vibration.

The provision of natural lighting from windows set high in the walls of the balance room is a feature of modern design. These lights occupy the full length of the room and should be fitted with blinds or curtains to provide control. The light is thrown from behind and above the operator on to the balance, the bench running parallel to the walls.

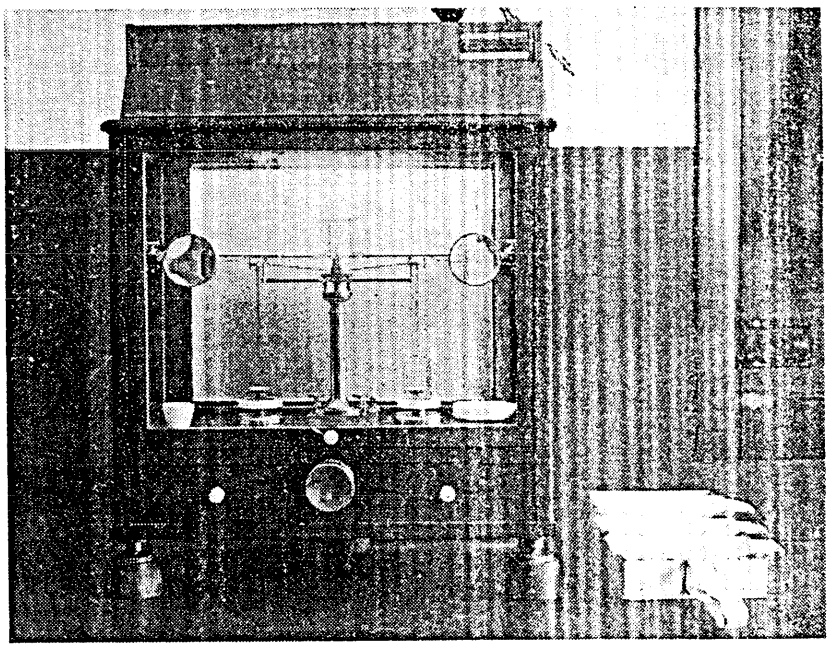


Fig. 40. An Oertling balance fitted with Fluorescent Lighting on Top.

(With acknowledgment to Modder East Ltd.)

The installation of fluorescent lighting for assay balances is becoming increasingly popular, however, and whether provided from powerful tubes on the ceiling or from smaller types fitted to individual balances, it would seem that this form of illumination has rendered all other methods obsolete. The concentration of a light on the beam of the balance, and the absence of shadow, are factors much in favour of fluorescent lighting.

THE BALANCE.

The balance consists, essentially, of a rigid beam or lever, having a central fulcrum and two arms of equal length; the two ends of the beam carry prism edges upon which the balance pans are supported by means of a suitable suspension.

If a body or mass is placed in the left-hand pan the pointer will be deflected. To restore the pointer to its original position, bodies of known mass, termed "weights" are added to the right-hand pan. When equilibrium has been restored it follows from the fundamental laws of mechanics that the body under consideration is equal to the sum of the known masses or "weights" that balance it.

Strictly speaking, the balance determines mass and *not* weight. At any given place, however, the weight is proportional to the mass and it has become customary to employ the term "weight" synonymously with mass.

As an assay balance is a very delicate instrument it must be carefully stored and housed; in practice it is usually kept in a glass case in a special room.

The beam of the balance is constructed with the greatest possible rigidity consistent with lightness. The beam moves about a central point on a horizontal fulcrum, or knife edge, and carries, suspended from either end, a pan, usually made of platinum or aluminium, on one of which—conventionally that on the right—are placed the standard masses, and on the other the body under investigation. The fulcrum of the beam consists of an agate knife edge, resting across two parallel agate planes carried by a central pillar, while the two pans are suspended from agate planes resting on knife edges of similar material. Attached to these agate planes are stirrups and from these are suspended the pans.

The most important constant of a balance is its sensitivity, which may be defined as the increase in the deflection of the beam for a given small additional load on one pan. Maximum sensitivity is attained in practice by having a long beam, by reducing the mass of the beam, by making the distance of the centre of gravity from the central knife-edge small, and also by the use of a long pointer. These conditions, while increasing the sensitivity, at the same time increase the time of oscillation of the beam, and therefore the time occupied in weighing. In general, a compromise has to be made, some of the sensitivity being sacrificed to reduce the time of swing.

In precision balances, one of the qualities mentioned—viz., the distance of the centre of gravity below the central knife edge, is made variable by means of the gravity bob, a nut with milled edge, moving on a screw attached to the beam vertically above the centre.

As the gravity bob is moved up, the sensitivity and time of swing are increased until a point is reached where the balance becomes unstable. The use of very long beams is not so popular now, because equal sensitivity with a shorter time of swing can be secured with a short beam and long pointer. This has been made possible by improved adjustment of the knife edges.

The three knife edges should be exactly parallel and, in general are so arranged that they all lie in the same plane with no load on the balance. If the beam were perfectly rigid the edges would remain co-planar for all loads. In most balances this is not so, and the end edges fall below the central one for heavy loads. For this reason it is sometimes arranged

that the terminal edges are above the central ones for small loads, thus, as the load is increased, the beam bends slightly and the edges become co-planar. With still greater loads the terminal edges fall below. This gives maximum accuracy at medium loads.

The centre of gravity of the loads and balance pans should always be vertically below the knife edges. When not in use the pans of the balance rest on two supports, while the weight of the beam is also taken off the central plane and knife edge.

ASSAY OFFICE BALANCES.

The Fine Assay Balance.

The balance most commonly used on the Rand is the "Oertling 14A", and that is the example chosen for description. The most important part of this instrument is the beam. It is constructed on the most scientific principles, and should never be handled by an inexperienced person. Its principal parts are the *beam proper*; the *pointers*, one at either end of the beam; the *central bearings*, one on either side, front and back, and at right angles to the beam, which are fitted with agate knife edges; the *end bearings* which support the pan hangers, and which are also fitted with agate knife edges; the *adjusting vane*, which is fastened to and movable on a fine threaded rod rising from the top centre of the beam; on this thread and above the vane is fitted the *gravity bob* by means of which the sensitivity of the balance is altered or adjusted.

The adjustment effected by the vane is that of bringing the beam into equilibrium. It may be stated here that with this very sensitive instrument it is a tedious process to bring the beam into equilibrium by means of the vane, hence it is customary to obtain an approximate adjustment by the vane and a final and exact one by placing a half-milligram rider on the left-hand side of the beam.

Both halves of the beam are graduated or divided into ten principal sections numbered from 1 to 10, which are again divided into five subsections.

The adjustment of the sensitivity by means of the gravity bob is effected by screwing the bob upwards away from the centre of gravity to render the balance more sensitive and incidentally increase the oscillation "period". It follows that if the balance is rendered very sensitive its speed is thereby lowered. The object of the adjustor should be to obtain the closest precision compatible with the greatest speed; rapidity, however, must always be a minor consideration with the balance under review. A well-cared-for and perfectly adjusted "Oertling 14A" should turn to one two-hundredth of a milligram. There is a limit of adjustment; should the bob be raised too far the balance is thrown entirely out of gear, but recovery of equilibrium immediately follows the subsequent lowering of the bob.

Next in order of importance and delicacy are the pans and hangers and their bearings. The pans hang from the end bearings of the beam, each having an inverted agate plane which rests on the agate knife edges mentioned above. It will be noted when inspecting the beam that the end agates are two in number at each end. This is to ensure that the agate planes of the hangers shall rest on them without pivoting, which might occur if the knife-edge agates were in one unbroken line. Such pivoting would, of course, at once upset the equilibrium. The hanger is

divided into two sections which hook together. This joint permits the pan to swing without displacing the agate plane and consequently upsetting the adjustment.

The beam support arrests the motion of the beam and brings it to rest with all knife edges and planes very slightly separated. Similarly the pan supports rise from the floor of the balance case and support the pans. This ensures that the knife edges are protected from undue wear and from injury during the transfer of weights, etc., and it is obvious that the balance must never be left swinging except during the act of weighing.

The balance is enclosed in a dust-proof, draught-proof case glazed on all four sides and the top. When weighing gold of more than ·5 mgm. flat weights are used, which are placed in the right-hand pan when the balance is at rest, and the glazed front, raised for access to the inside of the case. When flat weights to an amount within ·5 mgm. of the weight of the gold have been placed in the pan the front of the case is lowered and the final exact reading is made by a ·5 mgm. weight, known as a rider, which is moved along the right half of the beam until equilibrium is reached.

The movement of the rider along the beam with the case closed is effected by means of a sliding rod and a carrier which engages a loop in the rider, enabling it to be lifted from and placed on any part of the right side of the beam. In this balance a similar mechanism is installed on the left side of the beam for the adjusting weight mentioned earlier.

Inside the case and slightly behind the beam pointers, are placed two ivory scales (so-called verniers). Each scale extends to 40 divisions, both above and below the central zero mark. The scales are so placed that when the beam is at rest in its supports the beam pointers both mark slightly above zero. In front of each scale is placed a lens fixed in a focussing slot which renders the reading of the scale easier and more precise.

The floor of the case is made of thick plate glass, and two spirit levels are fixed on the brass stand plate at right angles to each other to assist in adjusting, and to ensure that the beam and it supports are respectively horizontal and perpendicular. This is performed by three adjusting screws which form the legs of the balance case. Brass discs with a countersunk shallow cavity in the centre for these adjusting screws to rest in should form the bases of the supports, and under these discs should be placed pieces of hard rubber about $\frac{1}{2}$" thick.

This balance should never be required to carry more than ·5 gram in each pan at a time, the slightest overstrain of the beam being sufficient to destroy its extreme precision.

Mine Sample Assay Balance.

A typical mine assay balance is the 12 S.B./A. Oertling.

This balance is similar in construction to the one described above, excepting that it is much stronger in build. The main point of difference between it and the "Oertling 14" is that the indicator is vertical and swings like a pendulum across a scale at the base of the supporting pillars, the divisions being coarse enough not to require a lens for exact reading.

This balance has a 6" (15·2 cm.) beam, a maximum pan capacity of two grams, and a sensitivity of ·01 mgm. Its action is much more rapid than that of the "14A".

The beam has a central agate knife edge which rests on two flat agate planes when the balance is in movement. These planes support the ends of

the central knife edge, the balancing point of the beam. The beam is divided, on either side, into 50 divisions, counting outwards towards either end. The pans are carried on loose skiffs, suspended from agate planes, operating on agate knife edges. These planes are grooved at one end and centre-popped at the other, in order to centralize them and allow a constant position to be maintained each time the balance is brought to rest.

The beam rest is actuated by a milled knob in front of the balance case, and functions through a double pillar support. This support carries the graduated scale used for reading the pointer showing the oscillations of the beam. The pointer extends down from the beam centre and moves across the graduated scale. This scale has 20 divisions on either side of a central zero. With this type of balance the possible parallax error is minimized as the operator is seated directly in front of the scale held in the centre of the balance system. This pointer also carries the gravity bob near the top. Most balances of this type have adjusting wheels at the top of the pointer attachment but older models have a vane, similar to the "Oertling 14A".

The Sartorius Assay Balance.

This is an air-damped balance which automatically shows readings up to 0·25 mgm. (representative of five assay dwt.). The beam, which is approximately $3\frac{1}{2}$" in length, is supported in a manner similar to that of the Oertling 12 S.B./A. and when in motion the balancing point is carried on flat agate planes supporting the central knife edge. The beam is marked from "0" on the left hand side to 10 on the right hand side with sub-divisions of 0·1. Using a half-milligram rider, this gives readings from 0 to 20 dwt.

The damping device consists of two aluminium pistons which fit into brass cups. These pistons hang from the stirrups.

Adjustment is made by means of two side wheels, one of which can be operated from outside the balance case. Adjustment for sensitivity is by means of two gravity bobs—a fine and a coarse.

The pointer is replaced by an arm which carries a transparent graticule. The graticule is a glass lens about $\frac{1}{8}$" in diameter and has markings from 1 to 5, with sub-divisions of 0·1, on each side of a central zero.

A beam of light is transmitted from behind the balance through the graticule, thence through a lens and a magnifying glass to a mirror set at an angle to the path of light. This mirror reflects the light back to a second mirror. The second mirror causes the light to travel in its original direction. The final reflection is on a ground glass screen where the shadow of the numbers opposite the beam of light is shown. Down the centre of the screen is a fine vertical line. The screen may be moved in order to place the vertical line exactly opposite the zero mark when the balance is in equilibrium.

When the beam is supported the figures from +2·0 to −2·0 are shown on the screen, the fine line intersecting the figure 0. When it is put into action with empty pans and with the rider off the beam, it will be noted that the right hand side of the beam drops. This is due to the fact that the right hand side of the beam is heavier than the left by a weight representative of 10 assay dwt. The half-milligram rider must, therefore, always remain in position on the beam during weighing.

When a 2 dwt. bead is placed in the pan the graticule will swing the

Checking of Weights and Riders.

For this purpose two sets of weights are required, a standard set of National Physical Laboratory weights and another set, in addition to the weights to be checked.

Method.—Place a standard weight on the right hand pan and a corresponding weight from the other set on the left hand pan. Find the point of rest. Now substitute the weight to be checked for the N.P.L. weight. Again determine the point of rest. As the sensitivity, or in other words the weight value of each division of the balance is known, the difference, if any, between the two points of rest gives the amount by which the weight varies from the N.P.L. weight.

(*Note:* An N.P.L. weight is one which has been weighed by the National Physical Laboratories. A Certificate is issued with the weight giving its exact mass. Thus an N.P.L. weight is not necessarily correct, it is merely one whose divergence from its marked mass is known, and without the Certificate, it is useless as a standard.)

Routine Methods of Weighing.

On the Rand it is customary to adjust the balance until the zero point is at 0 and then to place the bead to be weighed on the left hand pan and to use a rider on the right hand side of the beam. The rider is moved until the rest point is again 0 and the position of the rider is noted. This gives the weight of the bead. For large beads a weight is used in the pan in conjunction with the rider.

In some offices the zero point is a quarter of a division away from the 0, as the balance is adjusted to read as follows:—

	UP	DOWN
	4	− 4
	3	− 3
	2	
	9	− 7
Average ..	3	$-3\frac{1}{2}$

Point of Rest $\dfrac{3 + (-3\frac{1}{2})}{2} = -0{\cdot}25$

In such a case the rider is moved until the swings are the same.

The disadvantage of this method is that if the balance is checked by taking the "up" swing first then all weighings must be done in the same way and unless a fixed method is adopted this may lead to mistakes.

CHAPTER V.

THE CRUCIBLE ASSAY.

THEORY OF THE ASSAY FUSION AND ITS APPLICATION TO THE RAND ORE.

An assay fusion consists in heating a mixture of the finely pulverized ore with about three parts of flux until the product is fluid. One of the ingredients of the flux is litharge (lead oxide), which becomes reduced to minute globules of metallic lead by other constituents of the "fusion". These globules, as they are generated, adhere to the particles of gold in the ore, and when the temperature becomes high enough to make the whole fusion fluid, fall through the mass and coalesce into a button at the bottom of the crucible, leaving, above, a clear molten glass known as slag. Thus the whole of the gold is collected in the button by this "rain" of metallic lead.

The object of the fusion is to convert the gangue of the ore by means of fluxes into a slag which shall be so fluid while hot that the reduced lead globules simultaneously formed shall be certain to fall to the bottom of the mass. The amount of soda used must in practice be at least sufficient to produce sodium silicate (Na_2SiO_3) from the silica present and in addition another low-melting compound should be present (but is not absolutely essential), which in practice is either sodium metaborate, $NaBO_2$ from fusion of borax and soda, or sodium fluoride, NaF from fusion of fluospar and soda. The mixture of silicates and metaborates then melts much more easily than silicate or metaborate taken separately, and so results in a more fluid slag.

NOTE.—Silicates are classified according to the ratio of oxygen present in the base (RO) to the oxygen in the silica (SiO_2).

Name.	*Formula*	*Oxygen Ratio.*
Sub-silicate	.. $4RO.SiO_2$	2 : 1
Ortho- or mono-silicate ..	.. $2RO.SiO_2$	1 : 1
Meta- or bi-silicate	.. $RO.SiO_2$	1 : 2
Tri-silicate	.. $2RO.3SiO_2$	1 : 3
Sesqui-silicate	.. $4RO.3SiO_2$	2 : 3

The meta-silicate, Na_2SO_3 (i.e. $Na_2O.SiO_2$), is more fluid, when molten, than either the sub-silicate or the ortho-silicate, hence the formation of this compound in the assay fusion is to be preferred.

Metallic lead can be reduced from litharge by pyrites alone if this is present in sufficient quantity; the equation

$$FeS_2 + 7PbO + 2Na_2CO_3 = FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$

which represents the action when carbon is not used as a reducing agent, requires litharge equal to 13 times the pyrites. Hence if 30 grams litharge is to be used and fully reduced, the corresponding amount of pyrites is 2·31 grams, which on 1 Assay Ton (see Appendix) of ore equals about 8 per cent. Carbon must, therefore, be used if the pyrites in the ore is

sub = 1:2

Mono = 1:1

Seq = 2:3

Bi = 2:1

much less than 8 per cent, whilst if the pyrites is much over 8 per cent, no carbon should be used, and an oxidant along with metallic iron may become necessary.

The alumina in the ore appears in the slag as an alumino-silicate of the type $Na_2O.Al_2O_3.2SiO_2 = 2(NaAlSiO_4)$, i.e. a compound in which alumina functions as a base. Sodium aluminate is probably not formed unless the quantity of soda used is excessive. All the other bases of the ore (lime, magnesia, ferrous oxide, etc.) form (meta) silicates of the type $RSiO_3$, which have the effect of preventing the mass of the slag (which, as shown above, is sodium metaborosilicate, or sodium silicate, if borax has not been used) from crystallizing on cooling. The final slag is thus a complex glass in which *all* the bases are present both as *borates and as silicates*.

Application to Rand Ore:— Assume that 1 A.T. of ore is fused with 52 grams anhydrous sodium carbonate (equal to about 54 grams of the commercial article, which is usually slightly hydrated) along with 17 grams of borax and 29 grams of litharge, making 100 grams of flux.

The following is known to be contained in the 1 A.T. of ore, assuming it to contain 3 per cent pyrites, and to be an average of the whole Reef:

SiO_2	25·60	grams	
Al_2O_3	1·48	,,	
FeS_2	0·88	,,	
MgO	0·38	,,	
K_2O	0·23	,,	
FeO	0·18	,,	
Water of constitution	0·18	,,	(in sericite)
TiO_2	0·14	,,	
CaO	0.04	,,	
ZrO_2, Cr_2O_3, NiO, CoO, etc.	0·07	,,	together.
Total	29·18	grams	(1 A.T. approx.)

These materials then are to be equated to 52 grams sodium carbonate, with 17 grams borax, 29 grams litharge and the theoretical quantity of carbon required to reduce all the litharge, allowing for the effect of the pyrites.

Theoretical quantity of carbon =

$$\left(\frac{\text{M.W. of C}}{\text{M.W. of 2PbO}} \times \text{grams of PbO in flux}\right) - \left(\frac{\text{M.W. 7PbO}}{\text{M.W.FeS}_2} \times \text{grams FeS}_2 \text{ present in ore}\right) \text{grams}$$

$$= \left(\frac{12{\cdot}0}{446{\cdot}4} \times 29\right) - \left(\frac{1{,}562{\cdot}4}{120{\cdot}0} \times 0{\cdot}88\right) \text{grams}$$

$$= 0{\cdot}47 \text{ grams.}$$

To produce $NaAlSiO_4 + FeSiO_3 + MgSiO_3 + K_2SiO_3 + CaSiO_3$ sodium silicate must first be formed. The quantity of sodium carbonate may then be calculated from the silica present in the ore which is taken for this calculation to be 25·72 grams, i.e. the real silica plus the corrections for counting titania and zirconia as silica.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

Quantity of sodium carbonate required to combine with the silica

$$= \frac{\text{M.W. of } Na_2CO_3 \times \text{grams } SiO_2}{\text{M.W. } SiO_2} \text{ grams}$$

$$= \frac{106{\cdot}0 \times 25{\cdot}72}{60{\cdot}1} \text{ grams } Na_2CO_3$$

$$= 45{\cdot}36 \text{ grams } Na_2CO_3.$$

The pyrites reacts with sodium carbonate as in formula:—

$$FeS_2 + 7PbO + 2Na_2CO_3 = FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$

$\therefore$ 0·88 grams FeS_2 react with

$$\frac{\text{M.W. of } 2Na_2CO_3 \times \text{grams } FeS_2}{\text{M.W. of } FeS_2} \text{ grams } Na_2CO_3$$

$$= \frac{212 \times 0{\cdot}88}{120} \text{ grams } Na_2CO_3$$

$$= 1{\cdot}56 \text{ grams } Na_2CO_3.$$

The borax in the flux will react with sodium carbonate according to the formula:—

$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2$$

$\therefore$ 17 grams $Na_2B_4O_7$ react with

$$\frac{\text{M.W. } Na_2CO_3 \times \text{grams } Na_2B_4O_7}{\text{M.W. } Na_2B_4O_7} \text{ grams } Na_2CO_3$$

$$= \frac{106{\cdot}0 \times 17{\cdot}0}{201{\cdot}2} \text{ grams } Na_2CO_3$$

$$= 8{\cdot}96 \text{ grams } Na_2CO_3.$$

The total sodium carbonate required for these reactions is 55·88 grams.

The basic ingredients of the ore are calculated to their equivalents of sodium carbonate for the purpose of obtaining the total sodium carbonate in the charge.

The basic ingredients and their equivalents are calculated as follows:—

$$K_2O + SiO_2 = K_2SiO_3$$

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

$\therefore$ 1 mol. $K_2O \equiv$ 1 mol. Na_2CO_3

94·2 grams $K_2O \equiv$ 106·0 grams Na_2CO_3

$$0{\cdot}23 \text{ grams } K_2O \equiv \frac{106 \times 0{\cdot}23}{94{\cdot}2} \text{ grams } Na_2CO_3$$

$$= 0{\cdot}26 \text{ grams } Na_2CO_3$$

0·23	grams	K_2O	$\equiv$	0·26	grams Na_2CO_3
0·38	,,	MgO	$\equiv$	1·00	,, ,,
0·04	,,	CaO	$\equiv$	0·08	,, ,,
0·04	,,	NiO or CoO	$\equiv$	0·06	,, ,,
1·48	,,	Al_2O_3	$\equiv$	1·54	,, ,,
0·02	,,	Cr_2O_3	$\equiv$	0·01	,, ,,
0·18	,,	FeO	$\equiv$	0·27	,, ,,
0·53	,,	FeO from FeS_2	$\equiv$	0·78	,, ,,
		Total	=	4·00	,, ,,

The 52 grams of sodium carbonate in the flux is added to this figure making a total of 56·00 grams sodium carbonate present in the charge, but it will be noticed that only 55·88 grams sodium carbonate were required leaving 0·12 grams sodium carbonate which will appear in the slag as sodium orthosilicate (Na_4SiO_4). Thus from the above it will be seen that one assay ton of ore and the 98·47 grams of flux (slightly over 3 parts flux to 1 part of ore) almost exactly match. The total ingredients of the charge are 127·65 grams.

Examination of the fused mass will show:—

(*a*) Metallic lead.
(*b*) Ferrous metasilicate ($FeSiO_3$).
(*c*) Magnesium metasilicate ($MgSiO_3$).
(*d*) Sodium alumino-silicate ($NaAlSiO_4$) including the chromic oxide (Cr_2O_3).
(*e*) The potassium, calcium and nickel metasilicates.
(*f*) The residual sodium metasilicate (Na_2SiO_3).
(*g*) Residual sodium metaborate ($NaBO_2$).
(*h*) Residual sodium sulphate (Na_2SO_4).
(*i*) Residual sodium carbonate calculated as sodium oxide (Na_2O) in sodium orthosilicate (Na_4SiO_4).

(*a*)
$$2PbO + C = 2Pb + CO_2$$
$$446{\cdot}4 \text{ grams PbO} \rightarrow 414{\cdot}2 \text{ grams Pb}$$
$$29{\cdot}0 \text{ grams PbO} \rightarrow \frac{414{\cdot}2 \times 29{\cdot}0}{446{\cdot}4} \text{ grams Pb}$$
$$= 26{\cdot}91 \text{ grams Pb.}$$

(*b*)
$$FeS_2 \equiv FeO$$
$$0{\cdot}88 \text{ grams } FeS_2 \equiv \frac{71{\cdot}8 \times 0{\cdot}88}{120{\cdot}0} \text{ grams FeO}$$
$$\equiv 0{\cdot}53 \text{ grams FeO}$$
$$\text{Total FeO} = 0{\cdot}53 + 0{\cdot}18 \text{ grams.}$$
$$= 0{\cdot}71 \text{ grams.}$$
$$FeO + SiO_2 = FeSiO_3$$
$$71{\cdot}8 \text{ grams FeO} \equiv 131{\cdot}9 \text{ grams } FeSiO_3$$
$$0{\cdot}71 \text{ grams FeO} \equiv \frac{131{\cdot}9 \times 0{\cdot}71}{71{\cdot}8} \text{ grams } FeSiO_3$$
$$= 1{\cdot}30 \text{ grams } FeSiO_3.$$

(*c*)
$$MgO + SiO_2 = MgSiO_3$$
$$40{\cdot}3 \text{ grams MgO} \equiv 100{\cdot}4 \text{ grams } MgSiO_3$$
$$0{\cdot}38 \text{ grams MgO} \equiv \frac{100{\cdot}4 \times 0{\cdot}38}{40{\cdot}3} \text{ grams } MgSiO_3$$
$$= 0{\cdot}95 \text{ grams } MgSiO_3.$$

(*d*)
$$Cr_2O_3 \equiv Al_2O_3$$
$$152{\cdot}0 \text{ grams } Cr_2O_3 \equiv 102{\cdot}0 \text{ grams } Al_2O_3$$
$$0{\cdot}02 \text{ grams } Cr_2O_3 \equiv \frac{102{\cdot}0 \times 0{\cdot}02}{152{\cdot}0} \text{ grams } Al_2O_3$$
$$= 0{\cdot}02 \text{ grams } Al_2O_3$$
$$\text{Total } Al_2O_3 = 0{\cdot}02 + 1{\cdot}48 \text{ grams } Al_2O_3$$
$$= 1{\cdot}50 \text{ grams } Al_2O_3.$$

$$Na_2O + Al_2O_3 + 2SiO_2 = 2NaAlSiO_4$$
$$102{\cdot}0 \text{ grams } Al_2O_3 \equiv 284{\cdot}2 \text{ grams } NaAlSiO_4$$
$$1{\cdot}50 \text{ grams } Al_2O_3 \equiv \frac{284{\cdot}2 \times 1{\cdot}50}{102{\cdot}0} \text{ grams } NaAlSiO_4$$
$$= 4{\cdot}18 \text{ grams } NaAlSiO_4.$$

(*e*)
$$K_2O + SiO_2 = K_2SiO_3$$
$$94{\cdot}2 \text{ grams } K_2O \equiv 154{\cdot}3 \text{ grams } K_2SiO_3$$
$$0{\cdot}23 \text{ grams } K_2O \equiv \frac{154{\cdot}3 \times 0{\cdot}23}{94{\cdot}2} \text{ grams } K_2SiO_3$$
$$= 0{\cdot}38 \text{ grams } K_2SiO_3$$
$$CaO + SiO_2 = CaSiO_3$$
$$56{\cdot}1 \text{ grams } CaO \equiv 116{\cdot}2 \text{ grams } CaSiO_3$$
$$0{\cdot}4 \text{ grams } CaO \equiv \frac{116{\cdot}2 \times 0{\cdot}04}{56{\cdot}1} \text{ grams } CaSiO_3$$
$$= 0{\cdot}08 \text{ grams } CaSiO_3$$
$$NiO + SiO_2 = NiSiO_3$$
$$74{\cdot}7 \text{ grams } NiO \equiv 134{\cdot}8 \text{ grams } NiSiO_3$$
$$0{\cdot}02 \text{ grams } NiO \equiv \frac{134{\cdot}8 \times 0{\cdot}02}{74{\cdot}7} \text{ grams } NiSiO_3$$
$$= 0{\cdot}04 \text{ grams } NiSiO_3$$
$$\text{Total } K_2SiO_3, CaSiO_3 \text{ and } NiSiO_3 = 0{\cdot}5 \text{ grams.}$$

(*f*)

1·30 grams	$FeSiO_3$	contains	0·59 grams	SiO_2	
0·95 ,,	$MgSiO_3$	,,	0·57	,,	,,
4·18 ,,	$NaAlSiO_4$	,,	1·77	,,	,,
0·38 ,,	K_2SiO_3	,,	0·15	,,	,,
0·08 ,,	$CaSiO_3$	,,	0·04	,,	,,
0·04 ,,	$NiSiO_3$	,,	0·02	,,	,,

Total silica = 3·14 grams.

Therefore 25·72 — 3·14 grams silica is left to combine with sodium carbonate to form sodium metasilicate.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$
$$60{\cdot}1 \text{ grams } SiO_2 \equiv 122{\cdot}1 \text{ grams } Na_2SiO_3$$
$$22{\cdot}58 \text{ grams } SiO_2 \equiv \frac{122{\cdot}1 \times 22{\cdot}58}{60{\cdot}1} \text{ grams } Na_2SiO_3$$
$$= 45{\cdot}87 \text{ grams } Na_2SiO_3.$$

(*g*)
$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2$$
$$201{\cdot}2 \text{ grams } Na_2B_4O_7 \equiv 263{\cdot}2 \text{ grams } NaBO_2$$
$$17{\cdot}0 \text{ grams } Na_2B_4O_7 \equiv \frac{263{\cdot}2 \times 17{\cdot}0}{201{\cdot}2} \text{ grams } NaBO_2$$
$$= 22{\cdot}2 \text{ grams } NaBO_2.$$

(*h*)
$$FeS_2 + 7PbO + 2Na_2CO_3 = FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$
$$120{\cdot}0 \text{ grams } FeS_2 \equiv 284{\cdot}2 \text{ grams } Na_2SO_4$$
$$0{\cdot}88 \text{ grams } FeS_2 \equiv \frac{284{\cdot}2 \times 0{\cdot}88}{120{\cdot}0} \text{ grams } Na_2SO$$
$$= 2{\cdot}08 \text{ grams } Na_2SO_4.$$

(*i*) $2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2$

212·0 grams $Na_2CO_3 \equiv 184{\cdot}1$ grams Na_4SiO_4

$0{\cdot}12$ grams $Na_2CO_3 \equiv \frac{184{\cdot}1 \times 0{\cdot}12}{212{\cdot}0}$ grams Na_4SiO_4

$= 0{\cdot}10$ grams Na_4SiO_4.

Carbon dioxide is evolved from the reactions between:—

(1) Litharge and carbon.
(2) Sodium carbonate and silica.
(3) Borax and sodium carbonate.

(1) $2PbO + C = 2Pb + CO_2$

12 grams C → 44 grams CO_2

$0{\cdot}47$ grams C → $\frac{44 \times 0{\cdot}47}{12}$ grams CO_2

$= 1{\cdot}72$ grams CO_2

(2) $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$

106·0 grams Na_2CO_3 → 44·0 grams CO_2

52·0 grams Na_2CO_3 → $\frac{44{\cdot}0 \times 52{\cdot}0}{106{\cdot}0}$ grams CO_2

$= 21{\cdot}59$ grams CO_2.

(3) $Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2$

106·0 grams Na_2CO_3 → 44·0 grams CO_2

8·96 grams Na_2CO_3 → $\frac{44{\cdot}0 \times 8{\cdot}96}{106{\cdot}0}$ grams CO_2

$= 3{\cdot}72$ grams CO_2.

It will be noted that the sum of the ingredients put in (127·65 grams) almost exactly matches the sum of the products (131·12 grams).

It is to be noted that this theoretical fusion will give the same balancing of the ingredients if the borax is assumed combined with the iron, magnesia and alumina instead of with soda; i.e., instead of aluminium silicate and sodium metaborate we can have aluminium borate and sodium silicate. These alternative mixtures are "borosilicates".

The above is, of course, purely theoretical. It assumes a temperature control which is difficult to obtain in practice. In commercial assaying on the Rand the composition of the flux is, unfortunately, partly dependent upon the local furnace conditions. Hence it is important that the furnace shall be built on a pattern which will ensure that the requisite temperature is easily obtainable at any time.

Fluxes and their Practical Application.

Every assayer should thoroughly understand the principles governing the accomplishment of a satisfactory ore fusion.

Fluxes are divided into two classes:

Basic Flux.	Acid Flux.
Sodium carbonate (Na_2CO_3)	Borax ($Na_2B_4O_7$)
Litharge (PbO)	Silica (SiO_2)
Red Lead (Pb_3O_4)	
Haematite (Fe_2O_3)	
(Fluorspar) (CaF_2)	

A basic ore requires an acid flux, an acid ore requires a basic flux.

Sodium carbonate (anhydrous) fuses most readily, its chief function being the formation of sodium meta-silicate during fusion with the quartz.

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The silicate of soda is readily fusible and makes a clear slag.

1 part of silica requires 1·75 parts of sodium carbonate.

Litharge (PbO) and Red Lead (Pb_3O_4).—These serve several purposes, for besides forming very readily fusible silicates, both basic and double, molten lead oxide readily dissolves most metallic oxides, even those not easily amenable to ordinary treatment. The slags, thus formed, are strongly basic and attack crucible or scorifier, and care should be exercised when using the oxides of lead for fluxing purposes, that enough quartz or silica is present in the charge to counteract this strongly basic influence. As is shown in the theoretical part, this fluxing use of litharge is unnecessary unless the furnace is inefficient or unless shale is present in the sample.

Where, in addition to its use in giving a lead button, litharge is used as a solvent or flux, the fusion should be carried out at a preliminary moderate temperature; too high an initial temperature will cause the molten litharge to run through the charge without performing its work on the quartz particles.

Where an oxidizer is required red lead is preferable to litharge owing to its greater oxygen content. As soon as red lead is melted it splits up into oxygen and litharge.

$$2Pb_3O_4 = 6PbO + O_2$$

As stated before, litharge forms with silica a very fusible silicate, and also forms double silicates.

$$PbO + SiO_2 = PbSiO_3$$

From the equation 1 part of silica requires 3·7 parts of litharge.

Ferric Oxide.—Ferric oxide is infusible until reduced to the ferrous state by means of carbon; in this condition it readily fuses with silica, forming ferrous silicate.

$$2Fe_2O_3 + C = 4FeO + CO_2$$
$$2FeO + SiO_2 = Fe_2SiO_4$$

In its ferrous state, oxide or iron is readily taken up by the mixture of borax and soda.

From the foregoing it will be seen that with heavily pyritic ores, which require roasting, the roasted product will require addition of charcoal and silica to give a satisfactory fusion of the ferric oxide produced.

Borax.—Borax is an acid flux used to dissolve metallic oxides. It is also employed on account of its effect in rendering the slag more fluid. It forms borosilicates with silica, in which capacity it is sometimes classed as a neutral flux.

Silica.—Silica is mainly used in ores where the metallic oxides predominate, or for strongly basic ores. It unites with these forming silicates.

Fluorspar.—Beyond being suitable for refractory phosphates, silicates of alumina (e.g., slime), and certain infusible earths, fluorspar does not appear to be a very active fluxing agent, but to some extent it increases the fluidity of the slag; chemically, it is a neutral flux, and is thus bracketed in the table on the preceding page.

For fluxing purposes 1 part sodium carbonate is the equivalent of 2 parts litharge, or 2 parts borax, and where it is desired to replace one agent by another it should be effected in these proportions.

Testing of Fluxes for Presence of Gold and Silver.

Although most of the litharge and red lead supplied, is bought under a certificate of purity in regard to gold and silver, the assayer should satisfy himself on this point by making occasional tests.

For this purpose the following charge will produce a button of lead weighing about 30 grams:—

Litharge	90 grams
Charcoal	1·3 ,,
Silica	10 ,,
Sodium carbonate	25 ,,

The resultant lead button must be cupelled, too high a temperature being avoided; the bead obtained is weighed, flattened and dissolved in nitric acid to test for the presence of gold which remains undissolved.

Both lead foil and granulated lead should be examined in a similar manner by scorifying, say, 3 assay tons down to about 30 grams and cupelling.

Although other fluxing materials seldom if ever contain gold and silver, there is always the possibility of contamination from outside sources, and it is a wise precaution to run "blank" fusions periodically to obviate any possible chance of error from this source.

These tests should be made on each freshly made up "bulk" of fluxing material.

Fusion.

The object of the assay fusion is to concentrate the precious metals in a button of lead; and to retain the gangue in the slag.

The chemistry of the process has been dealt with and reference will be made only to the mechanical and practical side.

Reverberatory furnaces are generally used on the Rand as this is the only type, so far designed, that can cope with the large number of samples assayed in the average mine office daily.

The fluxed samples are loaded into the furnace by means of tongs or forks. The use of the latter is preferable as the whole batch can be loaded at one time, the complete operation taking less than one minute. The size of the batch varies in different offices, some assayers preferring to fuse 40 crucibles at a time, while others prefer larger batches of up to 80 crucibles.

No special measures to reduce the furnace temperature at the time of loading need be taken, as the introduction of a whole batch of crucibles lowers the temperature sufficiently to prevent a too rapid initial heating.

After loading, the furnace is stoked and the flame passes over the crucibles. This heating from above prevents boiling over and spitting, provided the crucibles are not too full. The fluxed sample should about half-fill the crucible.

The crucibles are allowed to remain in the furnace until they have attained a temperature of between 900° and 1100° Centigrade. Although it is possible for the reaction between the sample and the flux to be completed at about 800° Centigrade, the slag at this stage is not fluid enough

to allow all the lead to sink to the bottom of the crucible. Consequently, the temperature must be raised considerably before the assay is poured, to ensure that no lead is held up in the slag.

It may be said, therefore, that provided the increase in temperature is gradual, the higher the final temperature and the more fluid the slag, the less chance of any hold-up of lead and the better the assay.

The construction of most types of reverberatory furnaces used in Rand offices, and the method of loading the crucibles, aims at preventing too rapid an increase in initial temperature, which, by causing the crucibles to boil over, may lead to appreciable loss. Moreover the effect of this rapid fusion upon the flux reaction must also be considered.

If the temperature is raised suddenly it is possible for the litharge to be reduced before the remainder of the flux has reacted with the sample. Consequently the "rain" of lead may take place before all the particles of gold have been freed from the gangue or the pyrites by the action of the flux, and ineffective collection of the gold particles may result. The mechanical action of boiling caused by the reaction is much more violent in the case of the rapid fusion. This violent action causes the particles of lead to come into contact with one another and coalesce. In a correct fusion, therefore, where the temperature is raised gradually, a "rain" of lead is produced which consists of innumerable small particles; while a rapid increase in temperature tends to produce a much smaller number of large particles.

This effect can sometimes be seen if a single large crucible is placed in a white hot furnace and withdrawn after a few minutes. Occasionally large globules of molten lead are found on the surface of the partly fused sample.

The success of the fusion thus depends largely upon the fact that the "rain" of lead must continue until the flux has completely reacted with the sample, and this is best accomplished by starting the fusion at a low heat, with a gradual increase in temperature until the maximum is reached just before pouring.

Fusion time for a one assay ton charge is usually about 25 minutes while a five assay ton charge takes about 40 minutes.

The crucible farthest from the fire is withdrawn and examined to ascertain whether the fusion of the batch is complete. The fusion should be tranquil and the heat between light orange and light yellow. The contents of the crucible are swirled and if no particles rise to the surface the batch is ready to be poured into cast-iron moulds.

The moulds used are conical in shape and must be clean and lightly oiled to prevent sticking. Some assayers prefer to blacklead the moulds.

After pouring, the crucible should contain no shots of lead. If the sample consisted of clean quartzite the slag should be clear with a green or yellow-green colour. The presence of pyrites makes the slag black but it should still have a vitreous lustre. A dull slag without lustre generally indicates that the sample was incorrectly fluxed or that insufficient flux was used. Iron makes the slag brownish-black, while copper imparts a dull red colour. This copper colour is frequently seen in the slags from solution samples assayed by the cuprous chloride method.

Care must be taken to prevent excessive cooling of the furnace during pouring but if the original temperature was 1000° C. or more, well trained workers can usually pour the whole batch before the last crucible has cooled off too much.

Crucibles are usually withdrawn and poured one at a time by means of tongs, but multiple tongs have recently been developed which enable the operator to pour up to six crucibles at a time. These are more fully described under "Furnace Equipment" in Chapter III.

Preparation of the Lead Button for Cupellation.

After pouring, the sample should be allowed to cool in the mould until the lead has solidified. It is then tipped out and the lead is detached from the slag by striking the junction of the lead and the slag with a hammer.

The cone-shaped lead button is flattened on an anvil to detach most of the adhering slag. This procedure produces a shaped button which the operator can conveniently handle with the cupel tongs. Powdered slag is removed from the anvil by frequent brushing or by allowing a jet of compressed air to play on the surface of the anvil.

Occasionally, during hammering, it may be noticed that the button is brittle. This may be due to several causes but on the Rand is usually a sign of excessive sulphur or a very high proportion of gold in the lead button. In all cases, except the latter, brittleness is an indication that the sample has been incorrectly fluxed and that different treatment is necessary to prevent interfering elements coming down with the lead button. Although the lead button can be purified by means of scorification, it is better to eliminate undesirable elements before or during the fusion. These elements interfere with the cupellation and may cause incorrect assay results.

As mentioned before, however, the most common cause of a brittle lead button on the Rand is the presence of excessive sulphur in the sample. This brittle lead button is almost certain to have been accompanied by a matte, which by holding up some of the gold will lead to a low result. Owing to the large number of samples being handled, it is possible for this matte to escape detection when the lead button is detached from the slag, and for this reason a brittle button should be viewed with suspicion.

If the presence of a matte is detected it can be collected and scorified along with the lead button, but since any departure from the set routine interferes with the flow of work it is better to re-assay the sample after an examination has determined the correct treatment and flux.

Cupellation.

The object of cupellation is to separate the lead from the gold and silver in the lead-gold-silver alloy.

The principle of the process is the oxidation of the lead and the subsequent absorption of this oxide into a small, shallow, porous cup, called a cupel (hence the term cupellation).

The cupel may be manufactured from any material with a high melting point, which is not attacked by litharge, and which is in a granular form. The most common materials used in the manufacture of cupels are bone ash and calcined magnesite, the latter being generally used on the Rand.

A cupel should have a smooth surface and readily absorb its own weight of litharge without cracking. The cavity of the cupel should approximate the surface of a sphere, with a radius equal to half the diameter of the cupel and a depth of three-fifths of the radius.

The separation of lead from gold and silver by cupellation depends upon the high surface tension of the precious metals and the fact that they do not oxidize. This prevents the precious metals from sinking into the

pores of the cupel, while the molten lead oxide is readily absorbed. The lead oxide carries with it, into the cupel, limited amounts of other metallic oxides and the process may, therefore, be used for the purification of bullion. Most of the lead is absorbed by the cupel in the form of litharge but a small proportion is volatilized and carried away as lead fumes.

Cupellation is carried out in a muffle type of furnace. The opening in the back of each muffle, which is connected to the flue, ensures that an ample supply of air for the oxidation of the lead is drawn through the muffle.

The cupels are placed in the muffle which should be heated to between 900°C. and 1,000°C. The cupels are allowed to attain this temperature before being charged in order to drive off any moisture. This is very necessary because cupels are made by mixing the cupel powder with water and then pressing. They are air-dried and a certain amount of moisture invariably remains in the cupel.

When the cupels have attained the temperature of the muffle they are charged with the lead buttons. The position of the cupels in the muffle should correspond to that of the buttons on the tray. The lead may be placed in the cupels by means of tongs or by means of a Monckton transferrer. The transferrer is to be preferred as it charges the whole batch of cupels simultaneously. If the charging is done singly by means of tongs the cupels at the back of the muffle should be charged first as this means that the buttons are being passed over empty cupels and should one be dropped it does not fall into a cupel that already contains a lead button.

The button melts within a few seconds and the surface is at first covered with a scum of lead oxide. As the temperature rises this cover becomes fluid and is absorbed by the cupel; from this stage the bath of lead presents a bright appearance. Oxidation is now continuous until all the lead has been removed. Some of the lead oxide passes off as a vapour, but the remainder is absorbed by the cupel. The bath of molten lead gradually decreases in size. If other base metals are present, certain of these are oxidised and carried into the cupel by the litharge. Others, however, are left behind and, as the size of the lead bath diminishes, form a ring around the hollow of the cupel. This ring is called a scoria. Some lead is invariably retained by the scoria and is only absorbed after the lead bath has receded. Consequently the gold contained in such lead is left in the scoria. As these particles of gold are microscopic in size, it is impossible to detect them and an incorrect assay results. For this reason it is necessary to re-assay any sample which leaves a scoria, using a method which will remove the offending metal before cupellation. The most common scoria-forming metal found on the Rand is nickel, which is associated with the pyrrhotite found in the Main Reef. Nickel forms a distinctive green scoria and can be eliminated by scorification of the lead button prior to cupellation.

When all the lead has been removed the bead loses its brilliant appearance and looks somewhat duller. If the bead consists mainly of gold the cupel may be withdrawn immediately, but if it is predominantly silver more care must be taken as molten silver dissolves or occludes oxygen. This oxygen is given off when the bead solidifies and gives rise to minor eruptions which may cause loss of silver and gold. This phenomenon is known as "vegetation". This can be prevented by withdrawing the cupel by degrees or by placing a second hot cupel over it and then withdrawing. This prevents rapid cooling.

A small amount of copper added to the lead will prevent "vegetation".

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Therefore, when dealing with samples known to contain a large percentage of silver, it is customary to add copper to the lead.

The presence of silica in the lead, usually due to incomplete removal of the slag before cupellation, causes corrosion of the cupel and results in the surface of the cupel becoming pitted. This may cause the bead to split into two or more pieces. As some of the particles of gold may be too minute to be detected this breaking up of the bead must be avoided at all costs. If the amount of slag is large it will form a globule which covers the bead. In either case a re-assay becomes necessary.

Temperature of Cupellation.—The muffle temperature during cupellation plays an important part and should be carefully studied, especially when the silver value is required.

All metals will volatilize if the temperature is high enough but it may be accepted that when two metals, having different melting points, are alloyed and heated, the one with the lower melting point has a protective effect on the other.

Thus if a mixture of lead, silver and gold is melted in a cupel very little silver or gold will be volatilized while there is still an appreciable amount of lead present. As the proportion of lead decreases, however, so the volatilization of silver will increase.

Therefore if the silver value is required, the final temperature of cupellation should be below the melting point of silver, because at the end no lead remains to protect the silver.

Similarly, in the cupellation of a lead-silver-gold button, where only the gold value is of importance, the muffle temperature could be higher because of the protection afforded by the lead and silver. Although gold will volatilize, the loss will be extremely small while a large proportion of silver remains in the alloy.

It can be seen, therefore, that the temperature of cupellation depends on the type of assay being performed.

In the assay of by-products and bullion, for example, where both the gold and silver values are required, the cupellation should be completed at a temperature of approximately 900°C.

Mine samples are not, as a rule, parted and an allowance is made for the amount of silver in the bead. Since this allowance, or silver factor, is determined by assaying a collection of mine sample beads, it follows that all samples to which this factor is to be applied must be assayed under similar conditions of cupellation temperature. It is important, therefore, that this temperature should not only be the correct one for the type of assay being performed, but should also be constant from day to day.

In the case of reduction works samples, where the excess silver added for parting purposes allows a certain latitude in cupellation temperature, the importance of these assays makes it essential that a uniformly correct cupellation temperature be maintained.

For reduction works samples, therefore, as well as for mine samples a muffle temperature slightly below the melting point of gold, or between 950°C. and 1,000°C., should be aimed at. Automatic heat control by a thermostat is an advantage.

Parting.

Parting is the name given to the process of removing, by means of acid, the silver from a silver-gold alloy, or silver and platinum from a silver-platinum-gold alloy or gold from a gold-osmiridium mixture.

Silver is readily soluble in hot dilute nitric acid and in concentrated sulphuric acid.

Platinum and gold are soluble in aqua regia, while nitric acid readily dissolves a platinum-silver alloy.

In this process the soluble metal must predominate in the alloy. The need for this predominance can be seen when the nature of such an alloy is considered.

As an example, let us consider a gold-silver alloy in which the silver predominates. This alloy consists of many crystals of silver completely enclosing the crystals of gold. When this alloy is attacked by nitric acid, the acid has access to all the silver because as each crystal is dissolved the way is opened to the next until all the silver has been removed.

If the gold predominates, however, only the silver crystals on, or near, the surface of the alloy will be dissolved and the acid will be unable to attack the remainder because they are totally encased by the gold crystals.

It is for this reason that when gold is the predominant metal sufficient silver must be added to the alloy to reverse this condition. This addition of silver is termed "inquartation".

It also follows, that if the gold is present in sufficient quantity for the crystals of that metal to be in contact with each other, it will remain as a spongy mass when the silver has been removed by the acid; but if the silver predominates to such an extent that the crystals of gold have no contact with one another, the gold will be left as a fine powder after the removal of the silver.

The ratio of silver to gold is of great importance, and the assayer endeavours to produce a bead in which the proportion of silver is sufficient to part the bead completely without causing it to break up.

The critical mixture for silver and gold is a proportion of 2½ silver to 1 of gold. If the proportion of silver is less than this, parting will be incomplete, while a higher proportion of silver will cause the gold bead to break without increasing the amount of silver dissolved.

The breaking of the bead causes much inconvenience during weighing and increases the danger of losing small pieces of gold.

The parting of gold from a gold-osmiridium mixture differs from the above because the one metal is dispersed through the other without being alloyed, and the ratio of gold to osmiridium is, consequently, of no importance.

Parting: Method.—The bead is flattened on an anvil and dropped into hot, dilute nitric acid. The acid is boiled for a standard period, usually ten minutes.

As with most processes in assaying, the silver content of the parted beads must be kept constant. This is achieved by standardizing the method of parting. All beads are hammered to a uniform thickness, the period of boiling is the same for all samples and the strength of the parting acid is not varied.

It is impossible to remove all the silver from the bead by boiling in nitric acid, but this slight "gain" is balanced by the small losses which occur during fusion and cupellation.

It is possible to determine the amount of silver remaining in the parted beads by assaying a collection of these beads in a manner similar to a bullion assay and the loss occurring during fusion and cupellation can also be estimated by assaying synthetic samples containing known amounts of "check" gold.

For example, if a particular method of parting shows a "gain" of 1·5 per cent and the weight of the final bead, which is thus known to contain 1·5 per cent of silver, agrees with the amount of "check" gold added to the synthetic sample, it can be said that the "gain" exactly balances the losses.

It has been found that the silver content of what is considered a well-parted bead is in the vicinity of 1·7 per cent. but if the time of boiling is altered the silver content may vary from 1·5 to 2·5 per cent. If the acid temperature is allowed to fall below the boiling point of water, the silver content may be as high as 5 per cent, although the bead may appear to be parted.

For this reason particular attention should be paid to the parted bead before annealing, because it is easy, at this stage, to judge whether the bead has completely parted or not.

Annealing.

After parting, the sponge gold will disintegrate at a touch, unless it is annealed. Annealing causes the bead to contract and become more coherent. The beads are annealed by heating to a temperature not in excess of 1,000°C., i.e., just below the melting point of gold. Annealing can be done at temperatures much lower than this but the time taken is longer. After annealing, the beads should be malleable and have a bright golden colour. Care should be taken not to melt the beads.

Weighing.

The ability to use the assay balance correctly is acquired with practice, but it is essential that the theory of weighing should be thoroughly understood. The balance and the method of using it, is described in the section dealing with the balance room. The following observations deal with the practical aspects not mentioned elsewhere.

The assay balance is very susceptible to variations in weather conditions and should be insulated from changes of temperature as much as possible by even heating of the balance room.

The balance must be cleaned and checked before the start of each day's weighing and should be checked frequently during weighing.

Each bead will have a certain amount of cupel material adhering to it. Unparted beads should be hammered to remove as much of this adhering material as possible. Once again the question of standardization is important and it is essential that an absolute minimum be left adhering to each bead as this is the only method by which a constant factor can be calculated.

It is advisable that the assayer should be taught to use the balance correctly in his early training. He should be required to weigh accurately from the start and practices such as weighing to the nearest pennyweight should be allowed only after the correct technique has been thoroughly mastered.

Chapter VI.

THE SAMPLING, TREATMENT AND ASSAY OF SAMPLES FROM THE REDUCTION WORKS.

Introduction.

A constant check on the efficiency of Reduction Works practice is maintained by sampling the ore at different stages of the process, and carrying out grading analyses and assays on the samples taken.

The determination of the correct assay value of the different products is of primary importance, since these values show the amount of gold being sent to the Reduction Works as well as the efficiency of the extraction methods. In conjunction with the tonnage figures these values are used to calculate the amount of gold which should be produced, or the "gold called for" as it is termed. Moreover, these samples indicate, by means of the grading analyses, the crushing efficiency of the stamp mill, crushers, tube mills, etc.

It can be seen, therefore, that the taking of accurate and representative samples is a matter of paramount importance. (See "Gold Metallurgy on the Witwatersrand" by A. King.)

Methods of Sampling.

Pulp or Screen.—To sample a stream of pulp it is necessary that the stream should overflow from a projecting edge or lip. The sampling vessel, which is usually triangular in section with a narrow slot at the top, is passed transversely through the falling stream, thus removing a representative portion. Best results are obtained by taking increments at regular intervals during the shift. The sampling vessel should be smooth inside, easy to clean and large enough to ensure that no overflow takes place from the sampler during the taking of the sample. The width of the slot on the top of the sampler should be at least four times greater than the diameter of the largest grain of pulp. The increments taken during the shift are collected in a suitable container (e.g. an enamel bucket) which is kept for that purpose.

Rod or Tube Samples.—To sample slime in a tank a rod or tube sampler is used. This is a pipe, 2″ in diameter, long enough to reach the bottom of the tank, and fitted at its lower end with a rotary foot valve.

The sampler, with the valve open, is pushed down through the slime until it touches the bottom of the tank. The foot valve is closed by twisting the rod. The sample is then withdrawn and run into a suitable container. This process is carried out along a radius of the tank, starting at the centre. Experience and local conditions determine the number of increments to be taken for a representative sample.

Butters Slime Residue Sample.—The sample of Butters slime residue is usually taken by scraping off a small section of the cake, at various points, from leaves selected at random.

The sampler is a scraper, long enough to reach at least half-way down the cake and fitted with a narrow blade which can be passed between the caked leaves.

Sample from Rotary Filters.—In most Reduction Plants the Butters filter has been superseded by the rotary filter. These rotary filters are sometimes installed in two parallel rows with a conveyor belt, running between, carrying the residue to a sump for pumping to the slimes dam.

The sample is taken by placing a rectangular enamel dish on the conveyor belt. The length of the dish is equal to the width of the conveyor belt, and it travels down between the filters. As the residue drops off each filter, portions are caught in this travelling dish. These samples are taken at regular intervals during the shift.

Sample from the Residue Discharge Column.—The sampling of the residue from the residue discharge column is a method which is becoming increasingly popular.

A 1″ pipe, connected to the residue discharge column, allows a continuous stream of residue to by-pass into a return launder. An automatic sampling device samples this stream at regular intervals. The type of automatic sampler used at this point can be varied to suit the circumstances, but the tilting box type of sampler, introduced at the Modderfontein B Gold Mine, is one which is found to be very efficient.

This sampler consists of a V-shaped beam which tilts on a horizontal spindle. The beam carries a shallow scoop-shaped water container at one end and a counterweight at the other. The beam is attached by means of a link to the discharge end of a flexible rubber hose which in turn is fitted to the end of the 1″ pipe. Immediately above the scoop end of the beam is a tap or valve which allows a controlled flow of water into the scoop. When the scoop fills it tilts the beam which in turn forces the link backwards and causes the discharge from the attached rubber hose to pass over a sample box placed in the return launder. As the scoop empties, the counterweight tilts the beam back and causes the link to return to its original position and the discharge end of the rubber hose to pass over the sample box again. Each time the hose passes over the box the discharge is caught by the sample box instead of falling into the launder and so two increments are taken with each forward and backward tilt of the beam. It is usual to adjust the flow of water to ensure that the sampler will tilt at intervals of five minutes.

The sample box has two separate compartments, each of which has a half-inch slot on the top. A short pipe is fitted to each compartment to lead the increments to a suitable container. In this way duplicate samples are taken.

Other Mechanical Sampling Devices.

Mechanical sampling devices or automatic samplers can be divided into two general types.

(*a*) Stationary devices which sample part of the stream all the time.

(*b*) Moving devices which sample all of the stream part of the time.

Stationary samplers are not entirely satisfactory since their use presupposes that there is no variation in the character of the part of the stream of ore being sampled. This is very seldom true.

Moving sampling devices sample all of the stream part of the time and this eliminates errors due to variations in the character of the stream across its section and by making cuts at frequent intervals any changes in the character of the ore will be represented in the sample.

Many different samplers of this type are in use, and although some have become standardized, the usual practice is to design and build samplers to suit local conditions.

PRELIMINARY TREATMENT OF SAMPLES.

Except in a few cases where cyanide is present in the milling circuit the only sample requiring preliminary treatment is the slime residue. This differs from other Reduction Works samples in that the moisture it contains is a weak cyanide solution containing gold. To ensure a correct assay it is essential that none of this solution should be lost and since it would be a long and tedious process to dry off this moisture, without loss, the gold in solution is usually precipitated by the addition of cuprous chloride or copper sulphate—sodium sulphite solution. The moisture is then expressed, the sample dried, broken up, sieved and mixed before assay.

The precipitation is carried out by adding 40 to 50 ml. of cuprous chloride to the sample in an enamelled bucket and thoroughly mixing before pressing. Another method in use is to add to the sample of residue 40 to 50 ml. of five per cent copper sulphate, 20 ml. of 20 per cent sulphuric acid and a few ml. of sodium sulphite.

To determine the amount of undissolved gold, a duplicate sample of the residue is taken. This sample is immediately treated with an excess of alkaline potassium permanganate to destroy the cyanide present and to prevent any further solution of gold. It is then thoroughly washed

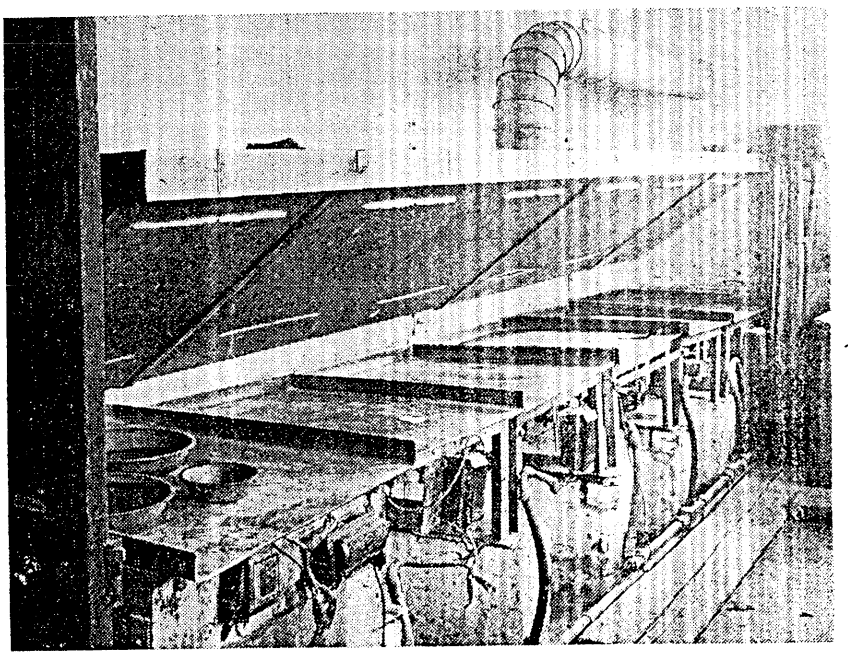


Fig. 41. Hotplates for drying Reduction Works samples with hood for removing dust.

(With acknowledgment to Rand Leases (Vogels) G.M. Co.)

through the press, at least six washings being advisable to ensure that all the gold in solution is removed. Finally the sample is dried, broken up, sieved and mixed before assay.

Drying of Samples.

When the Reduction Works samples are received at the drying department, each sample is thoroughly mixed and emptied into a clean, flat-bottomed, enamel or stainless steel tray, care being taken to see that the whole sample is transferred to the drying dish. The dish is then placed on the drying furnace or hot plate.

A common drying furnace is the coal-fired one with a cast-iron top. Electric drying plates with variable heats are also much used. These are designed either to heat the sample tray or to dry the sample on the hot plate itself.

Whatever method is used, it is essential that too great a heat be avoided. The sample is stirred during drying to prevent "spitting" and also to ensure that no roasting of the lower layers of the sample takes place. Should roasting occur the composition of the sample will be altered. The sample will be lighter and consequently slightly more of it will be taken for assay. For this reason the drying temperature should not be allowed to exceed 150°C. The sample should be removed from the heat just before the last of the moisture is driven off, since there is generally, at this stage, sufficient heat in the sample itself to complete the process of drying.

Crushing and Grinding.

Although certain samples from the Reduction Works require no further crushing or grinding before assay, samples such as the "screen", the "tube mill pebbles", the "conveyor belt", the "waste rock" and the "bin feed" have to be crushed and pulverized.

Crushing is done in a jaw crusher where the large pieces are reduced in size by the "squeezing" action of the crusher jaws.

Grinding or pulverizing is performed in a disc grinder, in which the ore is ground between a stationary and a revolving disc, the final product being thrown out from between the grinding surfaces as a fine powder.

Although it is generally recognised that the finer the material of the sample the better will be the agreement between the individual assays, only samples that are too coarse to be assayed in their original state should be pulverized.

Contamination can be avoided by having a separate pulverizer which is used only for Reduction Works samples, by pulverizing low value samples first and by thoroughly cleaning out the pulverizer between the grinding of each sample. It is excellent practice to crush a low grade ore, after the crushing of each sample, so that any possible contamination can be absorbed by this material.

Dividing and Packeting.

Coning and Quartering.—This method, if carefully carried out, gives very good results.

The crushed material is worked into a cone by shovelling it on to a centre point in such a way that the particles roll down in all directions from this centre point. Irregularities in composition are thus distributed as concentric layers of the cone. This coning may be repeated several times to

ensure thorough mixing of the material. The top of the cone is then flattened by spreading the material equally in all directions. This flattened cone is now marked into quarters and these quarters are separated. Two diagonally opposite quarters are rejected, care being taken to remove each rejected quarter completely.

The remaining quarters are thoroughly mixed and the process of coning and quartering is continued until a sample of suitable size is obtained.

Greater accuracy will be obtained if the size of the particle in the material is reduced to half its previous size between each coning and quartering.

Splitting (or Dividing).—Splitting or dividing is the reduction of a mass by some type of splitter consisting of a series of parallel troughs which alternately retain and reject a series of equal sections from a stream of crushed material poured over them.

The Jones Type of Riffle Sampler.—This sampler gives satisfactory results. It consists of a rectangular hopper supported on a stand. Across the bottom of the hopper is an even number of equally-spaced, steeply-angled chutes. Alternate chutes face the same direction. When the sample is poured into the hopper the material runs down these chutes and is caught by a container on either side and an accurate split is obtained. One half is rejected and the process is repeated until the sample is of the desired size.

When a sample of suitable size has been obtained, it is thoroughly mixed and divided into three portions by taking dips with a spatula. These three portions are placed in separate paper bags, which are marked with the relative information, viz., name of sample, shift, date taken, etc. One sample is sent for assay, another for grading, while the third is stored in case of dispute.

After these samples are assayed they are stored for a pre-determined period of, say, two weeks. It has become customary in many offices to check the standard of work by selecting samples at random and re-assaying them. The results are then compared with those originally reported.

Another method of ensuring that the work is up to standard is to make a composite sample by taking equal portions from, say, all pulps assayed during the month. This composite sample is very carefully assayed and its value compared with the arithmetical average.

SAMPLES.

Screens.—In some plants which have stamp batteries the "screen sample" is looked upon as an important sample since it represents the ore crushed during the previous 24 hours. However, modern practice employs discharge screens of $\frac{1}{2}''$ to $\frac{3}{4}''$ mesh and the reliability of sampling is poor. Hence most plants rely more on samples taken after final grinding. The sample is taken as the crushed ore passes through the screen of the mortar boxes. When the sample is received at the drying room it is allowed to settle, the excess water is decanted off, care being taken to prevent the escape of any slime. It is dried at a temperature not exceeding 150°C. A portion (about 300 grams) is sent to the grading room while the remainder is carefully quartered down until about 1,200 grams remain. This final portion is pulverized to pass 100 mesh, thoroughly mixed and is then ready for assay.

Mill Pulp.—This is the name given to the crushed ore entering the cyanide works, after having passed through the tube-mill classifiers, whence

it flows either to sand and slime separators or direct to slime collectors. This sample is prepared for assay in the same manner as the screen sample but requires no further pulverizing.

The preliminary treatment consists merely in drying, breaking up, mixing and packeting before assay.

Sand Charge.—This sample represents the sand or the coarse portion from which the slime has been separated.

The sample is dried, broken up, quartered if necessary, a portion set aside for grading and the remainder, after thorough mixing, is ready for assay.

Slime Charge.—This is the fine portion of the mill pulp, usually about 70 per cent minus 200 mesh, before cyanide treatment. It is dried, broken up, thoroughly mixed and is ready for assay.

Sand Residue.—This is the sand charge after the extraction of the gold amenable to cyanide treatment. It is prepared for assay in the same manner as the sand charge. To get concordant results it may be necessary to pulverize this sample.

Slime Residue.—This is the slime from which the available gold has been extracted by cyanidation. The moisture in this residue is a weak cyanide solution containing gold. The gold in this solution is precipitated by means of cuprous chloride or copper sulphate (see Preliminary treatment of samples). The sample is pressed, dried, broken up, thoroughly mixed and is then ready for assay.

Washed Residues.—The moisture in both the sand and slime residues is weak cyanide solution and invariably contains gold.

To determine the value of this dissolved gold, the residue sample is treated with an alkaline solution of potassium permanganate to destroy the cyanide and to prevent any further solution of gold. It is then washed repeatedly with fresh water until all the gold-bearing solution has been eliminated. The sample thus washed is assayed for gold, the value representing what is usually called "undissolved gold" and the difference in value between that and the original unwashed residue is called "dissolved gold". The washed samples are prepared for assay in the same manner as their unwashed originals, except that in the case of washed slime residue the precipitation must be omitted.

Tube-Mill Pebbles.—By means of this sample an attempt is made to arrive at the value of the ore being fed into the tube mills to act as grinding media.

One method of obtaining this sample is by catching the small pebbles which have been sufficiently ground to pass through the discharge grating. The pebbles are carefully washed, dried, coarsely crushed, quartered down, pulverized and the sample is then ready for assay.

On some mines, however, a grab sample of the original pebbles is taken as it is found that the ground pebbles are not representative of the original grinding media.

Waste Rock.—This sample gives the approximate value of the rock being discharged to the waste dump.

Under perfect conditions it should contain no gold, but, since the sorting has to be done at speed from a travelling belt, a certain proportion of reef invariably finds its way into the waste rock bin. Other possible sources of

contamination are the presence of adhering "fines" or pieces of reef adhering to the waste.

The sample is treated in exactly the same manner as the tube mill pebbles, special care being taken to avoid contamination from the crushers.

Bin Feed.—This is the crushed rock fed into the tube mills and represents approximately 90 per cent of the tonnage. Close agreement among the individual assays will only be obtained if this sample is carefully taken and very finely crushed.

The treatment is similar to that for tube-mill pebbles.

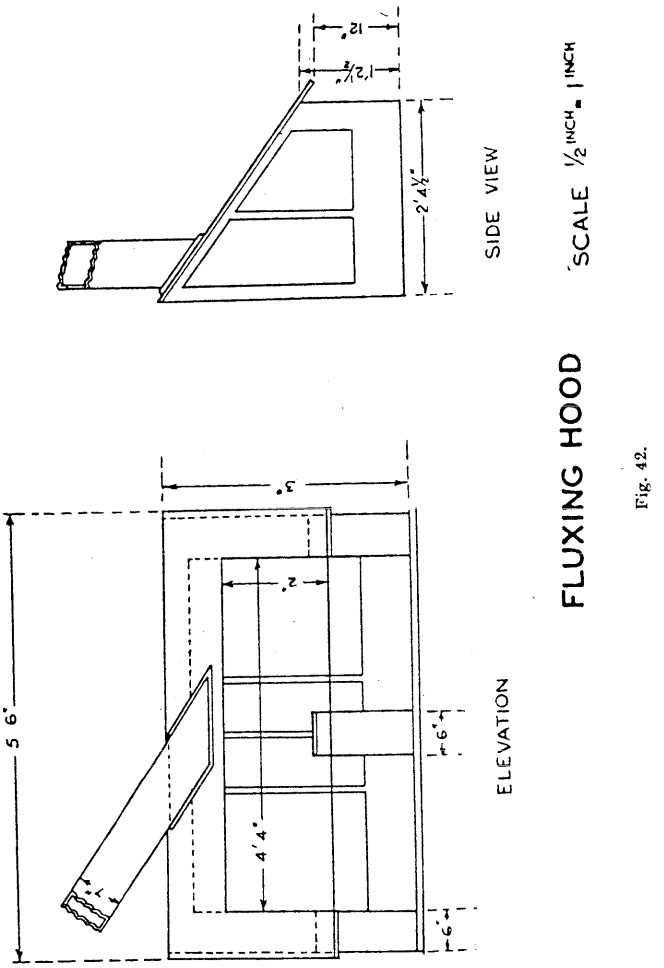


Fig. 42.

FLUXES.

Generally speaking, ores encountered along the Witwatersrand are highly acidic in character and the fluxes used to fuse these ores are, therefore, strongly basic.

A stock flux, which is generally made up in bulk and which is found suitable for most ores encountered in a Rand assay office, is one having the following composition: Sodium carbonate 50 per cent; Litharge 30 per cent; and Borax 20 per cent.

Because of variations in the composition of the ore, (e.g. black reef or other heavily pyritic ore) some assayers vary the proportions of the ingredients of this stock flux to suit local conditions. For example, in the case of a black reef or a heavily pyritic ore, the percentage of sodium carbonate may be reduced and that of litharge may be increased. Again, for reasons of economy, some assayers substitute a cheaper ingredient, such as fluorspar, to replace all or part of the borax, and some also reduce the proportion of flux to ore below the standard figure of three to one.

It should be stressed that it is the aim of the assayer to produce a good assay and the question of economy should, therefore, be one of secondary importance.

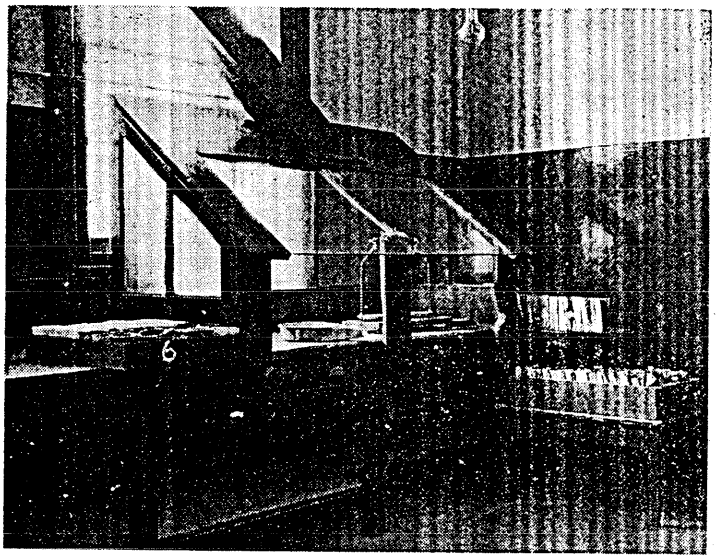


Fig. 43. A Fluxing Bench and Hood with plate glass front.

FLUXING.

To minimize the risk of contamination the fluxing of reduction works samples should, if possible, be carried out in a room reserved for this purpose. Many offices have separate rooms for the fluxing of reduction works and underground samples. If these facilities do not exist, care must

fluorspar allows slag to break away from Pb beads easier - higher coefficient of expansion! !! IS NOT cheaper !!

be taken to prevent contamination by demanding the most scrupulous attention to the cleanliness of the fluxing bench and balances at all times.

The balances used are the Becker type of pulp balance, either 500 or 1,000 gram, and all work is done under a glass covered canopy which is connected to an exhaust fan for the removal of dust.

Before fluxing, the samples are passed through a 30-mesh sieve to break up any lumps and are then thoroughly mixed by rolling on a piece of glazed paper or rubber sheet. It is usual to have separate sieves for residues and pulps and these are blown out with compressed air after use.

When fluxing, the operator takes the packeted sample and pours it out on to a piece of glazed paper in front of the balance. By drawing up each corner of the paper in turn the sample is left as a long mass in the centre of the paper. This is then spread out evenly with a spatula and dip samples are taken from various points until the balance pan contains slightly more than the weight required. The excess is removed with the spatula until the exact weight is obtained. It is usual to take triplicates of 2 assay tons for pulps and duplicate 5 assay ton or quadruplicate 2·5 assay ton charges for the residues.

The weighed portions are intimately mixed with the requisite amount of stock flux (see Fluxes), 6 assay tons of stock flux being used for each assay charge of pulp and 15 assay tons for each 5 assay ton charge of residue; with sufficient reducing agent, in the form of mealie meal or charcoal, to produce a lead button of 60 grams from the pulp and an 85 gram lead button in the case of the residue.

Silver for parting is added either as a solution of silver nitrate from a burette or a dropping bottle or as silver wire.

Fusion.

The fusion of a 5 assay ton charge will occupy about 40 minutes, and should be accomplished by the gradual raising of the temperature of the furnace. When the fusion is tranquil it is poured into an iron mould; after cooling, the lead button is detached and hammered ready for cupellation.

Cupellation.

The lead buttons are cupelled at a light red heat, about 900° C., which must be increased to a yellow heat at completion. Yellow heat is about 1000° C., i.e. slightly above the melting point of silver.

Parting.

After cooling, the beads or prills are detached from the cupels, flattened on an anvil and dropped into dilute nitric acid (1 part nitric acid to $2\frac{1}{2}$ parts water) which is at the point of boiling. When the silver has dissolved, the acid is carefully poured off and the gold discs are thoroughly washed with distilled water, dried, annealed and finally weighed.

The theory of parting has been dealt with elsewhere, and it is proposed to discuss here the methods of parting used in Rand assay offices.

There are two methods:

(*a*) Parting in test tubes in a water bath.

(*b*) Parting in small porcelain crucibles which are heated on a hot plate.

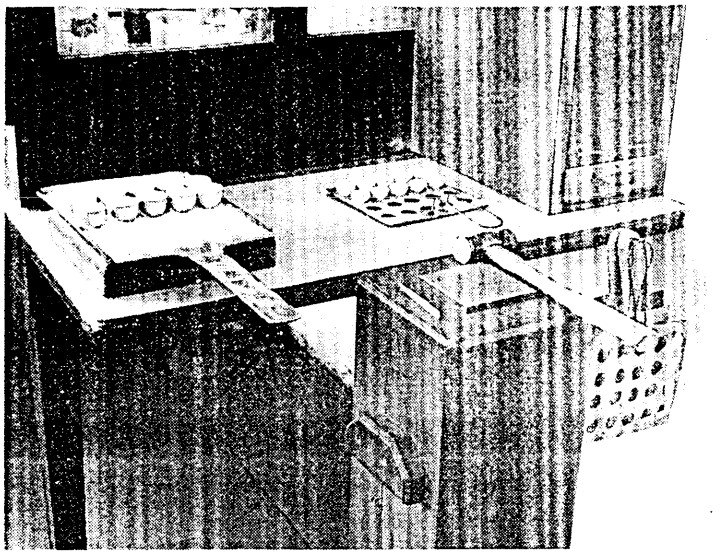


Fig. 44. Anvil for flattening gold prills prior to parting.
(*With acknowledgment to Rand Leases (Vogels) G.M. Co.*)

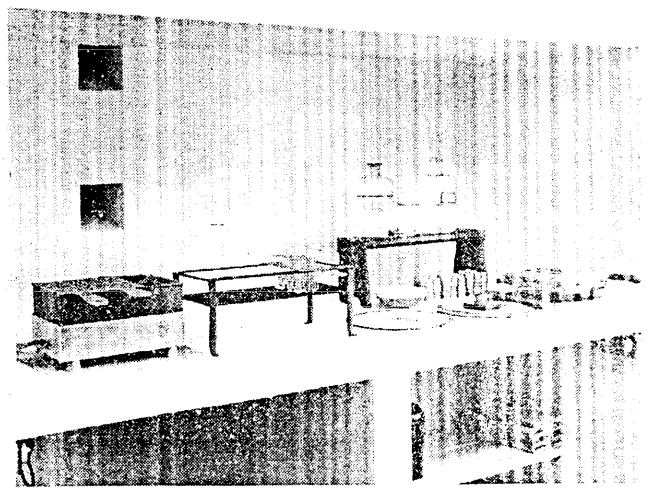


Fig. 45. Arrangement for parting Residue at Works [illegible].
(*With acknowledgment to Go[illegible] Proj[illegible] W[illegible] Ltd.*)

Parting in Test Tubes.—An electric water bath 18" long, 8½" wide and 4" deep, is fitted with an aluminium cover drilled with rows of holes $\frac{5}{16}$" in diameter. Pyrex test tubes 4½" x ½" are used for parting. When in position these protrude half an inch above the aluminium cover and stand in about three inches of boiling water. About 2 ml. nitric acid is added to each test tube and they are replaced in the water bath. The beads or prills are hammered on an anvil and one bead is dropped into each test tube. The test tube is allowed to stand in the boiling water for at least ten minutes, the acid is then drained off and the test tube filled with warm distilled water. A Battersea annealing cup is placed over the mouth of the test tube, the test tube and cup are up-ended so that the bead slowly sinks down the length of the test tube into the annealing cup. The water is drained out of the annealing cup, the porous nature of which ensures that the last traces of moisture are absorbed. The parted beads are annealed in a muffle at a temperature of about 900° C. After cooling, they are ready for weighing.

Parting in Small Porcelain Crucibles or in The Monckton Parting Tray.—In this method the bead is hammered and dropped into boiling nitric acid in small porcelain crucibles which are heated on an electric hot plate. After the silver has been dissolved the crucible is removed from the hot plate and the acid drained off. Distilled water is now added and the crucible replaced on the hot plate until the water boils. The crucible is again removed, the water thoroughly drained off and after the crucible has dried, the bead is annealed in a muffle.

A very effective method of removing the acid and the water from the crucible by means of a glass jet attached by a rubber tube to a filter pump has been evolved.

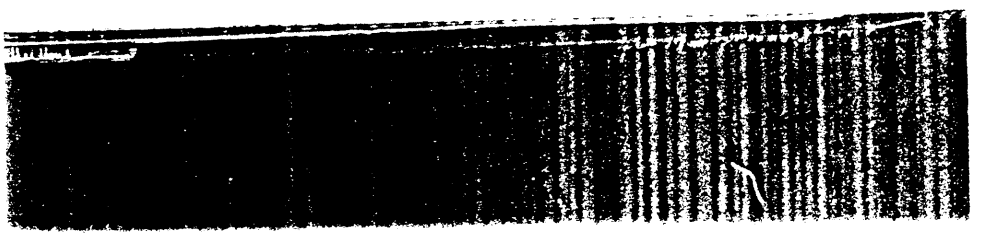
A collection of parted beads should be assayed periodically to determine the percentage of silver left undissolved. This is done in the same manner as a bullion assay.

Weighing.

Surface beads require to be weighed with the greatest accuracy. The balance is described elsewhere; it is highly sensitive but occasionally is found to be erratic in its action, possibly owing to physical differences between the state of the air inside the balance case and that of the balance room. The opening of the balance case for ten minutes before proceeding to adjust the balance will usually remedy this condition.

Before adjusting the balance, the beam, pan hangers, supports, etc., are carefully dusted with a fine camel hair brush, while the pans are cleaned with a piece of soft chamois. The balance is then "swung", the oscillations observed and the counter-balancing rider moved until the balance is brought into a state of equilibrium. This may involve a number of swings and the assayer should accept the balance as being in a state of equilibrium only after the most exhaustive checks have shown it to be so. The importance of ensuring proper adjustment cannot be over-emphasized, since the accuracy of this adjustment will have a bearing on all subsequent weighings. Special attention should be paid to the height of the balance bench and the position of the balance relative to the operator, in order to avoid errors due to parallax.

The balance is adjusted and each bead, in turn, is placed on the left hand pan and weighed as described in the chapter dealing with assay balances.



Chapter VII.

THE ASSAY OF ORE SAMPLES FROM UNDERGROUND.

The compilation of ore reserves and, indeed, the mining policy of a mine is largely dependent upon data derived from the systematic sampling and assaying of the mine ore. It will be appreciated, therefore, that in a Witwatersrand assay office "mine samples", as they are termed, are dealt with in far greater numbers than samples from any other source. Many offices handle from 500 to 1,000 such samples per day and on the larger mines it is not unusual for the daily total to be between 1,500 and 2,000. Moreover, as it is desirable that the assay values of mine samples should be available to the management with as little delay as possible (they are usually required within 24 hours of sampling), these samples should be dealt with as expeditiously, consistent with accuracy, as possible.

Working conditions, crushing facilities, furnace accommodation, availability of labour and labour saving devices, etc., vary on the different mines, and it is difficult, if not impossible, to lay down a standard system of manipulation. Many admirable systems are in operation, each designed to suit local conditions and to meet the requirements of the mine management. The essentials of a satisfactory system may, however, be summarized as follows:—

1. Clear and distinctive marking of samples.
2. Facilities for rapid sorting.
3. A ready flow of work in the process of crushing, dividing and pulverizing.
4. Installation of convenient, hooded work benches for fluxing.
5. The provision of strong but light trays to carry a convenient number of crucibles from bench to furnace room, and such labour saving devices as sample mixers, multiple crucible forks and tongs, cupel forks and transferrers.
6. A distinctive system of cupel marking to indicate clearly any deviation from the routine order of individual assays.
7. A system of check assaying and of filing samples for reference.
8. Assay balances preferably of a rapid weighing type, installed in a well-lit balance room.

Procedure.

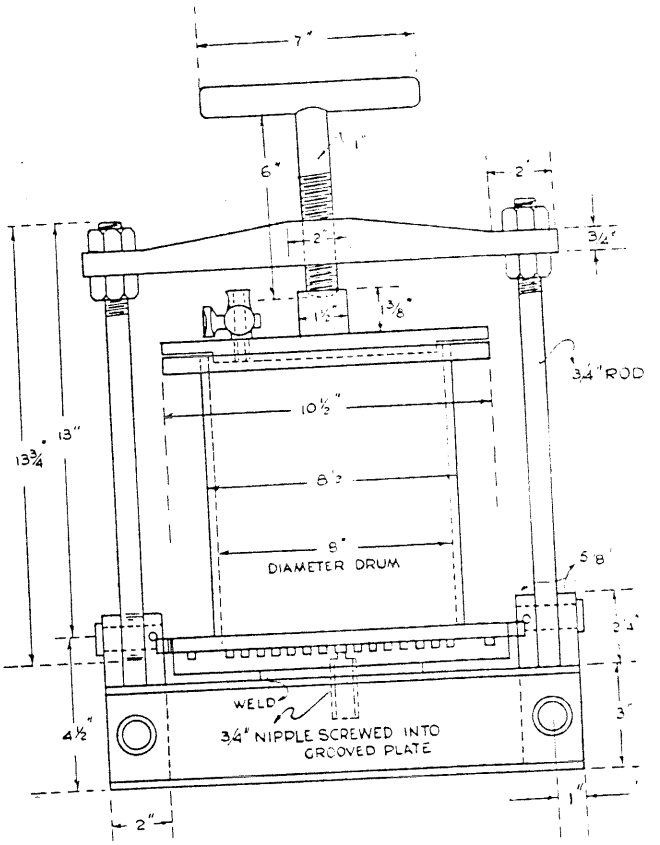
As described in the chapter dealing with the crusher house, mine samples are received from underground in canvas bags, and are transferred into metal dishes on arrival at the assay office.

Samples containing moisture should be dried before crushing and as the percentage moisture is generally low this can be done by placing the samples, in their dishes, on drying plates.

Another satisfactory method for the routine drying of mine samples is one designed by C. H. Coxon and C. A. Martin and installed in the assay office of the Blyvooruitzicht Gold Mines.

This method uses the heat given off by banks of infra-red lamps which are situated so that the samples are heated from above, the samples being carried under the lamps on an endless steel conveyor.

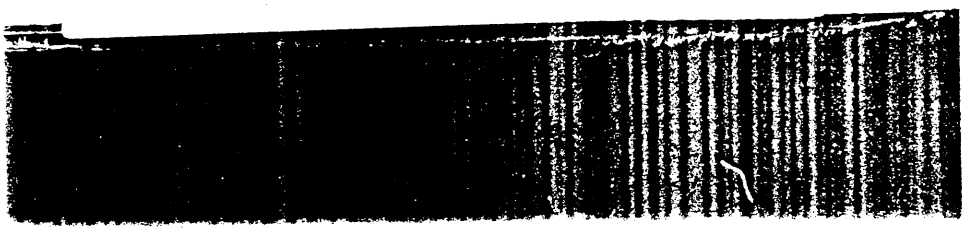
In this particular drier 300 50-ounce samples, containing an average of three per cent moisture can be dried per hour. It contains 266 lamps which are arranged in seven banks and are housed in five four-foot canopies. The canopies are hinged to provide access for cleaning and the replacement of lamps.



PRESSURE FILTER

SCALE 1/5" = 1"

Fig. 46.



By heating from above, "spitting" is eliminated and the heat generated, while sufficient to dry the samples thoroughly, is never sufficient to cause roasting nor to char the paper tickets which identify each sample.

A ticket accompanies each sample and on it the sampler's name or symbol as well as the number of the sample should be clearly marked. It is advisable to sort batches into numerical order before they are crushed and to retain this order throughout.

The canvas bags must be thoroughly cleaned after emptying so that no contamination will take place when the bag is used for further samples.

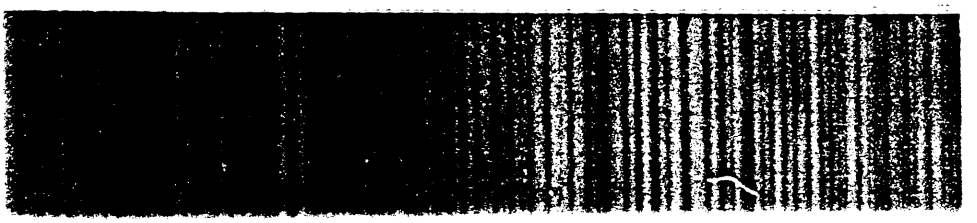
Fig. 47. Sample Storage Rack.
(*With acknowledgment to Geduld Prop. Mines Ltd.*)

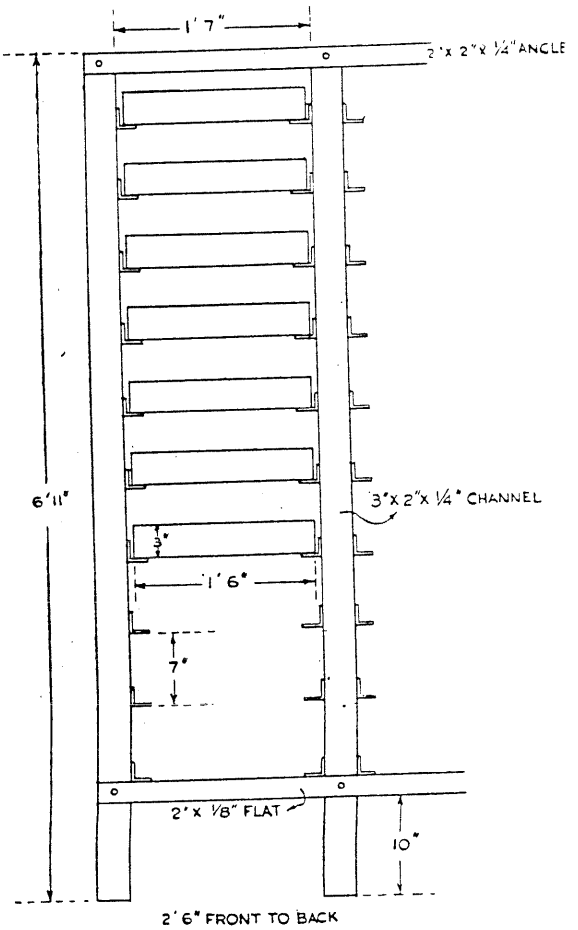
On some mines, bags of a distinctive colour are used for samples which are known to contain high values, and this excellent practice helps to prevent contamination in subsequent samples.

A sample should weigh about two pounds and the largest piece should not exceed two inches in diameter, but it is not always possible for the sampler to take such samples and samples may vary in weight from one pound to ten pounds and individual pieces may measure up to four inches in diameter. Generally, all samples weighing over three pounds are given a preliminary crushing. Here they are broken down to approximately half-inch diameter. The sample is then divided and one half is rejected. The sample, at this stage, is too coarse to be divided further.

Only in exceptional circumstances will more than 10 per cent of the samples require preliminary crushing.

The samples are now stacked in piles of five or more and passed to the secondary jaw crushers which crush the material to minus ½".

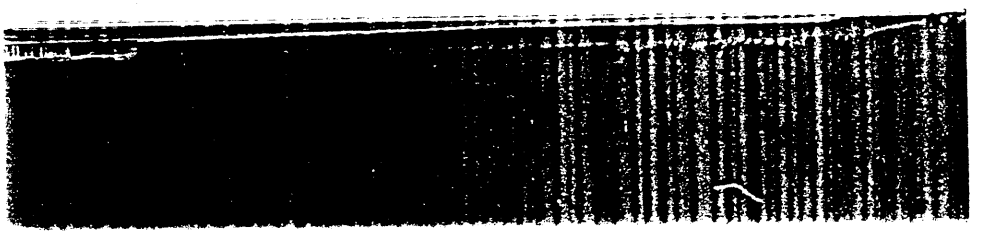




SAMPLE OR CRUCIBLE STORAGE RACK

SCALE 1/16"=1"

Fig. 48.



This system of having primary and secondary jaw crushers is only used in offices which have "Hush" jaw crushers to do the main crushing. These crushers are extremely robust and are comparatively inexpensive and as they will cope with 90 per cent of the samples received, they are extensively used.

In small offices it is often the custom to dispense with preliminary crushers and to break up large pieces with a hammer but in larger offices where "Hush" crushers are installed "Cupelite" or "Sturtevant" crushers are used as preliminary crushers. However, the modern tendency is to install the larger "Cupelite" crushers exclusively and thus abolish two-stage jaw crushing. The larger crushers will, when correctly set, reduce the largest piece of ore, likely to be found in a mine sample to minus ½".

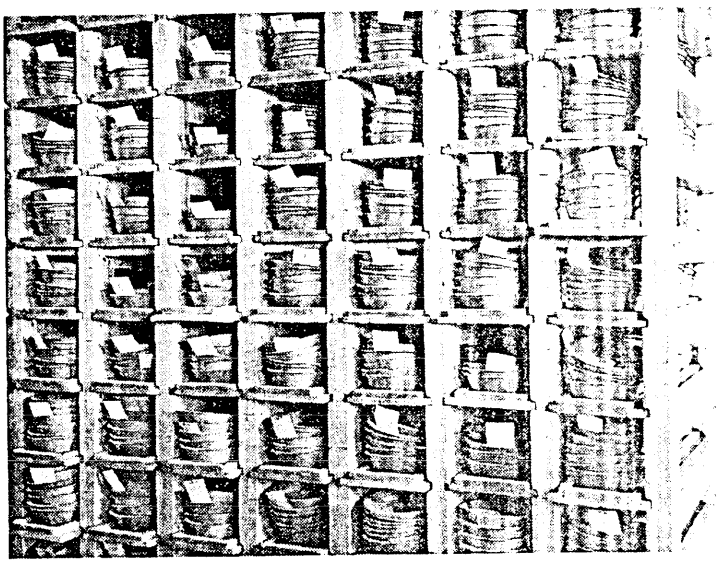
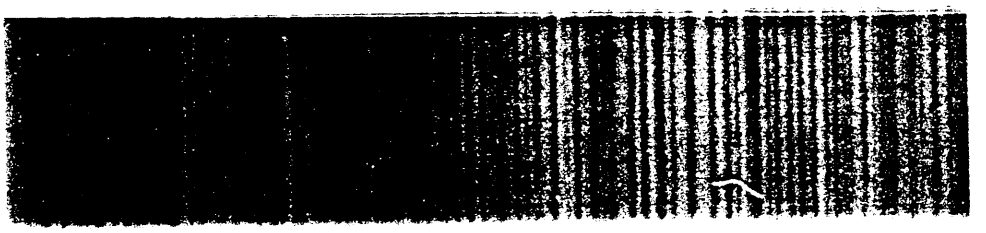


Fig. 49. Sample Storage Rack.
(With acknowledgment to Rand Leases (Vogels) G.M. Co.)

At this stage it is the usual practice to reduce the bulk of each sample, not only to facilitate handling but also to avoid unnecessary wear on the pulverizer discs. This operation, known as dividing or quartering, is carried out by means of dividers, mounted on a solid bench and covered by a hood connected to the exhaust system (See "Crusher House").

Each sample is passed through the divider one or more times, according to its original bulk, until the ultimate portion is approximately eight ounces in weight. To ensure that the final product is as representative of the original bulk as possible, no sample should be reduced to this small quantity if it contains fragments exceeding ¼" mesh.

Finally this representative portion of the original sample is pulverized. It is generally accepted that the degree of pulverization should be such



that the sample contains no plus 30 mesh material and not more than ten per cent plus 60.

Several points must be taken into consideration in fine grinding.

A. The heat generated in the pulverizer which may cause decomposition of the pyrite. However, unless the sample is to be used for "extraction tests" this aspect can be disregarded.
B. The finer the final product the better the assay.
C. The finer the grinding, the greater will be the dilution by fine iron from the pulverizer discs.

The above method is, of course, only used where the crusher, divider and pulverizer are mounted separately. When the machines are combined into a unit the whole operation is done at once. The divider in this unit provides for abnormally large samples and it is possible to allow all the sample to be pulverized in the case of a small sample or to reject up to three-quarters of a large sample (see Chapter II).

The action of pulverizing, where the sample is thrown out from between the discs, effectively mixes the samples and further mixing is usually unnecessary although some assayers prefer to mix each sample before it is "fluxed".

Before leaving the crusher house for the fluxing room the numerical order of each batch is checked.

Fluxing.

On receiving a batch of samples at the fluxing bench, the assayer records the numbers and weighs out the required amount from each sample. The sample may be poured on to a sheet of smooth paper, mixed, and dips taken from different portions to ensure a representative portion being taken for assay. In some offices, however, it is customary to take the amount for assay direct from the sample container.

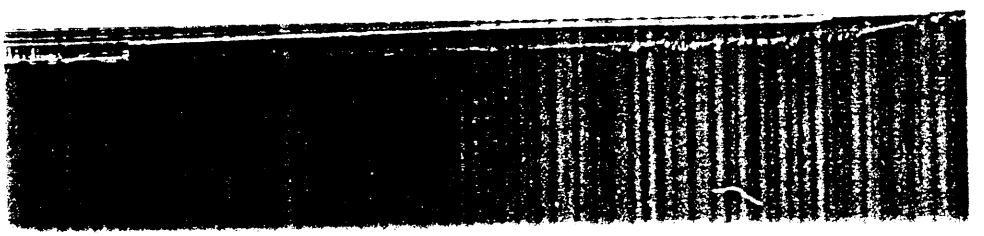
The weight of mine sample usually taken for assay is 1 assay ton (29·166 grams). This amount is weighed out and tipped into a mortar or sample mixer into which an assistant has placed approximately three times this weight of stock flux. After thoroughly mixing the ore and flux, the assistant charges them into a crucible, while the assayer prepares the next sample for weighing. The crucible commonly used is a No. 1 or No. 1G which has a capacity of approximately 300 grams (in terms of stock flux mixture).

After the assay quantities have been weighed out, the samples are stored, so that they are available for repeat or check assay. The samples are stored either on shelves or suitably designed racks, depending upon the type of sample container in use. The numerical order is maintained for easy reference.

The stock flux varies, on different mines, in the proportions of its constituents, but a reliable flux mixture for ordinary Main Reef has the following composition:—

Sodium carbonate	5 parts.
Litharge	3 ,,
Fused borax	2 ,,

Sufficient reducing agent is added to furnish a lead button weighing 25–30 grams per sample. On the Witwatersrand maize meal is commonly used as a reducing agent, and it has been found both practicable and convenient to add the meal to the stock flux when it is made up in bulk.



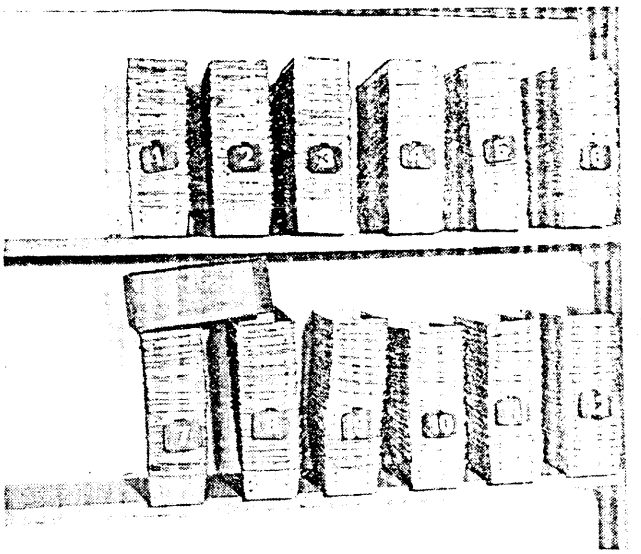


Fig. 50. Sample Storage Bins.
(With acknowledgment to Mackay East Ltd.)

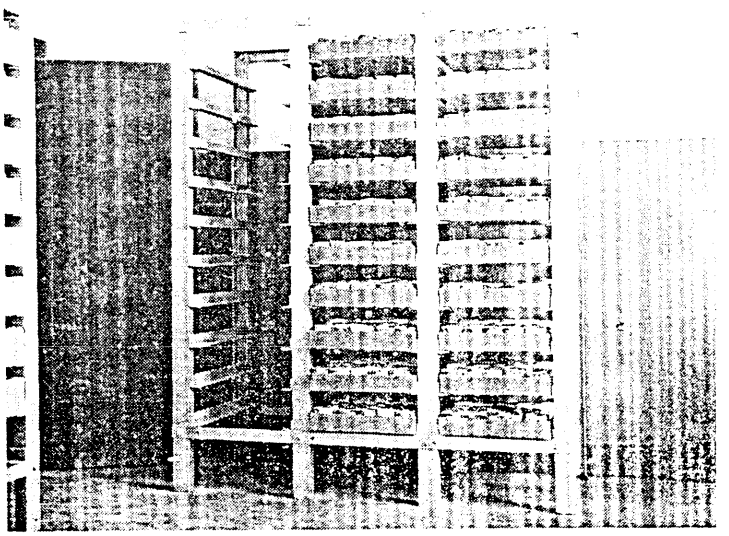
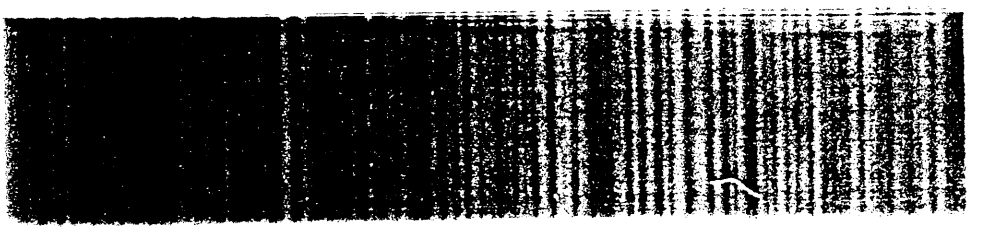


Fig. 51. Crucible Storage Rack.
(With acknowledgment to Geduld Proj. Mines Ltd.)



It will be appreciated that the flux recommended above is not necessarily suitable for all samples taken underground. It will suffice for the greater number, however, and occasional samples of ore observed by the experienced assayer as being of a refractory nature, are given appropriate treatment.

The chief cause of refractoriness is iron pyrite which, if present in excess of ten per cent, renders the lead button brittle. The assay of such ores is dealt with under "Complex Gold Ores".

The crucibles are generally contained in strong metal trays. The capacity of these trays varies from 16 to 35 crucibles. The number of crucibles constituting a normal charge also varies. Few assayers, however, place less than 48 crucibles in the furnace at one time while a few furnaces have a capacity of more than 72 crucibles.

Each tray is numbered and the identity of any sample is established by its position in a tray. It follows, therefore, that at each stage of the process, where a transfer of samples takes place (e.g. charging samples into the furnace, pouring fused samples, charging lead buttons into their cupels, etc.) the same order must be maintained and each sample must continue to occupy its original position in the tray.

As a check against inadvertent displacement of samples, use is made of the fact that if a small amount of copper is added to a sample, a green colour is imparted to the cupel. Before the tray of charged crucibles leaves the fluxing bench, therefore, the assayer introduces a small amount of copper, in the form of copper wire or as a solution of copper sulphate, to the appropriate charges. After cupellation each tray should contain a number of stained cupels conforming in design to the particular method used. An examination of the stained cupels not only identifies the number of the tray but also indicates whether any displacement of samples has taken place.

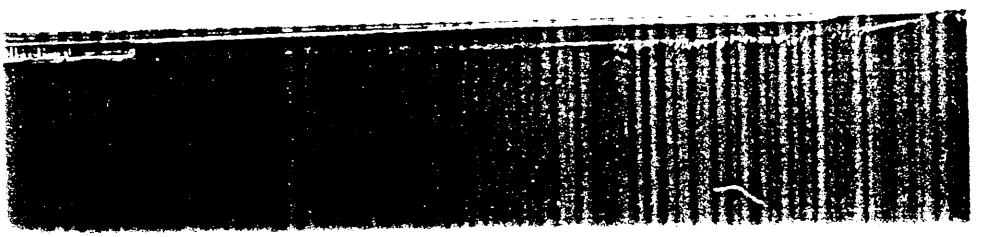
Some assayers "copper" to a definite pattern but others prefer an irregular system of "coppering" which is not easily remembered; the numbers of the "coppered" crucibles being entered into a book. The second method is more cumbersome but prevents any attempt at replacing samples which may have become disarranged. A tray which has any displaced cupels must be repeated.

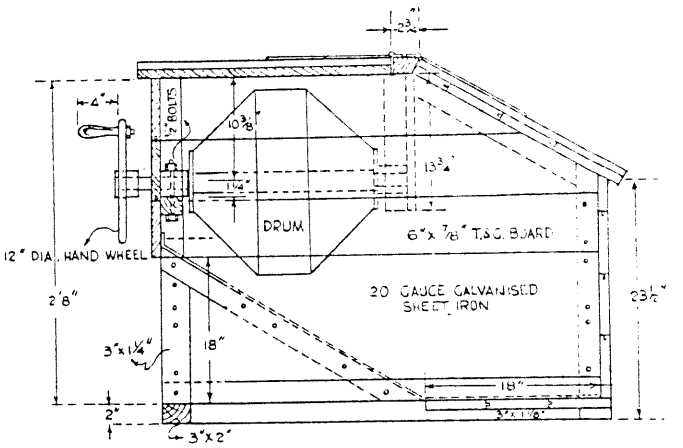
Charging the Furnace.

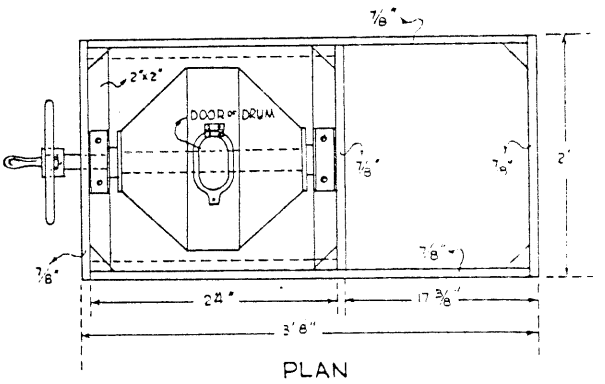
The crucibles of the batch are removed from the tray in consecutive order and charged into the furnace. Long iron tongs are used for this operation and in some cases these are designed to carry more than one crucible at a time. A "fork" capable of conveying a large number of crucibles is also in use, whereby it is possible to place the whole batch of crucibles on the furnace hearth in one operation.

The Fusion.

The period of fusion for this type of assay is approximately 30 minutes. At the end of this period the crucibles are examined, and if the fusion is complete the crucibles are withdrawn consecutively and poured into conical iron moulds, standing on an iron table or flat-topped iron trolley. After pouring each crucible is placed upside down on a specially designed rack so that residual molten slag may drain off.



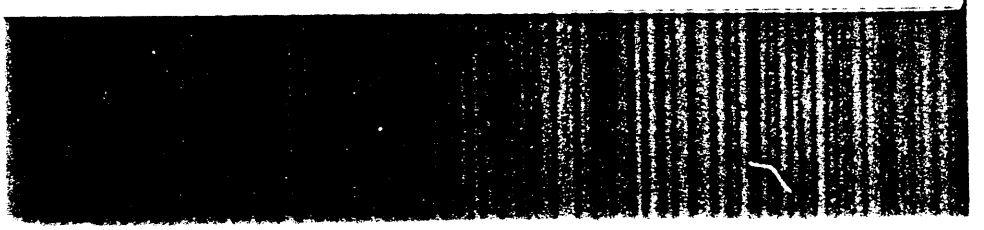




FLUX MIXER

SCALE 1/16"=1"

Fig. 52. A Combined Flux Mixer and Storage Bin.
(*Acknowledgment to Rand Mines-Central Mining.*)



When cool, each mould is inverted and tapped to remove the assay. The lead button is detached from the slag and placed in its correct compartment on a cupel tray or button transferrer. The buttons are then hammered into cubes to remove adhering slag before cupellation and to facilitate handling. The anvils upon which the buttons are hammered are sometimes fitted with a small compressed air jet from which air impinges on the face of the anvil and blows away the powdered slag. In the absence of this fitting the anvil should be brushed clear of slag after each button has been hammered. (See "Theory of the Assay Fusion").

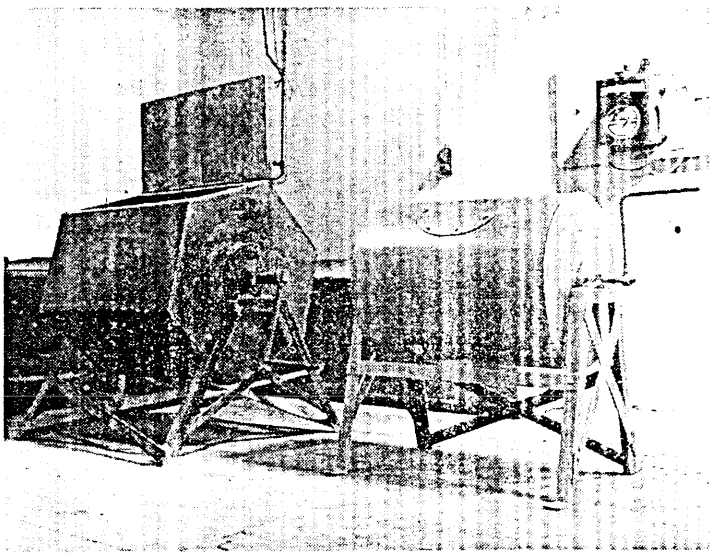


Fig. 53. Flux Mixing Barrels.
The barrel on the left is also used as a storage bin.
(With acknowledgment to Geduld Prop. Mines Ltd.)

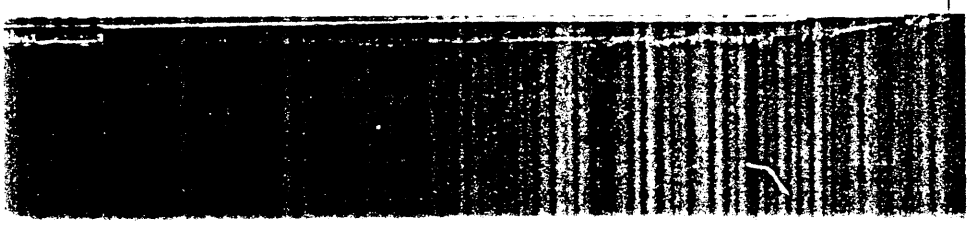
CUPELLATION.

The muffles in general use on the Witwatersrand are designed to hold cupels for a complete tray of mine sample assays. These cupels are placed in the muffle by means of a fork.

When the cupels have attained the heat of the muffle, the lead buttons are introduced. The cupellation temperature should not exceed 1,000°C.

The introduction of the buttons is greatly facilitated by the use of the Monckton transferrer. This device makes it possible to charge a complete tray of buttons into their respective cupels in one operation.

The use of the fork and the transferrer accelerates proceedings when a large number of assays are handled, and relieves the assayer of much of the strain of strenuous furnace work.



The period required for the cupellation of mine sample buttons is approximately 30 minutes. When cupellation is complete, the cupels are withdrawn. Flat trays without separate compartments are often used to carry cupels after cupellation. This type facilitates the use of the cupel fork.

WEIGHING.

After the copper stain design on each tray has been checked to ensure that no displacement of cupels has occurred, the cooled cupels are passed to the balance room for the weighing of the gold beads.

Each bead is removed from its cupel by means of a pair of steel forceps, placed on a small anvil and tapped with a light hammer to remove adhering cupel material, and weighed.

The balances most commonly used for this type of work are the Oertling 12 S.B./A and the Sartorious MK II, as these combine the necessary accuracy with reasonable speed of operation.

When sampling an ore body a comparatively large number of samples is taken, and consequently each sample represents a small proportion of the whole. Thus it is usually unnecessary to report high values in decimals of a pennyweight but in cases of low values it is sometimes the practice to weigh to the nearest 0·5 or even 0·2 dwt. per ton.

While a five milligram rider is sufficient for all beads representing values ranging from 5 to 100 dwt. per ton, it is more efficient to use a half-milligram rider for beads representing an assay value lower than 5 dwt. per ton. In fact, owing to the construction of the Oertling 12 S.B./A. balance it is difficult to weigh beads of a lower value than 5 dwt. per ton with a five milligram rider.

The advantages of using these two riders are explained in the article on the assay ton contained in the Appendix.

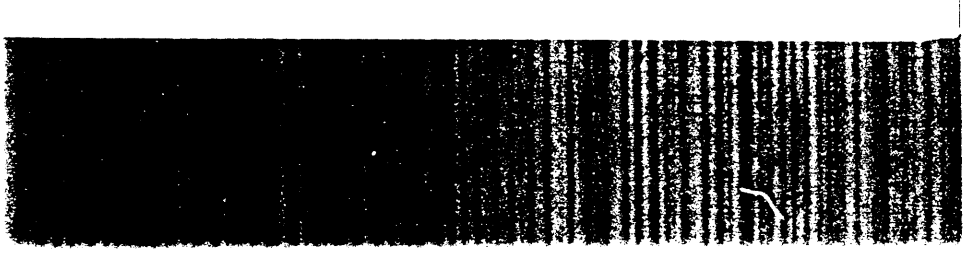
On the Witwatersrand it is not usual to part beads derived from routine mine ore samples, and it is necessary, therefore, to make an allowance for the silver which the ore is known to contain.

Research has shown that the percentage of silver remains constant within reasonable limits in the ore of each particular mine, and this knowledge provides a figure which may be used with reasonable accuracy, when making adjustments.

The assayer, therefore, deducts the accepted silver percentage from the weight of the mine sample bullion bead and thus returns a value closely approximating the fine gold content per ton.

In many assay offices the adjustment is made when the weight of ore sample is taken for assay, i.e. in a mine where the average percentage of silver in the ore is ten per cent, 0·9 assay ton is weighed out per charge, the resultant bead of gold bullion being regarded as fine gold.

The values, expressed in dwt. fine gold per ton, are entered on a certificate and returned to the sampling department.



Chapter VIII.

THE ASSAY OF GOLD-BEARING CYANIDE SOLUTIONS.

The assay of gold-bearing cyanide solutions is an important part of the work of the assayer, and, with the improvements in metallurgical practice on the Witwatersrand, this branch of assaying has assumed an even greater importance in recent years.

Accurate assays of these solutions are necessary, and for the efficient control of the cyanide process, the results of these assays should be made available to the Reduction Works as soon as possible.

Many solution samples have a very low gold content and, as these are often reported to an accuracy of 0·005 dwt. per ton, it is necessary to use a method by which a large volume of the solution can be rapidly and efficiently assayed, in order to give a weighable bead. It is equally true that in the case of solutions having a high gold content, greater accuracy is obtained by using a larger volume of the solution for assay. It is for this reason that the practice of evaporating the solution to dryness in a leaden dish, of comparatively small capacity, with subsequent cupellation of the lead, has been largely superseded by other methods.

The methods in general use are:—

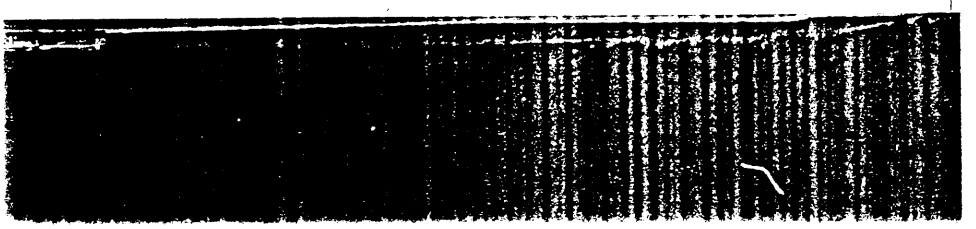
1. Evaporation in porcelain dishes.
2. The copper sulphate method.
3. The cuprous chloride method.
4. The zinc-lead acetate method.
5. Deposition on lead.
6. Electrolytic Deposition.

1. Evaporation in Porcelain Dishes.

One disadvantage of this method is the time necessary for evaporation which towards the end must be carried out at a low temperature to avoid loss by spirting. This is a serious drawback when a large number of rapidly conducted assays are called for daily.

Procedure.—Glazed porcelain dishes of a capacity of at least one litre are smeared with petroleum jelly, and about 30 grams of a stock mixture of litharge and carbon calculated to give a 20-gram button are dusted in. 10 to 20 A.T. of the sample are then introduced into the dish and the evaporation commenced, due precautions being taken to avoid overheating, otherwise the residue and litharge will adhere to the dish, causing trouble in cleaning out and possible loss. A water bath is the most satisfactory method of heating the sample.

When dry, the residue is wiped out into a crucible with a piece of clean filter paper, a small quantity of the flux being already in the crucible; the remainder of the flux is placed on top of the assay residue together with the piece of paper used for cleaning. The flux, of which one A.T. is taken, is the same as that used in the copper sulphate method with a little silica added to compensate for the extra litharge. The assay is now ready for fusion, and is completed in the usual way.



The use of petroleum jelly is advantageous as it obviates the tedious scraping which is necessary and often causes incorrect results when the dishes are not greased. The final traces may be removed by scouring the dish with about 10 grams of the stock flux.

2. The Copper Sulphate Method.

The use of five reagents for the precipitation in this method appears to make it a cumbersome and lengthy process. With a well-designed system however, it is possible to carry out the precipitation of 30 solutions in less than 30 minutes. The filtering and addition of fluxes should not involve more than another half-hour, and the fusing, cupellation and parting no longer than is necessary for an ordinary surface sample assay.

Reagents Used.

Solution of sodium cyanide (saturated)		
,, ,, copper sulphate	15	per cent.
,, ,, sodium sulphite	10	,, ,,
,, ,, sulphuric acid	20	,, ,,
,, ,, potassium ferro-cyanide	2	,, ,,

Procedure.—The solution for assay should be alkaline. To a conical glass beaker or other convenient receptacle a few drops of the sodium cyanide solution are added.

20 A.T. of the solution for assay are measured and transferred to the beaker. To this are added 20 ml. of each of the other reagent solutions, in the order given above, the beaker being shaken between each addition: the precipitated solution is allowed to stand for half a minute *until sulphur dioxide is being evolved freely.* It is then filtered through a medium texture folded filter paper.

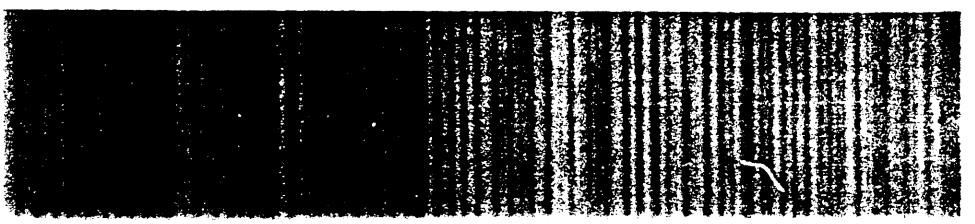
When the precipitate is thoroughly drained, a little (0·5 A.T.) of the stock "solution-flux" is added to the crucible, the filter paper with the precipitate is placed in the crucible, and 3·5 A.T. of the flux is dusted into the paper, which is folded in upon itself and covered with the remainder of the flux, of which a measure containing about 6 A.T. is taken in all. Some assayers prefer to drain the precipitate still further by squeezing the filter paper gently until most of the moisture has been expelled: after this the paper is opened and the flux is dusted over the precipitate. Another method is to add litharge or red lead to the filter paper before filtering, thus ensuring a better mixing of lead oxide and precipitate than can be obtained otherwise. This lengthens the time of filtering considerably but is said to give slightly more accurate results.

The requisite silver is added as silver nitrate solution from a burette, and the assay is then ready for fusion and treatment in the ordinary way. The silver nitrate solution should be of a known value, a useful strength being one which will impart a value of 0·5 dwt. silver per ton (20 A.T. having been taken) by the use of 1 ml. of silver nitrate solution.

The following is an efficient stock "solution flux":—

Sodium carbonate	36	per cent.
Litharge	25	,, ,,
Silica	25	,, ,,
Fused borax	14	,, ,,

Sufficient reducing agent should be added to the stock flux to produce a 30-40 gram button from the six assay tons.



By the exercise of a little thought and ingenuity, the assayer should devise a plant which will enable him to carry out a large number of assays by this method with a minimum of trouble while retaining complete accuracy.

Stock sodium sulphite solution may be stored indefinitely under a thin layer of paraffin in glass or stone-ware jars. The sulphite solution is siphoned off as required.

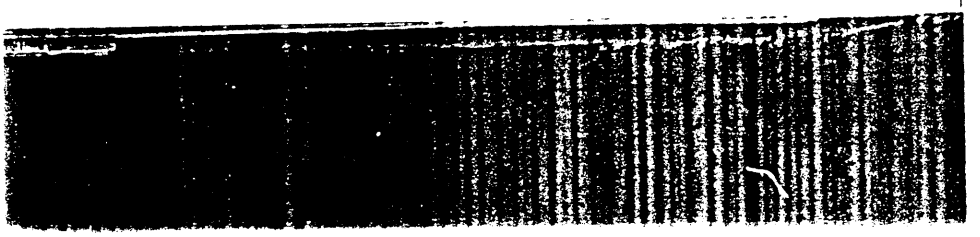
Fig. 54. Typical bench used for assaying solution samples.

3. The Cuprous Chloride Method.

An advantage in the use of this method is that only three reagent solutions, including the saturated sodium cyanide solution, are used. Further it is possible, by its means, readily to precipitate the gold from a large volume of solution of very low value, and thus obtain beads which may be weighed accurately.

Preparation of Cuprous Chloride Solution.—400 grams of crushed commercial copper sulphate are placed in a Winchester quart bottle which is then three parts filled with commercial hydrochloric acid, space being left for as much clean 16-gauge copper wire, previously flattened, as can be inserted. A minimum of 1,000 grams of copper should be used. The commercial hydrochloric acid is obtained in carboys, at a low price, and it is advisable to prepare 10 to 20 of these Winchesters at a time for stock.

After standing, with occasional shaking, for a few days, the copper reduces the mixture to the cuprous state, which is indicated by its becoming nearly colourless and clear; it however rapidly oxidizes to brown on exposure to air.



An alternative method of making cuprous chloride is to dissolve 250 grams of commercial copper sulphate, 400 grams sodium chloride and 150 ml. commercial hydrochloric acid in 2,000 ml. of tap water. When dissolved add 150 grams sodium sulphate. Bottle in a Winchester quart and add two or three pieces of clean copper rod to stabilize the solution. This solution is ready for use very shortly after preparation and should *smell strongly of sulphur dioxide*.

Procedure.—Similar flasks to those used in the copper sulphate method are employed. The sample bottle having been well shaken, the amount required for the assay is carefully measured out. It is usual to take ten assay tons of a solution expected to contain more than 3.0 dwt. per ton, and from 20 to 50 assay tons of those of lower value. Careful measurement of solutions is of great importance, and it is good practice to use a marked narrow necked flask, in which the required quantity runs high into the neck, for this purpose. A few drops of saturated sodium cyanide solution are first added to the sample and the flask is shaken. The cuprous chloride is now added, 10 ml. being sufficient for the 10 A.T. charges rising proportionately, according to the amount of solution, to 30 ml. for the 50 A.T. charges. A copious white precipitate appears. The flask is well shaken, allowed to stand for a few minutes, and shaken again.

The potassium ferrocyanide is now added. An exact amount cannot be stipulated, as this amount is entirely dependent upon the amount of cuprous chloride used. The aim is to render the precipitate coarse and flocculent and to leave a perfectly clear supernatant liquor. Even a

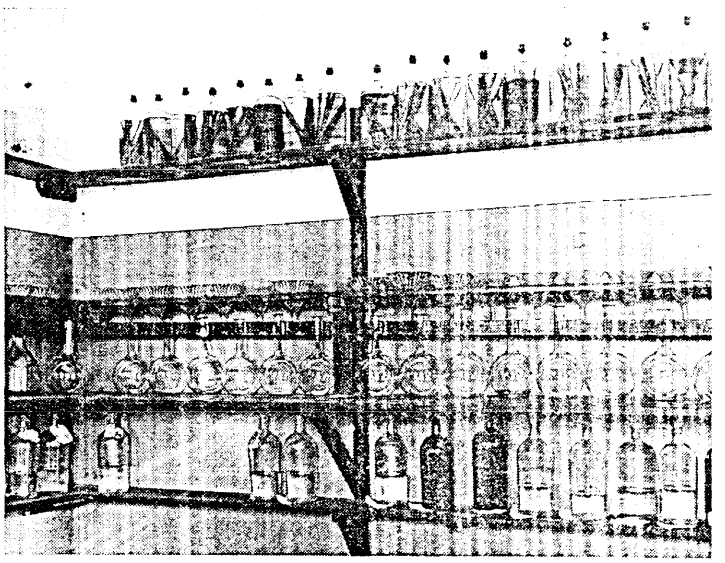
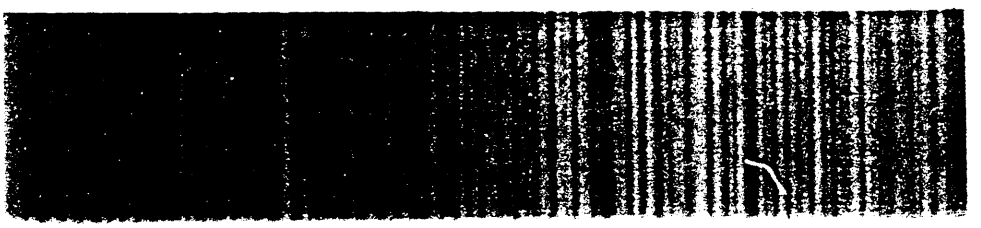


Fig. 55. Bench for assaying solution samples with Lacunder beneath the funnels for removing filtrate.

(*With acknowledgment to Gould Prop. Mines Ltd.*)



slight pink or brownish colouration of the precipitate indicates an excess of potassium ferrocyanide and such excess will lead to erroneously low results.

The sample should be well shaken and allowed to stand for a few minutes.

The solution is now filtered through a medium texture, folded filter paper and allowed to drain thoroughly. When draining is complete, the filter paper containing the precipitate is treated in exactly the same way as in the copper sulphate method.

NOTE:—It is imperative that colourless cuprous chloride solution be used, otherwise an excess of copper in the lead button will result and give trouble in cupellation. It will be observed that the precipitate turns a brownish colour after filtration. This is due to oxidation and has no deleterious effect on the assay.

This method is very popular and gives excellent results if the few simple precautions are observed.

4. THE ZINC AND LEAD ACETATE METHOD. - child's method

In this method advantage is taken of the fact that zinc being higher in the electro-chemical series than lead, displaces it from an electrolyte. Lead in turn, will displace gold and silver from solution. In this method, zinc shavings or dust and a lead salt are used to produce a lead sponge upon which the gold and silver is precipitated and subsequently separated by cupellation. The lead sponge serves a dual purpose by providing an excellent medium for holding the minute particles of gold and silver for subsequent handling. This chemical use of zinc and lead is technically known as "zinc-lead couple".

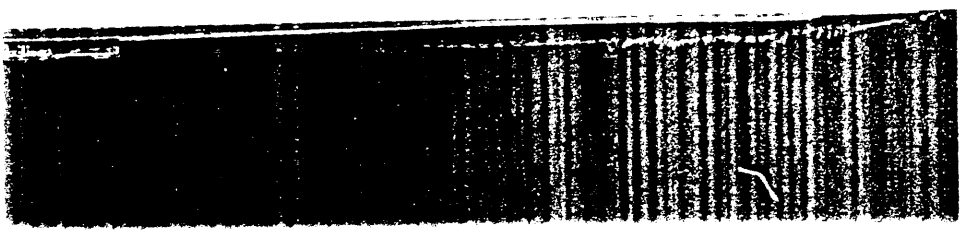
In routine work, when a large number of assays are called for in a limited time, the operation of boiling is one which has its disadvantages and can only be conducted conveniently by means of easily regulated electric heaters. The method given below has this objection, but the accurate results readily obtained amply compensate for it. No fusion is required and a saving in time and labour is thus effected.

Procedure.—The measured quantity of solution is poured into a beaker of suitable capacity, a few drops of saturated sodium or potassium cyanide solution and the necessary silver for inquartation are added, and the whole is brought to the boil on a hot plate. It is advisable to cover the beaker with a clock glass both to accelerate boiling and to avoid loss by spirting.

To the boiling solution add 4 to 5 grams of pure zinc dust or a loose ball of spun zinc of the same weight. Add 30 ml. of a saturated solution of lead acetate (1·25 specific gravity) and simmer until the solution clears. This should not require more than ten minutes.

When clear add 25 ml. of commercial hydrochloric acid and continue boiling until the excess zinc is completely dissolved.

Transfer the contents of the beaker to a porcelain dish and pour off the clear solution, wash several times in order to cool and to remove zinc chloride formed, and again decant. Manipulate the lead sponge so as to take up any detached pieces and squeeze between the fingers to form a compact cube. Dry carefully, cupel, part, anneal and weigh. Provided the lead button has not been too firmly squeezed it is unnecessary to



dry it thoroughly, as it is sufficiently porous to allow moisture to escape without causing the lead to spirt. Prolonged drying may cause oxidation of the lead and this must at all costs be avoided, as it has been found in practice, to cause loss of gold.

NOTE:—A saturated solution of lead acetate is essential and it is advisable to test the specific gravity before use. The solution must be at boiling point when the zinc and lead acetate are introduced, but *vigorous* boiling is not necessary and in fact tends to break up the lead sponge. Should the solution fail to clear readily a shortage of zinc is indicated. A little more may be added, but while this accelerates the clearing, it appears to render the button brittle. The process is rapid and little delay is caused by discarding a sample and repeating with more zinc.

The lead sponge should be coherent and soft. Excessive boiling, the presence of iron in the reagents used, and excess of lead acetate will all render it brittle. To ensure contact, when spun zinc is used, the ball should not be too compact.

The method calls for a little practice, but with attention to the few precautions enumerated above, accurate results will be obtained from high and from low value solutions.

5. DEPOSITION ON LEAD.

The following reagents and materials are employed in this method:-

Potassium permanganate solution : 6 grams per litre.
Hydrochloric acid.
Pure lead foil.

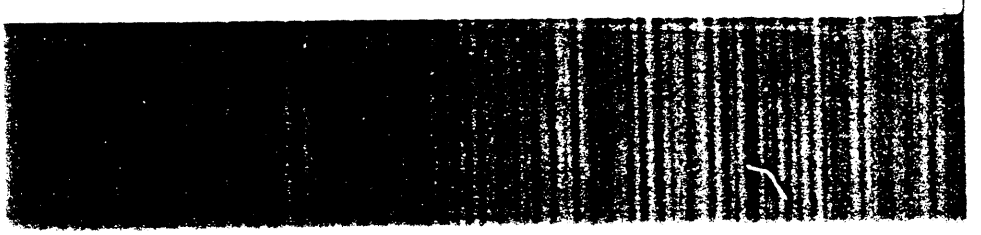
Commercial quality potassium permanganate and hydrochloric acid have been found to give satisfactory results.

Two pieces of lead foil are required per assay. The larger, approximately 6″ by 2½″, and weighing about 11 grams, should be folded in corrugations. A simple hand press, made of light metal has been devised whereby these corrugated sheets may be shaped rapidly, and the use of this implement greatly facilitates their preparation when a number of assays is carried out. The corrugations are about half an inch in depth. The second lead sheet, say 3″ by 2½″, is used as a wrapping when preparing the assay for cupellation.

Procedure.—The measured quantity for assay is placed in a beaker and brought to the boil on a hot plate. At boiling point the corrugated sheet of lead foil, 5 ml. of the permanganate solution, and 20 ml. hydrochloric acid are added, and the boiling continued for 30-35 minutes.

At the expiry of this period the solution is decanted, and the foil given two washes with cold tap water. By flipping the beaker with a wrist movement, the corrugated foil will close into a convenient shape for handling. Withdraw the foil from the beaker, using the thumb and forefinger at the ends to avoid disturbing the deposit, and dry carefully. A piece of metal screening, suitably shaped to hold the foil well clear of the hot plate is convenient for this purpose. When dry, fold into a compact shape, wrap in the second piece of lead foil, cupel, part, anneal and weigh.

Silver for inquartation should be added in the form of wire when wrapping, and not as silver nitrate to the solution. Samples of low gold content may be silvered by dropping the requisite small number of drops of silver nitrate on to the lead foil during drying.



NOTE.—Rapid circulation and agitation is essential and the solution should therefore be kept boiling *vigorously*. At no time should the foil become uncovered and it is advisable to have a supply of hot water available to maintain depth of solution during boiling. The deposit is a tenacious one, but in the interest of accuracy undue handling should be avoided.

With these simple precautions this clean and rapid method gives accurate results.

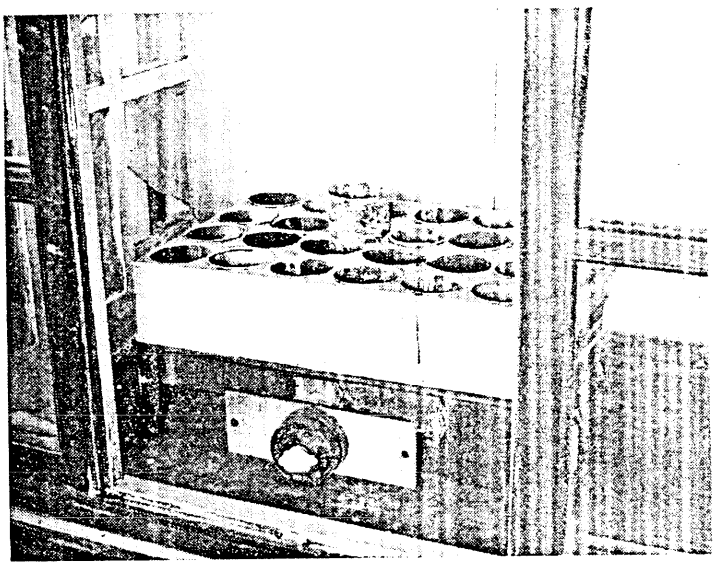


Fig. 56. A Holder used in the Deposition on Lead Method.
This holder heats the sides of the beakers as well as the bottom.
(*With acknowledgment to Rand Leases (Vogels) G.M. Co.*)

6. THE ELECTRO ASSAY OF GOLD-BEARING CYANIDE SOLUTIONS.

Although the assay of gold-bearing cyanide solutions by electrolysis is exceedingly simple and requires only a minimum of time, attention and technique on the part of the operator, a consideration of the elementary theoretical principles underlying the operation may be of assistance to those contemplating the use of this method for the routine assay of Reduction Plant solutions.

According to modern electrolytic theory, an electrolyte, when dissolved in water, is dissociated to a greater or lesser extent into its constituent ions; these ions being positively or negatively charged atoms or groups of atoms. The number of unit charges carried by the ions is determined by the valence of the elementary or compound groups in the given electrolyte.

e.g. $HCl \rightleftharpoons H^+ + Cl^-$

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^=$

$KAu(CN)_2 \rightleftharpoons K^+ + Au(CN)_2^-$

The degree of dissociation depends principally upon the electrolyte itself and the degree of dilution. All electrolytes tend to complete dissociation as dilution approaches infinity.

If electrodes are connected to the poles of a source of direct current and immersed in an electrolyte, the positively charged cations will migrate towards the cathode, whilst the negatively charged anions will move in the direction of the anode. If the voltage is above a certain critical value, which varies for different electrolytes, a current of electricity will flow through the solution. This current consists of a stream of electrons which enters the solution through the cathode and leaves by way of the anode. The passage of direct current through an electrolyte causes an electro-chemical change which is always one of oxidation at the anode and reduction at the cathode. From the electro-chemical point of view, oxidation involves the loss of electrons on the part of the anion, whilst reduction of the cation is associated with the gain of electrons. Taking as an example the electrolysis of an aqueous solution of hydrogen chloride we have,

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$2Cl^- - 2e \rightarrow Cl_2$$

$$2H^+ + 2e \rightarrow H_2$$

The hydrogen and chlorine are evolved as gases at the cathode and anode respectively.

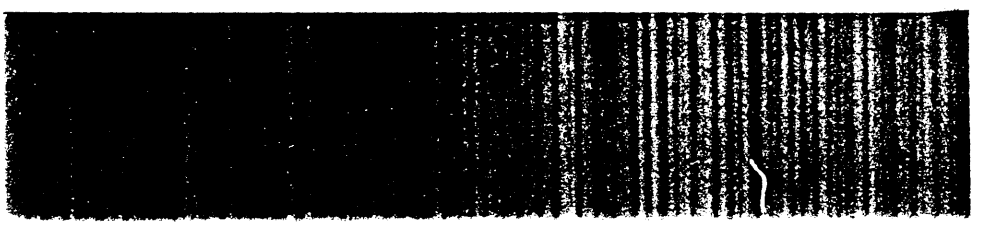
From the above discussion it will be evident that we are dealing only with the flow of negative units of electricity (i.e., of electrons). Atoms or atomic groups, which become positively charged ions, are those which have given up electrons to other atoms or groups of atoms in order that both may assume more stable electronic configurations. The positive units of electricity, in so far as chemical reactions are concerned, remain firmly bound within the atomic nucleus. The chemical change which takes place does so only at the electrodes themselves; passage of the current through the solution involves merely the physical migration of ions; further, the oxidation or reduction which takes place is that which is most easily effected under the prevailing conditions.

In the case of Reduction Plant solutions the gold is present in the form of an auro-cyanide, e.g., $K\,Au(CN)_2$, this compound is dissociated in the first instance into K^+ and $Au(CN)_2^-$, the gold being a constituent of the complex anion. This complex anion (which itself slowly dissociates into Au^+ and $2CN^-$) is not however discharged at the anode, since the most easily effected oxidation is that of hydroxyl ion, supplied, to a certain extent, by the dissociation of water, and to a very much greater extent by the lime normally present in the solution.

$$4OH^- - 4e \rightarrow 2H_2O + O_2$$

An equivalent quantity of hydrogen ions from the water is then discharged at the cathode in order to supply OH^- ions to maintain equilibrium with the calcium cations.

The gold cations, which are gradually formed as a result of the dissociation of the complex anion, migrate towards the cathode where, on reduction under suitable conditions, they remain firmly united to the cathode material. Owing to the slow dissociation of the $Au(CN)_2^-$ ion, and also to the comparatively low rate of ionic migration, low, that is in comparison to the speed with which the cathode can be made to discharge



the ions, the process is a lengthy one, if complete deposition of the gold is required, and must be expedited considerably in order to be of value as a means of practical quantitative analysis.

Accelerated rate of deposition may be effected to a certain extent by heating the solution, but much more satisfactorily by agitation, either by rotating one of the electrodes or by an independent stirring device.

If we consider Faraday's first law of electrolysis which states "the quantities of all substances deposited by an electric current in a unit of time are directly proportional to the strength of the current", we would suppose that the greater the current density, i.e., the strength per unit area of cathode surface, the more rapidly would the metal be deposited. However, in unstirred electrolytes, the solution in the immediate vicinity of the cathode rapidly becomes denuded of metal ions and the current is used up in the discharge of hydrogen ions. Increasing the current strength merely increases the quantity of hydrogen evolved and what metal ions are reduced will be deposited in a spongy non-adherent form, a type of deposit quite useless for accurate analytical work.

By thorough agitation of the solution the impoverished layer is continually being removed, and the cathode is then kept supplied with a far greater number of metal ions. For this reason, therefore, the current density may be greatly increased and the time of deposition shortened considerably. In the assay of gold cyanide solutions the rate of deposition is further accelerated by agitation owing to the fact that the complex anion which normally migrates towards the anode is brought into contact with the cathode where it accepts an electron and is reduced:

$$Au(CN)_2^- + e \rightarrow Au + 2CN^-,$$

the gold being deposited on the cathode and the cyanide anode establishing equilibrium with the alkali or alkaline earth cations. The cyanide is thus regenerated and oxygen evolved at the anode.

Before considering the design of apparatus and the technique of operation it is necessary to know something of the measurable factors of the current with which we are concerned. These are:—Current strength, resistance and electromotive force. These factors are related to one another as expressed by Ohms Law;

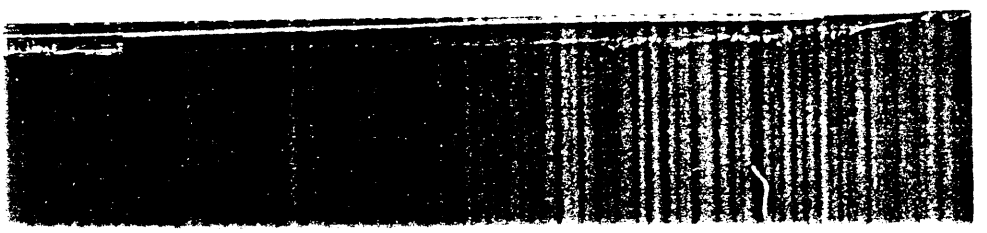
$$\text{Current strength (Amperes)} = \frac{\text{Electromotive force (Volts)}}{\text{Resistance (Ohms)}}$$

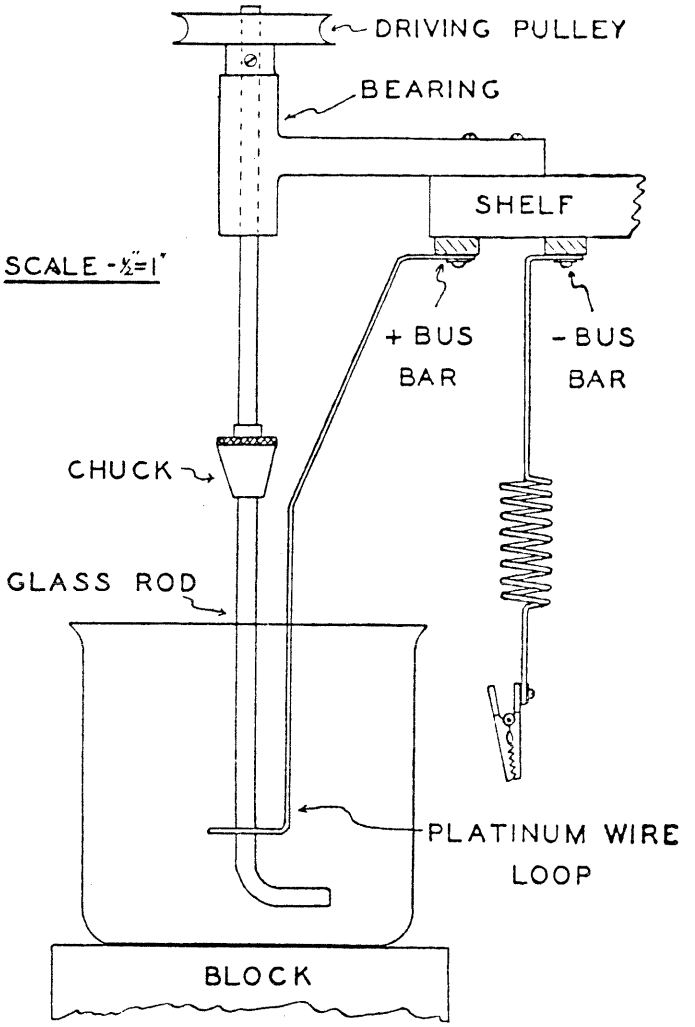
$$\text{or,} \qquad I = \frac{E}{R}$$

In the case of electrolytes a modification of Ohms Law is necessary in order to take account of the phenomena of polarization or back electromotive force which acts against the applied potential. This polarization potential is equivalent to the sum of the potentials required at the electrodes for the discharge of the ions. The modified law may be expressed as:—

$$I = \frac{E - (Ea + Ec)}{R}$$

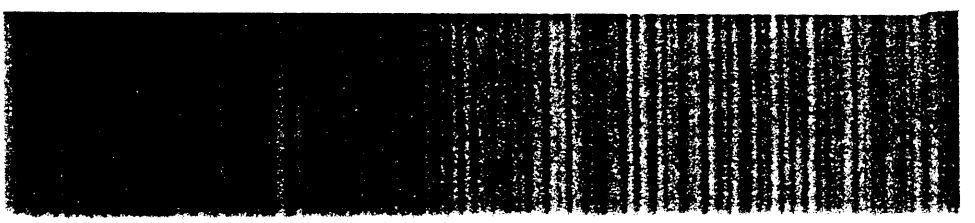
where E is the applied electromotive force, Ea is the voltage necessary for the discharge of the anion and Ec the required voltage for the discharge of the cation. The modified formula has been given here so that a clearer picture of what happens during the electrolysis of a solution may be presented. From the practical point of view however, the law as originally expressed will be sufficient.





STIRRING APPARATUS FOR THE ELECTROLYTIC DEPOSITION OF GOLD

Fig. 57.



Since we are concerned only with the deposition of gold and not with the separation of one metal from another, the applied voltage is unimportant, provided it is high enough to decompose the aurocyanide, and in accordance with Ohms Law to overcome the resistance of the circuit to an extent sufficient to permit a current of the required amperage to flow. From the assayer's point of view the current density is the important factor, and, in accordance with Ohms Law, this factor may be increased by increasing the voltage or by decreasing the resistance. For this purpose it is recommended that the source of direct current be supplied through a variable resistance in order that control of the current density may be exercised. It is of course possible to make use of a source of supply, say a 6-volt battery giving a constant voltage and to control the current density by increasing the conductivity, i.e., decreasing the resistance of the solution. This may be accomplished by the addition of a suitable electrolyte, e.g., sodium hydroxide or sodium sulphate. The former procedure is, however, to be preferred since it is obviously quicker and less troublesome.

It should be noted that the conductivity of an electrolyte varies considerably with change in temperature, increasing with the temperature by about 2 per cent per °C. For a given current density higher voltages will therefore be required in winter than in summer and this should be allowed for when designing electrolytic apparatus. Suitable sources of direct current are (1) full wave rectifiers, (2) motor-generators and (3) series-connected 6-volt auto type batteries. The best choice would probably be full wave rectification, since this on the whole would be less expensive than the installation of a motor-generator, and has the advantage over batteries in that the bother of periodical charging is avoided. If the D.C. generator is capable of supplying the required amperage at a maximum potential of about 15 volts this should be sufficient to meet all normal requirements.

Whatever source of current is decided upon it should be connected through a variable resistance and in parallel with the electrode terminals. The circuit must also incorporate a volt meter and a good quality ammeter capable of indicating Nx amperes where N is the maximum number of assays which will be carried out at any one time, and x is the required amperage per assay; the ammeter should also be capable of accurately indicating a change of 0·05 ampere.

The agitating mechanism may consist of a series of Edwards type laboratory stirrers which can be supplied with glass stirring rods and motor speed control. These units are, however, expensive to install on a large scale and in this case it would be more economical to set up an electrolytic table fitted with a central support carrying two banks of ball-bearing stirrers. These stirrers are commercially obtainable and are supplied complete with $\frac{1}{4}$" chuck and three speed pulleys. The two banks of stirrers may be driven by a $\frac{1}{6}$ h.p. vertical spindle motor, the power being transmitted by $\frac{1}{4}$" leather belting. If this method is adopted, the motor pulley should be of such a diameter as will impart a speed of approximately 550 r.p.m. to the stirrers. An adjustable idler pulley should also be provided in order to take up slack in the leather belting. Copper bus bars for carrying the current may conveniently be attached to the central stirrer support, the bar running along the top of the support being connected to the positive pole of the D.C. supply while that attached to the bottom of the support is connected to the negative pole. Flexible wire leads are soldered to the negative bus bar and fitted with alligator type clips for attachment to the cathodes.

Anodes should preferably be of platinum and of the form shown in the

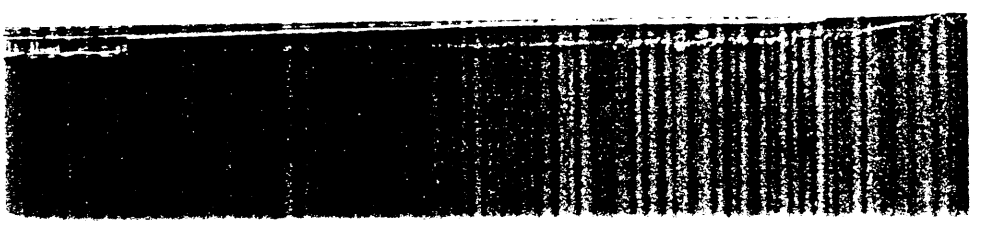
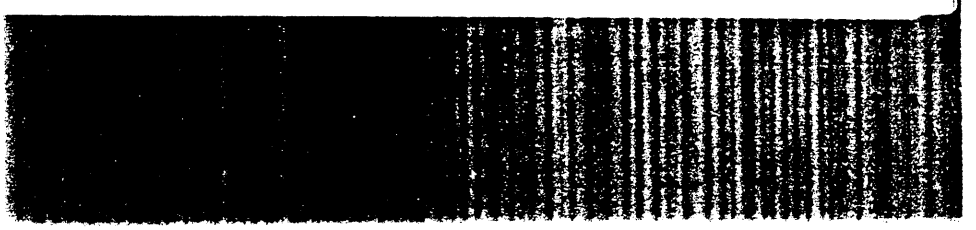


illustration. The diameter of the wire and of the loop encircling the stirring rod may be varied to suit the conductivity of the solution and of the voltage output of the generator, since the resistance offered to the passage of the electric current decreases by lessening the distance between the electrodes and also by increasing the electrode surface area. The anode should be constructed of wire sufficiently strong to resist the movement which the swirling motion of the liquid tends to impart. Platinum wire of about 12 S.W.G. is ideal for the purpose, but is rather expensive if a large number of units is required, and, in this case, an electrode support may be constructed from ¼" glass rod; it is then possible to make use of thin platinum wire by winding it spiral-wise around the glass. Although not recommended, anodes may also be constructed from heavy lead fuse wire. These are attacked by the cyanide solution but may be made more permanent by coating the wire with lead peroxide. This may be accomplished by dipping the anodes in a solution of alkali plumbate or by the electrolysis of a lead salt. The latter method is to be preferred and may be carried out by the electrolysis of a solution containing one gram of lead nitrate and 10 ml. concentrated nitric acid per 100 ml. Platinum or lead foil is used for the cathode and the current density should be about 0·05 ampere per 100 sq. cm.

Wide mouth one-pint Ball jars have proved to be excellent containers for 10 A.T. of solution and cathodes suitable for this type of container may be made up from strips of lead foil 12" by 2½". A convenient method of constructing the cathodes is to wrap the foil around a cylindrical block of wood which has a circumference of 11½", a strip of the foil is then almost severed from one end and bent upwards, the ends of the foil being united by cutting short slits, top and bottom, along the lines of overlap and twisting the two sections of foil together. Small V-notches should be cut from the bottom edge of the foil to allow free circulation of liquid which may otherwise become entrapped between the cathode and the walls of the container. After inserting the cathode the strip of foil is bent over the side of the jar and is ready for connection to the negative pole of the D.C. current supply.

With regard to the time required for complete deposition, this will vary with the current density, the efficiency of which is largely dependent upon the amount of agitation imparted to the solution. If high current densities are to be employed, the stirring rods at 550 r.p.m. will have to be larger and more efficiently designed than would be necessary when using stirrers of the Edwards type with which speeds of up to 5,000 r.p.m. are possible and simple L-shaped glass rods can be made to give ample agitation. The recommended current density is, however, between 0·15 and 0·30 amperes per 30 sq. in. of cathode surface, and between these limits the easily constructed L-shaped stirrers give satisfactory results with either type of stirring mechanism. At 0·15 amperes, deposition is completed in 1½ hours while at 0·30 ampere one hour is required for complete deposition. If, however, it is desired to complete the deposition in half-an-hour the current density must be increased to 1·5 amperes per 30 sq. in. Thus, it will be seen that, although an increase in current density decreases the time required for complete deposition, this decrease is not proportional to the current consumed, and, in fact, the higher the current density, the lower the efficiency of the machine. This loss of efficiency is of course, of little, if any importance from the assayer's point of view, but high current densities of the order of 1·5 amperes have two distinct disadvantages worth consideration; firstly, the passage of this comparatively



large quantity of electricity through the circuit heats the solution to near boiling point and, unless a current regulator is available, constant attendance on the part of the operator is necessary in order to control the current flow which increases with rise in temperature; secondly, the electrical equipment required to supply 1·5 amperes per solution will necessarily be much more expensive than that required to supply 0·3 ampere.

The deposition of the gold is not uniform throughout the operation of electrolysis but takes place much more slowly as the solution becomes poorer in metal ions. Thus the first 0·01 mgm. is deposited almost instantaneously, whilst deposition of the last 0·01 mgm. occupies a considerable proportion of the total time taken for complete deposition.

The actual assay is carried out as follows:—Ten Assay tons of head solutions or 20 A.T. of press tails or other low value solutions are measured into Ball jars or beakers into which the lead cathodes have previously been inserted. The containers are then placed in position on the machine, the stands for the containers' support being adjusted so as to leave the stirring rods and anodes in the centre of the solutions, the rod ends to clear the bottom of the containers by about $\frac{1}{4}$". The cathodes are now connected to the negative bus bar by means of the alligator clips and the stirring mechanism is started. The D.C. is switched on and the voltage adjusted to give a reading of Nx amperes on the ammeter. Here again N is the number of assays and x the desired current strength per assay.

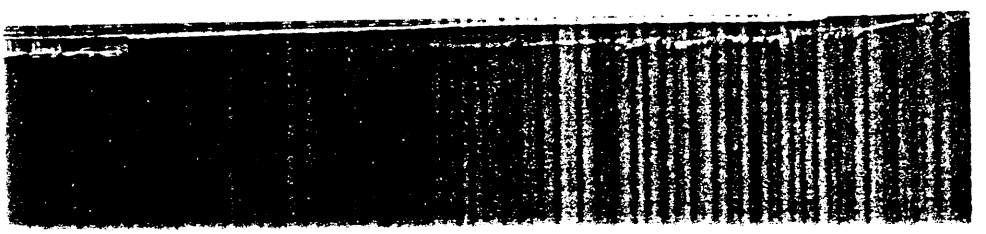
The machine is now allowed to run for the required time and during this period should require little attention from the operator. When deposition is complete the stirring mechanism is stopped, and with the current still flowing, the cathodes are removed one by one and immediately washed in running water. If the gold plated cathodes are left in the solution with the current turned off, the regenerated cyanide will tend to redissolve some of the gold, and for this reason it is important to leave the current on and to wash the cathode immediately it is removed from the solution.

The deposited gold should present a clear bright appearance and in the case of high value solutions should resemble good quality gold plating. The cathodes may be rapidly dried by shaking off the excess water, rinsing in methylated spirits and leaving for a few minutes on a low temperature hot plate. Silver for inquartation may be added to the solution before electrolysis in the form of silver cyanide, but is most conveniently added in the form of wire to the cathode, which, after drying is wrapped up and is ready for cupellation.

Purple of Cassius Test.

A rough test for the presence of gold in "tails" solutions may be useful at times and is carried out as follows:—

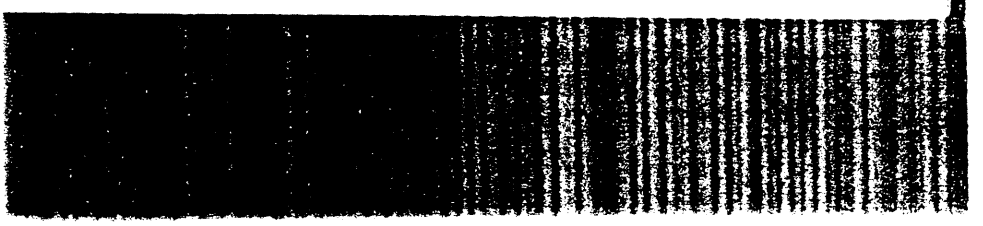
Place one litre of the solution to be tested in a bottle together with 10 ml. saturated sodium cyanide, three drops saturated lead nitrate or acetate solution and two grams zinc dust. Shake the stoppered bottle until the precipitate settles rapidly, decant the liquid and transfer the precipitate to a porcelain dish. Evaporate nearly to dryness with 10 ml. aqua regia, and take up with two ml. concentrated hydrochloric acid. Cool thoroughly and add a few drops of stannous chloride solution. A tint varying from slight yellow to purple is produced by solutions assaying from 0·02 dwt. per ton to 0·2 dwt. per ton respectively.



Care should be taken to ensure that the stannous chloride solution has not deteriorated otherwise poor results will be obtained. A few granules of metallic tin at the bottom of the bottle will prolong the effectiveness of the solution.

Gold from Gold Chloride Solutions.

The gold may be precipitated by means of sulphur dioxide but the precipitation is not always complete and therefore the evaporation method is safer.



Chapter IX.

GRADING TESTS.

Introduction.

The extraction of gold from the Rand ore has become such a highly specialized process that much detailed information is required to show the physical condition of the ore during the various stages of its reduction.

The most suitable product from all crushing, screening and grinding equipment must be ascertained. Where the product is too fine, the output of the machinery is reduced and the cost unnecessarily raised. Where insufficient grinding is the fault, subsequent stages of handling may be interfered with, or extraction affected.

Feed materials sent to crusher plants usually contain a proportion of fine material which does not need to be further crushed and which, if it enters the crushers, provides a cushioning effect for the coarse particles—thus interfering with the crushing action. Good reduction practice demands a removal of this fine material before it enters the mill.

In order to obviate faults of this nature a regularly supplied and permanent record must be made available. This record is possible only through the medium of frequent sieve tests. The feed materials and the final products must be constantly assessed by this means.

The assayer, with his sieving equipment, can provide data that leads to certain conclusions. Amongst these can be enumerated:—

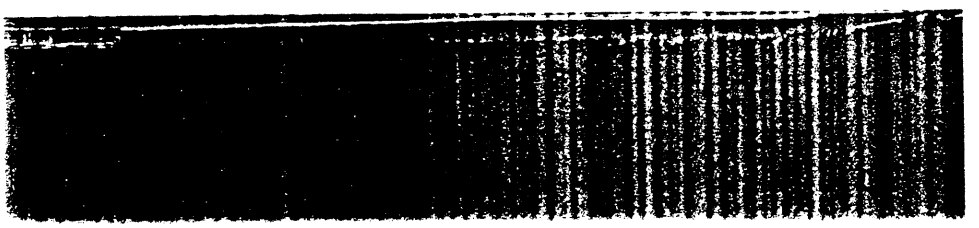
1. In the case of stamp mills, the tonnage of material crushed per stamp per 24 hours. The effect of varying screens and the speed and drop of stamps can be ascertained.
2. The duty performed by tube mills, showing the degree of grinding achieved at different speeds, rates of flow, feed and grinding media.
3. The efficiency of the classifiers under varying conditions of rate of flow, speed and height of overflow, etc.
4. Evidence confirming the reason for abnormal gold assay results.
5. In the case of coarse materials, the performance of crushers, vibratory screens, trommels, etc.
6. In the case of Newhouse or Symons Crushers, the stage at which cones and linings should be renewed.

All these can be assessed by the use of figures, supplied by the grading operator, and disclosing the percentage of coarse, medium and fine material produced by the different processes.

Theory of Grading.

Theoretically, sieving consists of agitating a weighed quantity of material in a sieve until no more material passes through. This procedure can give absolutely correct results only when the particles being sieved are all solid spheres and when the sieve apertures are all exactly the same size.

In practice these conditions do not apply and a grading test becomes, to some extent, an approximation. Standardization of procedure, however, makes possible results capable of reproduction within a narrow



margin of error and thus provides the guide needed in assessing the factors outlined in the introduction.

Examination of the particles of finely ground ore by means of a microscope, shows that while the majority tend towards a spheroid shape, from the point of view of their major axes, they are generally far removed from perfect spheres and certainly cannot be expected to behave as such. Some again show a flat cleavage and appear under the microscope as small elongated or rectangular planes. This means that many particles are, for a particular sieve aperture, both oversize and undersize, depending upon which side is presented to the aperture. Discrepancies in results are accounted for by the presence of these particles.

An ideal method might be defined as one that would retain as oversize, all particles having a volume greater than that of a sphere whose diameter is equal to the width of the sieve aperture.

As this is manifestly impossible, a compromise must be sought whereby the total weight of particles retained equals the total weight of the particles having a volume greater than the sphere described above. This can only be achieved by adopting a method which has been found and proved by experiment. Such a method will still be prone to error, but, if adopted as standard practice, will reduce the variation of error and thus give comparative figures from day to day.

Coarse Gradings.

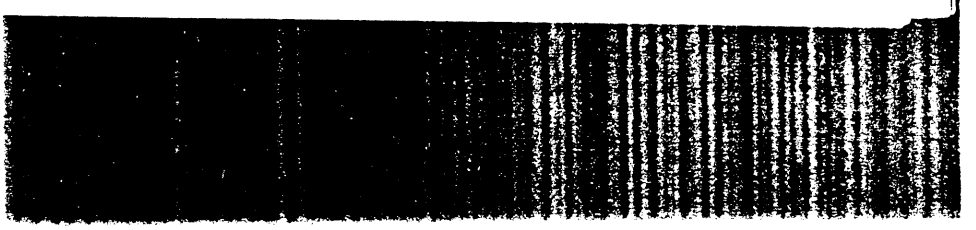
For coarse material (such as from Run of Mine ore, Newhouse Crusher and Symons Crusher, etc.) it is necessary to have a set of sieves with a depth of about 4″ and 18″ in diameter, equipped with steel wire screens with mesh ranging down 2″, 1½″, 1″, ¾″, ½″, ⅜″, and ¼″ to ⅛″. These sieves must be so made as to rest firmly one over the other in a tall "nest". The set-up is best operated in a deep trough-like concrete enclosure to prevent water spillage and yet to allow of all fines being washed away from the coarse products. A "rocker" arrangement must be placed below all these sieves so that the operator may shake or "rock" the set-up to induce the ore to pass through the openings until each sieve carries on top its respective "plus" product only.

For this type of grading a large sample is needed, i.e. from 200 to 4,000 ounces. This is weighed directly in its container on a platform scale (remembering to deduct later the weight of the container). The sample is then placed on the top screen in manageable lots, washed with a jet or spray of water and shaken until no more passes the screen being handled. If the sample is being handled in one batch, the procedure is simple and each plus fraction is merely weighed (in ounces) and the percentage of each calculated. For practical purposes, it is unnecessary to dry either the original sample, unless there is much wet slime present, or the fractions, as the degree of accuracy needed is well inside the error that may arise from this source. In the case of a very large sample, the relative fractions obtained from each portion must, of course, be added together until the whole sample has been put through the sieves.

A specimen of a "bench record" for a normal sample is:—

Newhouse Product No. 2

Mesh.	+2″	+1½″	+1″	+¾″	+½″	−½″	*Gross oz.*	*Container.*	*Nett oz.*
%	25·5	11·0	25·3	8·2	10·4	19·6	435	72	363
	93	40	92	30	38 oz. per fraction weighed.				



Grading of Finer Materials.

Requirements.—A set of sieves with accurate square mesh wire cloth with the desired mesh variations. For the daily analysis of reduction works products, such as Residues, Pulps, Screens, Classifier Overflow or Returns, etc., 48, 100 and 200 mesh are usual. (Some mines use the variation, 60 90 and 200.)

A Washing (or Bucket) Sieve.—This is a 200 mesh sieve with 8-inch sides to prevent material being washed or splashed over the edge of the sieve.

For reasons of economy some assayers make their own washing sieves by soldering an extension on to an ordinary 200 mesh sieve, but this practice does not meet with universal approval owing to the fact that faulty soldering may leave crevices in which a portion of the sample can lodge.

A Grading Machine.—There are several types of mechanical shakers but the one most commonly used on the Reef is the "Ro-Tap Testing Sieve Shaker".

A Balance and a Set of Gram Weights.—A pulp balance with a "chainomatic" attachment for weighing the fractions is suitable.

A set of gram weights from 0·1 gram is usually sufficient for ordinary routine work.

Drying Plates.—Electric drying plates with varying heats are the most suitable.

Other requirements are:—Several large buckets, 10" dishes, 6" dishes, brushes and spatulas.

Quantity of Sample.

This is governed by the proportion of oversize particles in the sample.

The number of oversize particles remaining at the end of the test should be large enough to give an average and yet should not be so large as to prevent each particle from having free access to the apertures.

For complete standardization the weight of sample taken should be such that the residual oversize is in each case the same weight. This is, of course, not practicable but, as the composition of each type of sample from a modern crushing plant varies but little from day to day, it may be said that, by taking a fixed weight for all samples, standardization for each type of sample is successfully achieved in this respect.

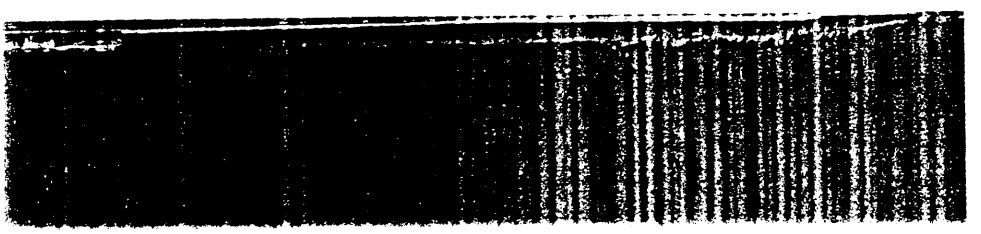
For normal reduction works products 100 grams is a suitable quantity, but for comparatively coarse material a larger quantity should be taken.

Methods of Grading.

There are two methods of grading, wet and dry. Each method has its advantages and it has been found that by combining the two, the advantages of each are retained without introducing any disadvantages.

Procedure.

Washing.—There are two methods of washing away the fine product. There is little to choose between them but, whatever the method adopted, one only should be used.



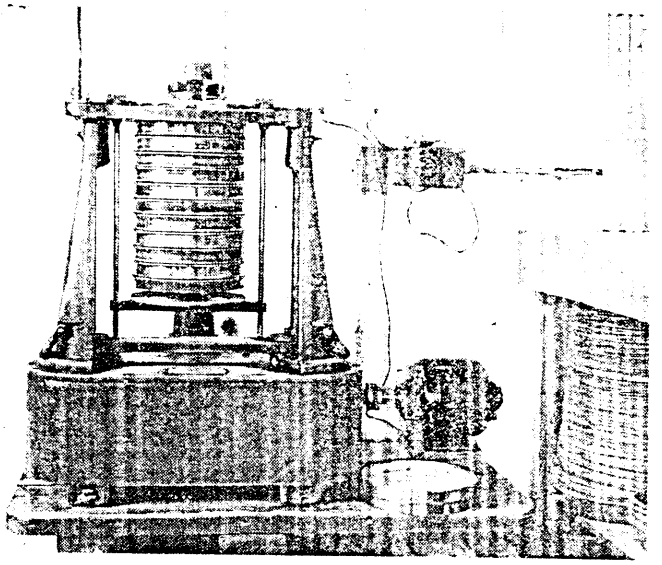


Fig. 58. Ro-Tap Sieve Shaker used in grading analysis

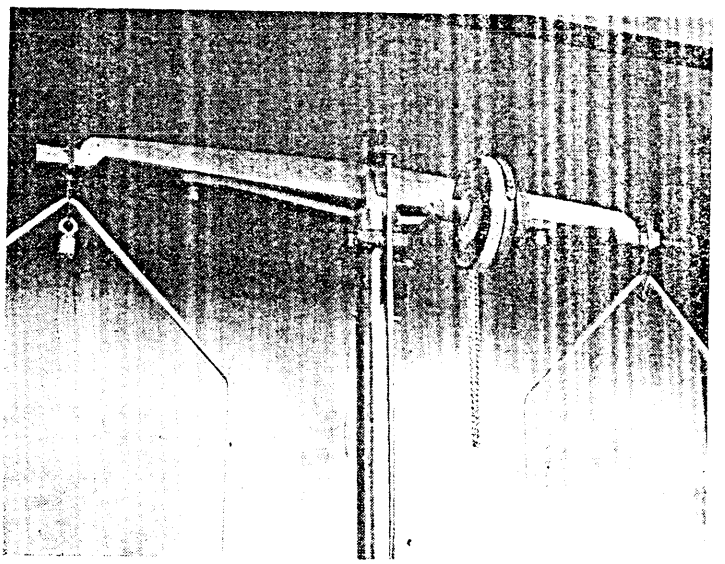
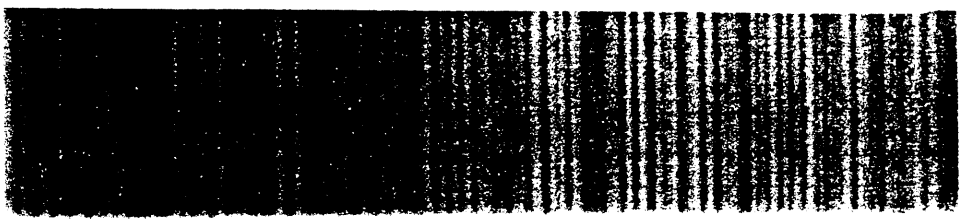


Fig. 59. Chainomatic attachment fitted to pulp balance for weighing grading samples
(With acknowledgment to Rand Leases (Vogels) G.M. Co.)



Washing in Buckets.—Two large buckets filled with water in the waste-water sink are used as "washing pools". The 100 grams of sample is placed in a 6" dish and wetted with about 200 ml. of water to avoid dust. It is afterwards washed into the washing sieve. This is then held with its sieve-base about one inch below the water surface in the first bucket and is then rotated sharply to and fro—in the manner of a balance-wheel of a watch—lifting it just above the water surface every few turns until it is seen that all lumps have disintegrated and most of the slime washed through. A few turns in a similar manner are performed in the second bucket of clean water.

The plus 200 is then washed into a 10" dish with a gentle jet of water. The water is decanted from the dish and the plus 200 dried at steam temperature.

This may be done by floating the dish on a hot water bath or by placing it on a hot plate the temperature of which is maintained at that of boiling water.

The Jet Method.—A weighed quantity of the ore is placed in a bucket sieve. The undersize is then washed through the sieve by means of a jet of water. A rose type garden spray provides a suitable jet. The time of spraying should be fixed within limits, as should the pressure of the water. (This last point is not over important, but aids standardization.) The sieve is then inverted over a dish, the diameter of which should be greater than the diameter of the sieve. The sample is washed into the dish and dried as above.

In practice a number of such washings are done in sequence, each having a numbered "bakelite" ticket in it for identification. Three such samples are then brushed respectively on to the 48 mesh or upper sieve of three interlocking nests of sieves that are put on the machine together. Each "nest" consists of 48, 100 and 200 mesh sieves with a pan to catch any minus 200 that comes through. (The washing sieve fails to remove all the minus 200 and the remaining minus 200 mainly of a sandy nature has to be removed in this way when dry.)

The grading machine should be fitted with an automatic timing device and all samples given a set time to ensure that no error arises as a result of varying lengths of time in the shaker.

The time usually given is seven minutes.

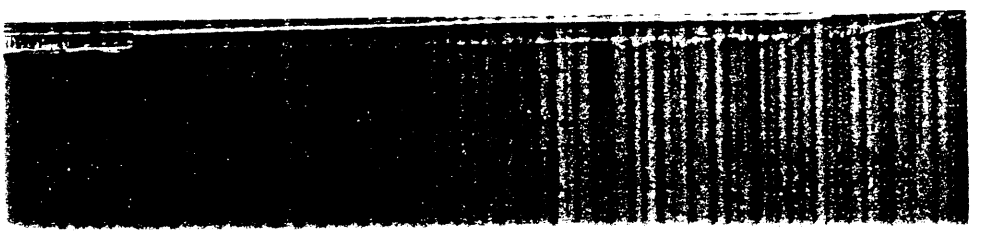
If the sieving is done by hand, a nest of sieves should be shaken in a standardized manner for a given time. A good procedure is to place the nest on a smooth surface, move it left to right, one move of 8" each half second, with a bumping action by the right hand on the leftward move: this to proceed for seven minutes for each set.

The fractions plus 48, plus 100 and plus 200 are now removed from each sieve by inverting over a piece of glazed paper, tapping the sieve perimeter gently with the handle of the brush, then brushing bottom and top.

This brushing must be gentle in order to prevent damage to the wire cloth. The fractions are then weighed on the pulp balance (to 0·1 gram) and recorded (in case of the 100 gram samples), directly as percentages.

Care of Sieves.

It is essential that the operator should examine his sieves very carefully after each day's work, holding them up to the light in order to enable him to detect any small rupture of the wire cloth. Such ruptures occur when the sieves get old, especially in the 200 mesh. (A carefully applied



solder patch can cure such a breach, and is justifiable if standardization shows the sieve to be otherwise efficient.)

Another point to be checked is the clogging of the sieve apertures. This takes place as a result of particles of ore becoming jammed into the aperture. Repeated brushing, top and bottom, with a hard brush will usually remove most of this trouble. The washing sieve, particularly, needs this attention. Care must, however, be exercised to see that the brush hairs do not enter the apertures and pull them out of shape during brushing.

Sieves should always be stacked in correct order after use and closed with the cover to prevent casual damage from any falling object.

Standardization of Sieves.

The standard grading sieves used on the Rand to-day are the Tyler.

Sieve Apertures.

These are, as a rule, fairly constant in any particular sieve, but two sieves will vary one from the other. Thus it is possible to find, to a certain degree, the difference between the two by sieving a number of portions of the same sample through each sieve. The difference between the average of the results from each sieve will show the variation in aperture sizes.

Therefore, if one sieve be accepted as a standard, all other sieves may be standardized against this one, and the relation between the aperture sizes may be ascertained and a correction factor calculated for each sieve.

It must be borne in mind, however, that different types of crushers and grinding units will produce particles of different shapes and also that different materials will break down according to variable size ranges of particles.

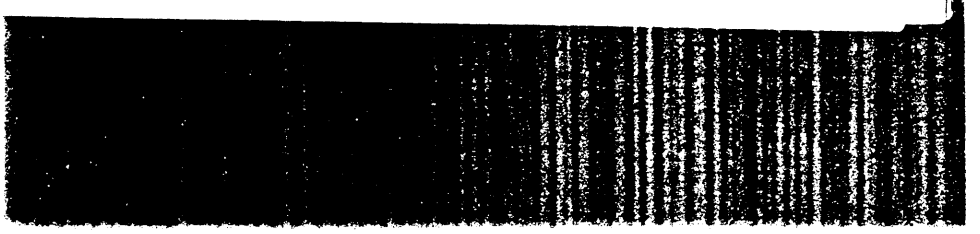
Thus it comes about that the correction factor applicable to cement may have to be modified when sieving crushed quartzite. Also, the correction factor for a tube mill product may not apply to a stamp mill product.

If a sieve is to be used on one particular mine it is safer to use the product of the grinding plant on that mine for standardizing the sieve.

Certificated standard sieves can be purchased, but, as these may have been standardized by using some material other than crushed quartzite—the factor given on the certificates cannot always be accepted as fully applicable to Witwatersrand ores. However, it is advisable for the assayer to procure a set of certificated sieves for standardization purposes.

Alternatively, a sieve of each mesh is found which gives satisfactory results, and these are accepted as "master" sieves.

As an example, ten or more portions of 100 grams are taken from a well-mixed slime residue sample. These are "wet" graded through a standard 200 mesh screen. After drying they are "dry" graded through the two sieves, i.e., the "master" sieve and the sieve to be standardized, alternate samples being graded by each sieve. The average of these two sets of figures show the percentage by which the sieve under test differs, in results, from the "master" sieve. This percentage difference, if added to or subtracted from all results obtained from this sieve, will bring these slime residue results very close to the results obtained from the "master" sieve. The same procedure should be adopted for coarse samples and for those of medium fineness.



On some mines a synthetic sample is used in place of the slime residue. By intensive wet and dry grading, four large portions are assembled, which are, respectively, all plus 48 mesh, plus 100 mesh, plus 200 mesh and minus 200 mesh. By combining various weights of these samples a synthetic mixture is obtained which is used as the standard test sample.

STANDARD AVERAGE EXAMPLE (medium grade):—

Mesh	Standard Av.	Set being Tested (Av.)	Error (gm.)	Correction	
				Grams	% of w'd material
48..	24·04	23·91	−0·13	+0·13	+0·54
100..	26·03	25·52	−0·51	+0·51	+2·00
200..	22·66	25·88	+3·22	−3·22	−12·44

The correction should then always be made as calculated from the percentage. As in the above, this would be 12·44 per cent of 25·88 = 3·22. This deducted from 25·88 = 22·66, which is the correct figure.

The following extract from "Profitable Use of Testing Sieves" Catalogue 53 of W. S. Tyler Company is of interest.

> "The ratio between the different sizes of the screen scale has been taken as 1·414, or the square root of two, as recommended by Rittinger in his work on ore dressing. The niceness of this will be apparent from the following: taking 0·0029 inch or 0·074 millimetre, the opening in the 200 mesh sieve, as the base or starting point, the width of each successive opening is exactly 1·414 times the opening in the previous sieve. It also makes the area or surface of each successive opening in the scale just double that of the next finer or half that of the next coarser sieve. In other words the widths of the successive openings have a constant ratio of 1·414, while the areas of the successive openings have a constant ratio of 2."
>
> "Another advantage in this selection of ratio is that, by skipping every other screen, you have a ratio of width of 2 to 1, by skipping two sizes you have a ratio of 3 to 1 and by skipping three sizes you get a ratio of 4 to 1, so that in selecting a screen scale for concentrating work, for instance, you can pick out from the table without any calculation a 1·414, 2, 3, or 4 to 1 ratio of opening."

GRADING ANALYSES

The economics of crushing and treatment in the reduction works can be brought nearest to perfection if a knowledge of the distribution of the gold is used as a guide.

In some ores the gold is so "free" that a fairly good extraction is obtainable from a coarsely ground ore. In others the gold consists mainly of submicroscopic particles locked up in the quartzite and the pyrites. A knowledge of the ore's characteristics from this point of view is essential to efficient reduction works practice.

It is necessary, therefore, for the assayer to be able to carry out this form of analysis.

The analysis consists of preparing a sufficiently large portion of the sieve products to make it possible to assay each one accurately. The Reduction Officer would, of course, select a large sample of his treated product, or residue, for such a test. For example, if a residue of the following comminution were to be analysed in this way, the smallest percentage would guide the assayer in his decision as to how much sample is to be graded:—

$+48 = 5{\cdot}0\%$, $+100 = 10{\cdot}5\%$, $+200 = 26{\cdot}5\%$, $-200 = 58{\cdot}0\%$.

An accurate assay would demand at least two 1 A.T. charges, i.e., 60 grams, or 12 times 5 for the plus 48 in this case. So that 1,200 grams will have to be put through the sieve for the test. The best way of achieving this is to wash 1,200 grams (200 grams at a time) through the 200 sieve into two or three litres of water in a bucket; and re-washing each batch of 200 grams into another such quantity. The minus 200 is recovered on a Buchner Funnel, dried, sifted to break up the lumps, and assayed along with the other products, i.e., plus 48, plus 100, plus 200, prepared from the dried plus 200.

The assayer would then have values, e.g.,

1·62 dwt. per ton of + 48
0·91 dwt. per ton of +100
0·30 dwt. per ton of +200
0·12 dwt. per ton of −200

(It is here obvious that the plus 48 and the plus 100 should be more finely ground.)

Calculation would then follow:

TABLE 1:

Comminution.

+ 48	5·0%	5·0	Tons would contain		5·0 × 1·62 =	8·100	dwt.
+100	10·5%	10·5	,,	,,	10·5 × 0·91 =	9·555	dwt.
+200	26·5%	26·5	,,	,,	26·5 × 0·30 =	7·950	dwt.
−200	58·0%	58·0	,,	,,	58·0 × 0·12 =	6·960	dwt.
		100·0			Total =	32·565	

The calculated value per ton would thus be $\frac{32{\cdot}565}{100} = 0{\cdot}32$ dwt.

The significance of these figures is brought out in a different way if the "distribution" of the gold is then calculated to a percentage.

5·0%	of each ton has	0·08100	dwt.	or	24·87%	of	0·32
10·5%	,,	,,	,,	,,	0·09555	,,	,,	29·33%	,,	0·32
26·5%	,,	,,	,,	,,	0·07950	,,	,,	24·41%	,,	0·32
58·0%	,,	,,	,,	,,	0·06960	,,	,,	21·49%	,,	0·32

Thus nearly 25 per cent of the residue gold is found to be in 5 per cent of the residue.

REPORTS ARE USUALLY SUBMITTED:—

TABLE 2.

Mesh	Comminution % by weight.	Dwt./Ton.	Gold Content: dwt.	% Distribution.
+ 48	5·0	1·62	·08100	24·87
+100	10·5	0·91	·09555	29·33
+200	26·5	0·30	·07950	24·41
−200	58·0	0·12	·06960	21·39
Calculated original residue			0·32565	100·00

Value in residue (by assay) 0·34 (or whatever the direct assay may have shown.)

Method for Quick Determination in Plant—When speed is important, a quick method of grading analysis with a reasonable degree of accuracy can be done in the Reduction Plant as follows:—A litre flask is filled with the wet pulp and weighed on a Stadler sp. gr. balance. The contents are tipped on to the appropriate screen and the fines washed through the screen which is then carefully dried on a moderately heated plate and the plus material weighed. As the quantity of solids in the flask is established from tables, the percentage plus material can be calculated. This method saves the drying of the whole sample before grading.

CHAPTER X.

THE SAMPLING AND ASSAY OF GOLD BULLION AND THE ANALYSIS OF BULLION AND GOLD SLIME.

THE ASSAY OF GOLD BULLION.

SAMPLING.

Three methods of sampling gold bullion are practised on the Witwatersrand. These comprise the withdrawing of a portion of the molten metal from the crucible before casting, the drilling of the bar after casting, or the removal of portions termed "clips" from the bar by means of a special machine. The samples thus obtained are described as "dip", "drill", or "clip" samples respectively.

It is generally accepted that more accurate and representative samples are obtained by dip sampling particularly when the bullion contains an appreciable percentage of impurities. Base metals tend to float to the top of the molten bullion, and segregate in this position in the bar after casting. Drillings and clips are likely to contain an undue proportion of either impurities or the gold itself and may not be representative of the whole mass. By thoroughly stirring the bullion in the molten state, a homogeneous mixture is obtained from which it is a simple matter to withdraw a small portion or dip sample truly representative of the whole.

While this method overcomes most difficulties of sampling, the presence of osmiridium, which is occasionally found in bullion, presents a problem more difficult to surmount. Osmiridium is not fused at the temperature of the ordinary mine smelting furnace and consequently remains distributed unevenly throughout the mass of the bullion. Close agreement between individual assays is difficult to obtain, hence it is usual to carry out a large number of assays (say 6-10) and to accept the average of these results as the fineness of the bullion.

The Dip Sample.—The molten metal is thoroughly stirred, the practice of the "Royal Mint" being to stir 100 times; a plumbago sampler, which has been previously heated to redness, is then inserted into the metal with a stirring motion; the sampler should reach at least half-way to the bottom of the charge.

The sampler is then withdrawn and without delay the metal is poured from the sampler through water into an evaporating basin which lies at the bottom of a bucket of clean water; the basin is removed, and as much of the slag as possible is panned off. The sample is then dried.

Plumbago bullion samplers may be purchased or they may be cut from old "salamander" crucibles.

The Drill Sample.—The bar to be sampled is first wiped dry, and a sharp $\frac{1}{4}$ inch drill is sent into it to a depth of $\frac{1}{8}$ inch; the resulting drillings are put aside with other scrap gold, and the same hole drilled into again to a depth of $\frac{1}{2}$ inch; this gold is emptied on to a clean piece of glazed paper; the same drilling operation is carried out on the reverse side of the bar, and at the opposite end to that first sampled. The resulting pieces of gold are

– Vacuume tube sample – best!

mixed with those from the first sample. A powerful magnet may then be used to remove any steel which may have come from the drill.

The Clip Sample.—In some cases clip samples are taken in addition to dip samples.

Two bars are melted together in a coke furnace and the dip samples are taken. The bullion is then cast into small moulds, each lot being cast into five bars.

The first and last bar of each lot is clip sampled. This is done in a machine similar to a metal planing machine. The tool is approximately $\frac{1}{8}$ inch wide and the clips are taken across the bar.

Four or five cuts yield sufficient gold for a sample.

The drill sample and the clip sample usually give a slightly lower value than the dip sample, the difference becoming more marked as the fineness of the bar decreases.

Bullion Assay.

The purity of gold bullion is expressed as "fineness" in parts per thousand, and the result of a bullion assay is reported in this way. A set of weights is used in the assay of gold bullion which are marked in thousandths of a half-gram. They are sometimes referred to as milliéme weights (1 milliéme being equal to 0·5 milligram). The usual quantity taken is 0·5 gram (1,000 parts) and the weight of fine gold resulting from the assay, when weighed with the same weights, will represent the fineness of the bullion in parts per thousand.

In practice, however, a small correction is usually required. There is sometimes an appreciable loss of gold during cupellation, while on the other hand, it is impossible to extract the last traces of silver from the cornets during the acid treatment.

To correct such errors a check assay is conducted; this is made up of an exactly weighed amount of proof gold, with copper and silver in as nearly as possible the same proportions as are contained in the bullion under examination.

This check is treated with the assays, and subjected to the same conditions throughout; any gain in the result of the check must therefore be subtracted from the result of the assay proper. This gain is called a "surcharge". A gain in the check is usual; losses are not frequent, and should be viewed with suspicion. It is almost impossible for losses to occur except as a result of one or more of the six causes given below.

1. Careless handling.
2. Cupel absorption; which becomes more marked in its importance as the proportion of lead to the precious metals increases.
3. The use of impure gold for check purposes.
4. A faulty cupel.
5. Excessive cupellation temperature.
6. The use of impure acid.

Whatever the cause of the loss, the assay should be repeated.

Method of Assay.

As it is somewhat tedious to weigh out exactly 0·5 gram (i.e., 1,000 parts) for assay, the weight taken is generally brought to within 0·25 of a mgm., or 0·5 of one thousandth, which may be either in excess of or less than 1,000; the exact weight is then noted.

Pieces of lead foil are cut and placed on a cupel tray. The amount of lead to be used should be governed by the fineness of the bullion, e.g.—

Bullion Fineness	*Lead Required*
950—1,000	2 grams
900— 950	4 grams
800— 900	6 grams

The last is a ratio of 12 to 1 when 0·5 gram of the sample is taken.

For bullion under 800, 4 grams of lead should be added for each 100 below 800.

To the conical lead cups, prepared for the assays, is added about 25 mgm. of electrolytic copper, and to that of the check about 40 mgm.

If the same gauge of copper wire or foil is always used the metal need not be weighed, as the required weight can be cut off by use of a template. The reason for the addition of this copper is to prevent the phenomenon technically known as "vegetation" when the cupels are removed from a hot muffle; extra copper is added to the check, there being no copper in the proof gold, the aim being to render the check as nearly representative of the assays as practicable. The weight of proof gold taken is usually the amount of the expected fineness of the bars. That is to say, if bars of 900 fineness are expected, the amount of proof gold taken is 900 half-milligrams or milliémes.

The silver for parting is usually added in the form of silver discs. Discs of various weights are obtainable from the Rand Refinery. A disc weighing 1·125 grams is usually added to bullion samples which have a fineness of over 850.

The amount of silver added should be such that the resulting alloy does not contain less than 2·2 parts of silver to one of gold, or more than 2·5 of silver to one of gold.

Method of Weighing the Gold.—The sample of bullion is first hammered, then rolled through the flattening mill (bullion rolls) and cut into small pieces with scissors in order that a representative small portion may be taken for assay. This is specially necessary for dip samples.

From the sample of bullion, pieces are placed in the left-hand pan till the amount is slightly heavier than the 1,000 weight already placed in the right-hand pan. The pan containing the sample is taken off, a large piece of the gold removed, held firmly in a strong pair of pliers, and cut with a pair of shears till the weight is, say, 1,001. In order to bring the weight to within 0·5 very small pieces are cut off until the weight is $1{,}000 \pm 0{\cdot}5$. The exact weight is noted.

When the desired weight is obtained, the contents of the pan are placed in the lead cone, and the pan carefully brushed to ensure that all is transferred to the cone.

The cone is now securely wrapped up and replaced in the cupel tray.

Duplicate portions of all bullion samples are taken and the weight entered in the bullion book.

The assays are placed in the cupels, which have already been put in the muffle and attained the muffle temperature, which should be between 1,000° and 1,050°C., the heat being kept constant during cupellation. An extra row of unused cupels will assist in maintaining a constant temperature. After 15 minutes the cupels may be carefully removed and allowed to cool on the plate in front of the muffle till the buttons have

solidified, when they are replaced in the cupel tray and taken to the anvil. Each button is gripped with the pliers, placed on its edge and struck lightly with a hammer to release any adhering cupel material, the last traces of which are brushed off with a hog's-hair or brass-wire brush.

The button is then flattened by a few sharp blows with a hammer, and when each has been treated in this way the batch is placed in a suitable receptacle and annealed in the muffle at a temperature of about 700°C. Alternatively they may be heated over a bunsen or a primus stove. If possible, bullion work should be done in the day-time, as muffle temperatures are sure to be over-estimated when working at night, unless the assayer is very experienced in light contrasts. After annealing, each button is rolled in the "flattening" mill to a ribbon of about three inches in length; these ribbons are again annealed (700°C.), rolled into a cornet with the fingers, and placed in the parting apparatus, which consists of a nest of small cups made of either platinum or silica supported in a frame of usually the same material; the first cup is identified by means of a handle or other distinguishing mark.

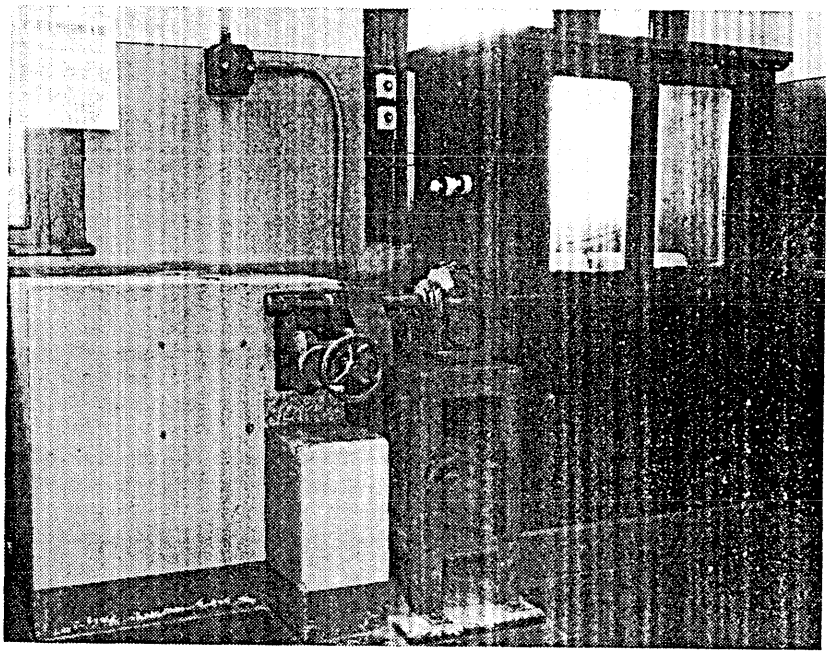


Fig. 60. Fume Cupboard for parting gold bullion assays.
Note power-driven rolling mill on left.
(With acknowledgment to Geduld Prop. Mines Ltd.)

Parting.—In this operation two acids are used, the first being 30 per cent nitric acid (1 vol. acid : 2 vol. distilled water), the second 70 per cent (2 vol. acid : 1 vol. distilled water). The parting apparatus is gently lowered into a glass beaker containing sufficient boiling weak (or first) acid by means of a hook-shaped glass rod or platinum wire. Ten minutes after the evolution of brown fumes has ceased, or 20 minutes after the

apparatus was placed in the acid, it is removed and placed in the boiling strong acid (70 per cent), where it remains for 20 minutes.

The apparatus is then removed and the cornets are drained, thoroughly washed in boiling distilled water, followed by several cold distilled water washes, drained, dried and annealed in the muffle at a dull red heat.

If a platinum apparatus is used, and the final annealing carried out at too high a temperature, there is a tendency for the cornets to stick to the cups; but this does not occur when the silica apparatus is employed, and is one of the reasons for the use of the latter.

After cooling, the cornets which have the colour of ripe corn and a characteristic silky appearance may be tipped out by inverting the cup and lightly tapping it. They are now weighed and the weights entered in the "Bullion" Book, e.g.:—

Description	Weight taken 1000 = ½ gram.	Weight Obtained.	Adjusted Weight.	Average.	Check.	Corrected Fineness.	Fine Gold Reported.
Mill 8 and Mill 9..	1000·1	918·5	918·4	918·3	·4	917·9	918·0
	1000·2	918·4	918·2				
	1000·2	918·4	918·2				
Check	900·2	900·6					

As shown above, it is usual to report to the nearest half part per thousand.

Estimation of Silver.—In order to estimate the silver in bullion, an extra assay is carried out precisely as in the case of the gold estimation, but omitting the inquartation and the addition of copper. The weight of the resulting button of bullion (gold and silver) is deducted from the weight taken, i.e. 1,000; the difference represents the base metal. The gold fineness plus the base metal deducted from the original weight taken equals the silver fineness. In work of any importance, a check of similar composition to the assay should be put through the process, in order to ascertain the error due to volatility of silver or cupel absorption.

All bullion samples should be kept until such time as it is known that they will not be required for checking purposes.

Lead Bullion.

The samples of this product are usually received at the assay office in the granulated form. If the bath of molten lead has been well stirred before taking the dip, the sample will be thoroughly representative. So perfect is the mixture of metals in the alloy that in disposing of lead bullion a difference of 0·2 per cent between the buyer's and seller's assays is the greatest variation allowed, without proceeding to arbitration.

Since the result of this assay is the earliest reliable information the reduction officer can obtain as to the quantity of gold he may expect from the cyanide clean-up, it is usually required as soon as possible. The method of assay, being merely that of cupellation and parting, is a very simple matter, requiring, however, certain important precautions.

(*a*) The sample must be thoroughly dry. The drying must never be forced, i.e. the temperature must always be well below the melting-point of lead.

(*b*) The granules must be freed from all slag (litharge) which may have formed during the act of sampling. This is done by rolling them on a hard surface, and blowing away the separated slag.

Of the lead thus cleaned and dried 5 grams, or such weight as is the assayer's custom, is carefully weighed on the chemical balance, wrapped in lead foil, put into a hot cupel and watched until completely molten in order to ensure that spirting has not taken place. The assay of lead bullion is usually done in duplicate or triplicate, and the first report is made at once in terms of bullion, the fine gold result being reported after parting.

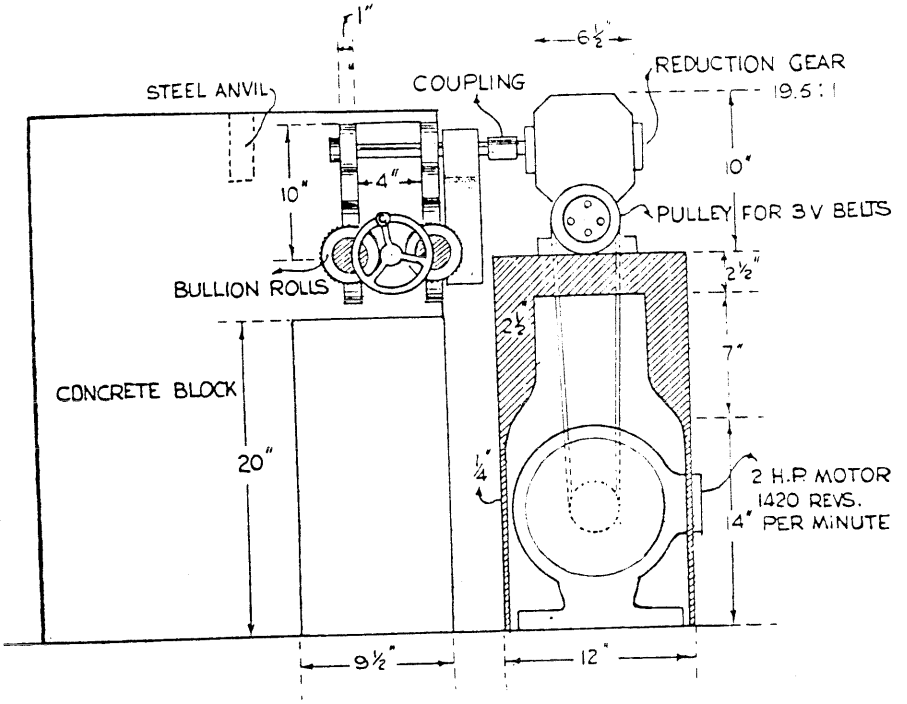


Fig. 61. Electrically-Driven Rolling Mill.
A 2 H.P. motor drives the rolls at 25 r.p.m.

Purchases of lead containing gold are sometimes made from smelting works, so that an estimation of gold content is called for. The lead will be in the form of pigs of about 1,000 oz. each.

Cuttings of lead are taken from a corner of each pig, or, if a large quantity is being handled, from every fifth or tenth pig. When these are received at the assay office they are hammered flat, each piece cut in half by shears, one half being retained for check purposes in case of disagreement, and from the other halves are cut small pieces as nearly as possible of equal weight for assay, which is conducted as in the case of the granulated lead described above.

It may sometimes happen that the lead bullion contains an appreciable amount of copper, in which case it may be found necessary to remove this by scorification prior to cupellation.

Base Metal Bullion Bars.

The most satisfactory method of dealing with samples from bars containing a high percentage of base metals is to remove the base metals by scorification. Weigh out one to five grams of the bullion, depending on the value, wrap up in assay lead foil and place in a scorifying dish. Add lead to bring the total lead to about 40 grams. Scorify and pour. If the percentage base metals is very high, re-scorification may be necessary. The lead button is then cupelled and treated as an ordinary gold bullion sample.

Silver losses are generally high when using the scorification method and the slag should be re-assayed by the fusion method. Most of the silver can be recovered by this method. Silver for inquartation should be added after scorification and prior to cupellation.

GOLD SLIME ANALYSIS.

This analysis is usually called for when difficulty is encountered in the precipitation of the gold, in the separation of the gold slime from the barren solution, or in the smelting of the gold slime.

The necessity for this analysis cannot be forseen and therefore when the need arises, a speedy analysis is required if the information is to be of any value.

The following rapid method will be found useful in such cases.

Method of Analysis.

The sample is dried at a low temperature to prevent any roasting or calcining effect.

One gram of the dry material is weighed out and decomposed with the minimum of aqua regia. When decomposition is complete sulphuric acid is added and the assay is heated to fumes, cooled, diluted, filtered and washed.

The residue consists of the silver, lead and silica, while the filtrate will contain gold, copper, zinc, iron, nickel and calcium.

To extract silver, the residue is washed in the filter with hot dilute ammonia until all the silver chloride has been washed out. This solution of silver is caught in a beaker, and treated with nitric acid, in which silver chloride is insoluble. The silver chloride is filtered off and the silver determined by the method described under Gravimetric Assay for Silver.

Lead.—The lead and silica remain in the original filter and the lead may be removed by washing with hot ten per cent ammonium acetate. The lead in the filtrate is estimated by titrating with ammonium molybdate using tannin indicator as described under the assay of lead. (See "Assay of Base Metals".)

Silica.—The remainder of the residue consists of silica, provided the decomposition of the sample with aqua regia was complete. This can now be dried, ignited and weighed as silica. It may happen that the

solution, before precipitation, contained some slime. This will be counted as silica and while not actually silica, may be counted as such for all practical purposes.

Gold.—The original filtrate is now warmed and treated with 0·5 gram of sodium sulphite. This generates sulphur dioxide which precipitates the gold. After standing for a few hours it is filtered off, dried, ignited and weighed.

Copper.—To the filtrate from the gold filtration a crystal of sodium sulphide is added and the mixture is warmed. The generated hydrogen sulphide will precipitate the copper as copper sulphide. This is filtered off and the copper is determined as described in the copper assay.

Calcium.—The filtrate from the copper is made ammoniacal, warmed and treated with yellow ammonium sulphide or a 5 per cent solution of sodium sulphide. Zinc, iron, and nickel are precipitated. The solution is brought to the boil and the coagulated precipitate filtered off and set aside. The filtrate is gently boiled with a slight excess of nitric acid or bromine and, if necessary, filtered to remove any sulphur. Warm 15 per cent ammonium oxalate is now added to the boiling solution and the beaker set aside for the fine precipitate of calcium oxalate to settle. The precipitate is filtered off and the calcium is determined as described in analysis of limestone.

Nickel.—The residue from the first calcium filtration which contains the zinc, iron and nickel is washed with cold hydrochloric acid. This removes the zinc and iron, leaving the nickel on the filter paper. This is dissolved in aqua regia and taken almost to dryness. Dilute acid is employed to dissolve the residue, the solution if necessary being heated. The solution is neutralized with ammonia and then two more drops of ammonia are added. About 10 ml., 1 per cent dimethylglyoxime is now added, and the solution heated to 60°C. After standing for ten minutes the nickel glyoxime is filtered off through a weighed Gooch crucible, dried at 110°C., cooled and weighed. Alternatively it may be ignited to nickel oxide, cooled and weighed as such.

Iron.—The filtrate containing the iron and zinc is oxidised as before, and the iron precipitated as iron hydroxide by the addition of ammonia. The iron is filtered off and the quantity determined as described under the estimation of iron.

Zinc.—The filtrate from the iron hydroxide is acidified with hydrochloric acid and the zinc is determined by titration with potassium ferrocyanide, using uranium acetate as external indicator.

Sulphur.—One gram of the gold slime is taken and boiled with sodium carbonate solution. The insoluble sulphates are converted to soluble sodium sulphates which can be filtered off. The filter is washed well and the filtrate is acidified with hydrochloric acid. The sulphates are precipitated by the addition of hot barium chloride. The precipitate is filtered, ignited and weighed. It is then reported as sulphate sulphur.

The residue, after filtering off the sodium sulphate, is washed into a beaker and oxidized by boiling and adding nitric acid and potassium chlorate. The nitric acid is removed by evaporating to dryness. The now soluble sulphates are taken up in hot sodium carbonate, filtered and precipitated as above. They are reported as sulphide sulphur.

ANALYSIS OF GOLD BULLION.

In analysing gold bullion for base metals the percentages to be determined are usually very small.

The chief impurities are lead and copper; traces of nickel, arsenic, and bismuth are often found.

Manganese and zinc have also been detected, the former having its source in the manganese dioxide used for fluxing the gold slime.

Considering the high temperature at which the metal is melted it might be expected that zinc and arsenic would be absent in a bullion bar, but these impurities have definitely been proved to be present. Zinc can be an annoying and extremely difficult base metal to remove, if it once gets into "smelt" as zinc oxide.

The gold and silver are estimated by cupellation assay as given in another part of this chapter; for the other metals a large quantity has to be taken; about 10 grams being suitable.

The sample is dissolved in aqua regia, and the solution evaporated down to a syrupy consistency, then diluted considerably, and the silver chloride settled and removed by filtration. Sulphur dioxide is then passed into the filtrate till a considerable excess is present and the mixture allowed to stand for three or four days in a warm place.

The gold is precipitated, possibly accompanied by some of the lead (as lead sulphate). The solution is filtered off and the filter well washed. The precipitated gold is warmed with ammonium acetate solution and the dissolved lead filtered off.

This filtrate (*a*) is put aside and the remainder of the lead afterwards added to it.

To the original filtrate from the precipitation of the gold by sulphur dioxide a little sulphuric acid is added and the solution evaporated until dense white fumes are given off. The solution is allowed to cool and is then diluted and an equal volume of methylated spirits added for complete precipitation of lead sulphate. It is allowed to stand for a few hours, (overnight if convenient) and, if any lead sulphate is seen, it is filtered and washed. The precipitate is dissolved in ammonium acetate solution and added to filtrate (*a*).

Lead is determined either by volumetric or colorimetric method as described in the chapter on base metals.

The sulphuric acid filtrate is neutralized with ammonia, made slightly acid with hydrochloric acid and hydrogen sulphide passed into the solution. This precipitates arsenic, copper and bismuth. The precipitated sulphides, after filtration, are digested with caustic soda solution, which dissolves the arsenic and leaves the copper and bismuth sulphides unaltered.

The alkaline filtrate is acidified and hydrogen sulphide is again passed to precipitate the arsenic as sulphide. Arsenic sulphide precipitate is treated in the same manner as that described in the determination of arsenic.

The copper and bismuth sulphides are dissolved in hydrochloric acid, made up to a known volume, which is then divided into two portions. The copper is determined in the one portion, employing the sodium thiosulphate-iodide method, the bismuth being determined in the other portion by adding ammonium carbonate, filtering, washing and igniting the precipitate which is weighed as bismuth trioxide.

Another method is to add ammonium carbonate after the titration. This precipitates the bismuth. The precipitate is filtered, washed, dried and ignited. It is weighed as bismuth oxide.

$$Bi_2O_3 \times 0{\cdot}897 = Bi.$$

The filtrate from the original hydrogen sulphide treatment—containing the iron, manganese, nickel and zinc—is boiled to expel the excess of hydrogen sulphide, nitric acid is added to oxidize the iron and it is boiled again.

Excess ammonium chloride is added, and then some ammonia. The precipitated ferric hydrate is filtered off, the precipitate is dissolved in dilute sulphuric acid and the solution is reduced in a "Jones Reductor". The iron is determined by titrating with standard potassium permanganate.

Bromine, in excess, is added to the filtrate from the iron precipitation. It is then rendered ammoniacal and allowed to stand at just below boiling point for some time. The manganese is precipitated and filtered off. The precipitate is redissolved and the manganese is determined by the sodium bismuthate method.

The filtrate from the manganese precipitation is treated with dimethylglyoxime which precipitates the nickel. The precipitate is filtered off through a weighed Gooch crucible, air-dried at 110° C., cooled, weighed and calculated to nickel. Zinc, if present, can be determined in the filtrate by titration with potassium ferro-cyanide. By using ferri-ferro-cyanide solution, an indicator, such as diphenylbenzidine, can be used internally.

THE ASSAY OF BY-PRODUCTS, COMPLEX GOLD ORES, AND OTHER MATERIALS CONTAINING GOLD.

Introduction.

The assay of these complex materials may involve the use of processes which are not used when assaying a normal Reef ore. This is due to the presence of certain elements which interfere with the normal assay in one or more ways.

Gold is often found associated with copper, arsenic, antimony, manganese, zinc and tellurium in nature and with calcium, osmiridium, iron, mercury, ashes, carborundum and fire-clay in the case of by-products; consequently it is advisable, when dealing with an unknown material, to make a qualitative analysis in order to guide the assayer in the selection of suitable fluxes.

Examples of Typical Interference.

1. Sulphur, which renders the lead button brittle, difficult to clean and causes trouble during cupellation. When present in larger quantities it forms a MATTE. This is a mixture of metallic sulphides which retains some of the gold and a larger proportion of the silver, and cannot be cupelled.

2. Metals which pass into the lead without affecting its malleability unless present in very large quantities, but which are not removed with the lead during cupellation and remain behind in the cupel in the form of a ring of metallic oxides. This ring invariably holds up some of the gold. The ring is called a scoria. Metals which exhibit this property are, amongst others, nickel and zinc.

3. Metals which break down the surface tension of the gold prill and cause it to be absorbed by the cupel. Tellurium and copper have this effect.

It thus becomes necessary to remove or neutralize the interfering substances. This can be done by using one or more of the following methods:—

(*a*) Acid Treatment.
(*b*) Roasting.
(*c*) The use of special fluxes.
(*d*) Scorification.
(*e*) Fritting.

Acid Treatment.

The necessary weight of ore is taken and placed in a suitable beaker. Sufficient of the required acid is added and the interfering substance is dissolved either by allowing to stand for the necessary period of time, agitating the mixture, or by heating.

Heating is the most common method used. The mixture is then filtered and washed and the insoluble residue is dried, fluxed and assayed.

Hydrochloric acid is used to remove antimony.

Nitric acid readily attacks mineral sulphides and most base metals and is used to remove these substances. Owing to the fact that it may liberate nascent chlorine from chlorides, it should not be used when chlorides are present as solution of the gold may result.

Sulphuric acid is used to remove metals such as copper and iron.

ROASTING.

Roasting is a process whereby volatile impurities are removed by means of heat, from material to be assayed. The heat is applied gradually and is not carried above a blood red colour (about 550° C.) until the reaction is almost completed. The heat may then be raised gradually until a full red heat (about 750° C.) is attained.

Too high a temperature at the commencement may cause fusion of the assay, while rapid evolution of the fumes of arsenic, antimony or zinc may cause mechanical loss. The operation is complete when no fumes can be seen or smelt—when the roast is said to be "sweet".

Roasting should be resorted to only when absolutely necessary, and the assayer should know what impurities are present, as certain materials cause volatilization of gold. The action of chlorides is particularly noticeable. A sample mixed with 10 per cent, by weight, sodium chloride will lose most of its gold if roasted at 750° C. for half an hour.

When roasting a sample the following procedure has proved effective.

Method.—The roasting dish should be large enough to enable the assayer to spread the sample very thinly over the dish and thus render stirring unnecessary. Sufficient gold-free silica is placed in the dish to cover the surface of the dish completely. The silica is flattened with a large rounded glass stopper or other suitable instrument until a smooth, packed, surface is obtained. Another method is to "pepper" the dish with silica from a sieve.

The necessary amount of ore is now weighed out and mixed with some silica. The amount of silica depends entirely on the nature of the ore. Ores containing only a small amount of easily fusible material may require no silica, but the higher the percentage of low melting point ingredients, the higher the percentage of silica required. Thus, for samples containing over 70 per cent pyrites, equal weights of ore and silica are necessary to prevent partial fusion and caking.

The mixture is sprinkled evenly over the prepared roasting dish. The dish is placed in the entrance of an open, red hot muffle and allowed to remain there for about ten minutes. Then the dish is moved gradually farther into the muffle until a dull red heat is attained. This temperature is maintained until no more fumes can be seen coming from the roast. The muffle is now closed and the temperature raised to about 750° C. Then the muffle is opened and allowed to cool somewhat. The dish is withdrawn and allowed to cool completely.

If copper sulphate is present, the sample must be cooled after roasting and ammonium carbonate mixed with the ore and the mixture again heated until the fumes have ceased. The sulphates are converted to ammonium sulphate which is volatile and passes off.

The presence of arsenic and antimony necessitates the addition of fine charcoal after the roast is apparently complete. This extra reducing agent is necessary to counteract the iron oxide. The charge is then re-

roasted in order to reduce and then re-oxidize and volatilize the oxides formed. Care must be taken to burn off all the charcoal.

For such work the use of an electrical thermocouple to register temperature is advantageous.

Special Fluxes.

By "special fluxes" is meant those fluxes not mentioned in the theory of the assay fusion as being necessary for the formation of a slag. The most common are:—

Sodium nitrate.
Metallic iron.
Caustic soda.
Sulphur.

Sodium nitrate ($NaNO_3$) is a powerful oxidizing agent and is used to oxidize metallic sulphides, causing the sulphur to pass off as sulphur dioxide, while the balance is converted to sodium sulphate.

$$4FeS_2 + 10NaNO_3 = 4FeO + 5Na_2SO_4 + 3SO_2 + 5N_2$$

Metallic iron is used as a desulphurizer. The iron combines with the sulphur to form iron sulphide which is readily dissolved in the slag provided excess sodium carbonate is used.

NaOH — Caustic soda is used as a flux for antimonial and arsenical ores.

Sulphur is used for samples containing large amounts of metallic iron. The action is the same as when adding metallic iron to sulphide ores. Excess sulphur should, at all costs, be avoided.

Scorification.

Scorification is an oxidizing fusion; the ore is mixed with granulat lead together with a little borax and placed in a scorifier in the muffle. The scorifier is a shallow dish made of fireclay: shallow so as to offer a large area for oxidation. Borax is used to lessen corrosion of the scorifier and to render the slag more fluid. The lead and borax melt, the ore floating on the bath of lead. Sulphur, arsenic, etc., are oxidized and volatilized; the lead then gradually oxidizes. The molten lead oxide, which is a solvent of metallic oxides, dissolves the non-volatile metals present and reacts with the gangue of the ore and the silica of the scorifier to form a slag. The precious metals remain in the molten lead, and scorification is usually complete when the slag entirely covers the lead. The scorifier is then removed from the muffle and the contents poured into a scorifier mould. On cooling, the slag is detached, and the button, unless found to be hard or brittle (when rescorification with additional lead is necessary), is hammered free from slag, and is ready for cupellation.

Method.—Amounts of ore varying from 0·05 A.T. to 0·25 A.T., depending on the value and from eight to twelve times this weight of lead are taken.

The ore and half of the lead are mixed and placed in the bottom of the scorifier; the remainder of the lead, together with 2 grams of borax, is used as a cover for the mixture.

Four distinct periods may be noted during the process viz., melting of the lead and borax, roasting, fusion, and finally scorification.

The scorifier is first placed at the mouth of the muffle and gradually brought to the desired temperature by moving it farther in. The slag,

as it forms, flows to the periphery of the bath of lead, where it accumulates in the form of a gradually closing ring until the whole of the bath is covered; this final stage is known as "the closing of the eye".

With rich samples a little charcoal wrapped in tissue paper should be dropped on the surface. The charge is poured when all action has ceased. This "cleans" the slag, but a safer method is to re-assay the slag and add the result to the original.

Except in the case of rich ores, especially silver, the scorification assay has been largely superseded by the crucible method. The latter is particularly useful with low-grade ores, as a much larger quantity is taken for assay. Scorification is very useful, however, in particular cases as an auxiliary to the crucible method for the purpose of purifying or reducing the size of lead buttons obtained from fusions prior to cupellation.

Fritting.

Fritting is defined in *The Condensed Chemical Dictionary* as follows:—

Frit. A term used in the ceramic industry and applied to a semi-fused mass, the constituents of which were originally soluble or insoluble, fusible or infusible. By "fritting" (i.e., preliminary fusing) the original properties of the constituents are changed; thus, the soluble materials become insoluble and the infusible materials fusible.

As applied to assaying it is a process whereby an ore is mixed with the required flux and is then heated to a dull red heat and maintained at that temperature long enough to enable reaction to take place.

This process becomes necessary when dealing with materials which are not oxidized or reduced rapidly or which unite more readily with other materials at a higher temperature.

Thus in the case of the assay of a tellurium ore for gold, fritting is resorted to in order to induce the tellurium to combine with the fluxes and so enter the slag rather than enter the lead which is what would happen if the temperature were raised to the fusion point at the start.

Method.—The sample and flux are well mixed and placed in a suitable crucible. This is then placed in the furnace and allowed to attain a heat of approximately 500°C. The temperature should be considerably lower than 500°C. at the time of charging and it should be raised slowly in order to heat the whole charge as evenly as possible.

Keep the temperature at about 500°C., until the whole mass has attained this temperature. Maintain these conditions for about ten minutes and then slowly raise the temperature until the sample is completely fused. Now allow the furnace to attain its maximum temperature (with the average Rand assay furnace this is about 1,100°C.) and pour the sample into an iron mould as described elsewhere. Again, as it is difficult to judge temperatures in the 500°C. range, a pyrometer should be used.

Material Containing Metallics.

It may happen that a sample contains both fine material, and coarse metallics which cannot be crushed. Since it is almost impossible to take a representative portion for assay, it is advisable that the fines be separated from the coarse metallics and the two assayed independently.

The method is as follows:—

The dry sample is passed through a 30 mesh linear screen. Should the metallics contain pieces of quartzite or other material which can be crushed,

these should be picked out by hand, pulverized and added to the fines. The two portions are then weighed.

The fines are well mixed and portions removed for assay. The number of assay tons taken and the flux used depends, naturally, on the type of material.

The whole of the metallics must be assayed, because as already stated, it is impossible to take a representative portion. Should the weight of metallics make it inconvenient to do the assay in one pot they may be divided into two or more portions.

Should the metallics contain large pieces such as bolts and nuts, the assay will present difficulties. With such material an exact gold valuation should not be called for and an approximation is all that can be provided. It may be assumed that such material will only have its surface impregnated with gold from other sources and therefore if the samples are mixed with a flux which will, when fused, remove a skin say one-eighth of an inch deep it may be assumed that the major portion of the gold will be recovered. Before pouring, the unattacked portions of iron are stirred in the slag to remove any adhering lead and removed. The charge is then poured in the usual way.

Should a more accurate assay be required or should the metallics consist of large pieces of material in which the gold may be evenly distributed, some method of comminution, such as by filing, must be attempted. Another method is to dissolve them, take the solution to dryness, and assay the residue.

The gold value of the original sample is then calculated by using the following formula:—

$$\text{DWT. VALUE} = \frac{(A \times B) + (C \times 29{\cdot}166 \times 20)}{A + D}$$

Where A is the weight of fines in grams.

B is the value of the fines in dwt./ton

C is the weight of gold recovered expressed in milligrams.

D is the weight of metallics in grams.

Panning.

A quick, but very approximate, idea of the value of a sample may be obtained by the method known as panning.

This is applicable with some degree of accuracy where the gold is "free" but can be very misleading where the gold is encased.

500 grams of the finely crushed ore are placed in a dish shaped like a large, deep frying pan (some prospectors have actually used a frying pan). Water is added and the contents of the pan are stirred by shaking with a circular motion. Simultaneously with the shaking the water is poured off. It naturally carries the lighter particles of the ore with it. This process is repeated until only a few grams remain. Then by washing all the material into the angle of the pan formed by the junction of the bottom and the sides and cautiously washing it along this angle a tail of gold is left behind. The length of the tail gives an indication of the value of the sample.

Crucibles are set in the fire and brought to a high temperature before charging the samples. Cupellation is carried out at as low a temperature as possible to ensure accuracy in the silver assay. The minimum number of simultaneous assays on any sample is four. In the case of "Fine Iron" six simultaneous assays are made.

The nature of the material to be assayed is taken into consideration, and sufficient litharge and reducer is added to produce uniform buttons weighing from 50 to 60 grams. The weight of each lead button is recorded. If buttons are over or underweight or not uniform for any particular group of assays the assays are repeated.

For metallurgical purposes samples are analysed by the Works' Chemist and thus the Assayer has the advantage of knowing in advance the main constituents of the material to be assayed. All assays are "washed" with a mixture of maize meal and litharge, litharge alone or, in certain cases, red lead. Silica is added to fluxes in exceptional cases. As crucibles are used once only, the silica required by the charge is obtained from the crucible in which it is fused.

The fluxes shown in the following section will serve as a guide for work carried out in the reverberatory type of assay furnace although they were developed essentially for assay fusion in "Cornish fires".

The basic flux used by By-Products, Limited, consists of sodium carbonate, litharge and borax in the proportions:—

Sodium carbonate	.. 2 parts by weight.
Litharge	.. 4 ,, ,, ,,
Borax	.. 1 ,, ,, ,,

This flux is referred to throughout the remainder of the chapter as By-P.B. Flux (By-Products Basic Flux). It may be modified to suit the material being assayed.

Crucible Reverberatory Furnace Slags (Borax Slags).

This type of slag contains from 26 to 36 per cent silica and from 5 to 25 per cent lead, the balance consisting of borax, soda, zinc, iron, manganese and copper.

Sample	.. 0·5 A.T. – 1.0 A.T. – 30 g
By-P.B. Flux ..	.. 3·5 A.T. – 7.0 A.T. – 210 g
Maize Meal	.. 4·5 grams. – 9.0 g

Reverberatory Pan Furnace Slags and impure Litharge from lead bullion cupellation may be fluxed as above.

Siliceous Concentrates, Ashes and Sweepings.

These are fluxed as follows:—

Sample	.. 0·5 A.T.
By-P.B. Flux ..	.. 3·5 A.T.

Maize meal 4·5 grams in the case of siliceous concentrates, varying the amount with the quantity of carbon present in the ashes and sweepings. These materials contain up to 80 per cent silica. The ashes and sweepings may contain as much as 10 per cent carbon.

DETAILS OF PROCEDURE.

Assay of By-Products.

Under this heading is classed materials collected in the reduction works and smelt house. They comprise:—Concentrates, black sands, borax slags from bullion smelting, bricks, pots and liners, coarse and fine iron chips from the stamps and tube mills, lime scalings from launders, ashes from burnt launders, corduroy blankets, etc.

Most mines on the Witwatersrand send these materials to a central co-operative smelting works where the gold is recovered by smelting.

Comparatively few by-product samples are received by the average Witwatersrand assay office and many assayers merely flux these samples with an excess of standard flux. The usual proportions are:—

Sample	0·5 A.T.
Soda	3·0 A.T.
Litharge	2·0 A.T.
Borax	1·0 A.T.

With sufficient reducing agent to give a 50-gram button.

New No. 3 crucibles are used and, to avoid the possibility of contaminating other samples, are destroyed on completion of the assay. Samples of graphite and carborundum pots and "sweepings" may require roasting but in nearly every case the excess flux causes all undesirable material to enter the slag.

This method gives excellent results but is rather expensive when large numbers of samples have to be assayed.

Should the sample not be amenable to this treatment its composition must be ascertained and a suitable flux employed.

All by-products and complex gold ores should be given a "wash" before pouring. This means that a mixture of litharge and mealie meal, or other reducing agent, is added to the sample after fusion is complete. The crucible is then replaced in the furnace until the reaction is complete and the fusion is again tranquil.

This "wash" provides a second "rain" of lead which, coming after complete fusion of the sample, picks up any gold which may have escaped the first "rain" and has remained suspended in the slag.

THE ASSAY OF GOLD-BEARING MATERIAL AT BY-PRODUCTS, LIMITED, JOHANNESBURG.

By-Products, Limited, is a private company which was formed and still operates as a subsidiary of the Transvaal Chamber of Mines. It was created primarily to treat any gold-bearing by-products produced on those mines which are members of the Chamber but which do not possess suitable equipment for treating the material themselves.

The gold- and silver-bearing material tendered to the Company for purchase and treatment consists mainly of the following:—

Crucible reverberatory slags (borax slags), reverberatory pan furnace slags, pyritic concentrates, furnace bricks, graphite and carborundum pots, fireclay liners, ashes, fine iron, sweepings, flue dust, matte, miscellaneous concentrates, litharge, lead bars, copper scalings, charcoal, hydrates and base metal bars.

BRICKS, POTS AND LINERS.

These mixtures average 65 per cent silica, 25 per cent alumina with the quantity of carbon depending upon the amount of graphite pot material present.

Sample	0·5 A.T.
By-P.B. Flux	3·5 A.T.
Maize Meal	0—4·5 grams.

GRAPHITE AND CARBORUNDUM POTS.

The samples usually contain from 30 to 35 per cent carbon.

Sample	0·25 A.T.
Sodium carbonate	0·5 A.T.
Borax	1·0 A.T.
Red Lead	4 to 5 A.T.

The following flux is used for samples containing approximately 20 per cent carbon.

Sample	0·5 A.T.
Sodium carbonate	0·5 A.T.
Borax	1·0 A.T.
Red Lead	2·5 A.T.

A sample consisting of practically pure carbon, e.g., charcoal used as a gold precipitant, is roasted prior to fusing with the following flux:—

Sample	0·5 A.T.
By-P.B. Flux	3·5 A.T.
Maize Meal	4·5 grams.

SCALINGS.

Composed mainly of silica and calcium carbonate.

Sample	0·5 A.T.
By-P.B. Flux	3·5 A.T.
Maize Meal	4·5 grams.

ZINC-GOLD SLIME.

Low Grade. This sample has an average gold content 3·5 per cent and is usually uncalcined.

Sample	0·25 A.T.
By-P.B. Flux	3·5 A.T.
Maize Meal	4·5 grams.

COPPER MATTE.

The following is the analysis of two typical mattes produced at these Works and the assay fluxes used:—

(*a*) *Low Grade Copper Mattes.*—Copper 10 to 20 per cent; nickel 2·3 per cent; lead 14·7 per cent; iron 50 to 40 per cent; total sulphur 21·9 per cent; arsenic 0·7 per cent.

Sample	0·5 A.T.
Sodium carbonate	1·0 A.T.
Borax	0·5 A.T.
Litharge	3·25 A.T.
Nitre	3—5 grams.
Silica	0·2 A.T.

(*b*) *Concentrated Copper Matte.*—Copper 35 to 45 per cent; nickel 3·4 per cent; lead 15·1 per cent; iron 30 to 20 per cent; total sulphur 20 per cent; arsenic 0·7 per cent.

Sample	0·25 A.T.
Sodium carbonate	1·0 A.T.
Borax	0·5 A.T.
Litharge	3·25 A.T.
Maize meal	1·5 grams.
Silica	0·2 A.T.

In both instances it is necessary to add silica to protect the crucible. In the case of (*b*) it may be necessary to scorify the lead button.

Copper Sweep ("Cement Copper").

This is composed mainly of copper oxide. It usually assays from 1 to 2 oz. gold per ton and from 400 to 500 oz. silver per ton. 0·25 A.T. of this material is treated either with dilute sulphuric or nitric acid to remove the copper. If nitric acid is used the silver present is dissolved. In that case ammonium chloride is added to the *cold* solution to precipitate the silver. The residue containing the gold and silver is filtered off and fused with the following flux:—

By-P.B. Flux	3·5 A.T.
Maize Meal	4·5 grams.

Calcines (Roasted Pyritic Concentrate).

Average composition:—Silica 20 per cent; total sulphur 1 to 3 per cent; balance mainly oxides of iron.

Sample	1·0 A.T.
Sodium carbonate	1·5 A.T.
Borax	1·0 A.T.
Litharge	2·0 A.T.
Maize Meal	6·0 grams.

It may be necessary to add silica if corrosion of the crucible is excessive, but as crucibles are used once only, the silica requirements of the charge are supplied with safety by the material of the crucible.

Black Sands.

Composition: Total sulphur 20 to 40 per cent as iron sulphide; silica 10 to 30 per cent.

Sample	0·5 A.T.
By-P.B. Flux	3·5 A.T.

To this flux, add an iron nail and 0·5 A.T. extra soda.

When these samples contain osmiridium, the parted prills after weighing are treated with WARM dilute aqua regia, filtered through an ashless filter, washed with hot water, dried, incinerated under hydrogen and weighed. The weight of osmiridium is then deducted from the previous weighing.

Fine Iron.

This material may contain as much as 35 per cent of metallic iron, the balance being made up of oxides of iron, silica from 10 to 20 per cent, and sulphur from 1 to 10 per cent in the form of iron pyrites.

A representative sample of the material is crushed until the iron is free from oxide. The percentage of iron metallics in the whole sample is then determined. The samples are assayed separately as "iron metallics" and "fines" (see methods described below), and the results calculated over the whole sample.

Fine Iron "Fines".

Approximate composition:—Silica 15 per cent; sulphur 1 to 10 per cent; the balance mainly oxides of iron.

Sample	0·5 A.T.
By-P.B. Flux	3·5 A.T.
Maize Meal	3 to 6 grams.

An iron nail may be necessary, depending upon the amount of sulphur present. If there is any doubt, iron is used (maize meal is not required if iron is used).

Fine Iron "Iron Metallics".

This sample is divided into 30 gram portions and the iron digested with 1 : 1 sulphuric acid. After digestion, the residue is filtered off, washed, dried and fluxed as follows:

By-P.B. Flux	3·5 A.T.
Maize Meal	4·5 grams.

This flux may need amending if the residue contains a fair amount of sulphur.

Arsenical Material.

Material containing arsenical pyrite (FeAsS), iron sulphide and silica.

General Analysis: Arsenic 18 per cent; total sulphur 31 per cent; silica 5 to 10 per cent.

To prevent the formation of speiss, red lead is used.

Sample	0·25 A.T.
Red Lead	3·5 A.T.
Sodium carbonate	1·0 A.T.
Borax	0·5 A.T.
Silica	1·0 A.T.
Maize Meal	4·5 grams.

BASE METAL INGOTS, mainly copper.

0·5 gram is taken for assay.

The sample is wrapped up in 10 to 12 grams of lead foil and cupelled at a high temperature. When cupellation is almost complete a small piece of lead foil is placed in the cupel. This operation is repeated to ensure the removal of the last traces of base metal from the bead.

If the gold content of the ingot is low, say under ten parts per thousand, more than 0·5 gram of the sample is taken and the scorification assay is used.

ANTIMONIAL SLAGS.

Composition:—Lead 30 to 45 per cent; antimony 5 to 25 per cent; copper 3 to 4 per cent; total sulphur 3 to 10 per cent; balance mainly silica.

Sample	0·5 A.T. - 1.0 A.T. - 30g
Litharge	2·5 A.T. - 5.0 A.T. - 150g
Sodium carbonate	1·0 A.T. - 2.0 A.T. - 60g
Borax	0·5 A.T. - 1.0 A.T. - 30g
Maize meal	4·5 grams. - 9.0g

As in the case of copper ores, a high percentage of litharge is used in order to oxidize the antimony and carry it into the slag.

SPEISS.

The assay of Speiss for both gold and platinum group metals is described in the chapter dealing with the platinum group metals.

OTHER BY-PRODUCT MATERIALS.

BATEA AMALGAM RESIDUE.

This sample is very complex and may contain large lumps of amalgamated material weighing as much as two ounces each, together with fine amalgam, concentrates and other gold-bearing material. It is, therefore, impossible to obtain a representative small portion for assay, and for this reason the whole sample is treated. The sample is weighed and placed in a sufficiently large tared glazed crucible and the mercury is driven off, preferably in the smelting works. The loss in weight of the sample is reported as mercury per cent. The crucible is then placed inside a graphite crucible for safety in case it should break, and a flux consisting of soda carbonate, borax and sand is placed on top and the contents fused. When fusion is complete the sample is thoroughly stirred and a dip sample taken. The metal is then poured into a mould, cleaned and weighed, the fineness being estimated by making a bullion determination on the dip sample. The percentage of the gold and silver in the original is then calculated.

HYDRATES.

This sample consists for the most part of the white precipitate from zinc boxes mixed with a small quantity of extractor house sweepings. Of the dried sample 0·5 assay ton is taken and mixed with the following flux:—

Sodium carbonate	1·0 A.T.
Litharge	1·5 A.T.
Fluorspar	0·5 A.T.
Silica	0·5 A.T.

Reducing agent to give a 30-gram button.

The assay is then completed in the usual way.

COMPLEX GOLD ORES.

Cupriferous Ores.

An ore containing more than one per cent of copper should be treated as complex, and becomes more difficult to assay as the percentage of copper increases.

When the ore contains less than 5 per cent of copper, and is sufficiently rich in gold to permit of half an assay ton being taken, it may be fused with 60 grams of standard mine flux plus 40 grams of litharge and sufficient reducing agent to bring down all the lead. The lead is scorified and the copper is removed as oxide; the resulting button should weigh about 20 grams, and may safely be cupelled in the ordinary way. One part of copper requires about 16 parts of lead for cupellation.

The slags from all fusions and scorifications of rich samples should be broken up and re-assayed with a suitable flux, as they are liable to contain gold and silver; the resultant button is cupelled, and the prill added to the original one for inquarting and parting.

When the copper content of the ore exceeds 10 per cent, or when the gold value is very low, so that a large amount must be taken for assay, it is necessary to dissolve out the copper by treating with either nitric or sulphuric acid, the latter being recommended where extreme accuracy is required.

Nitric Acid Method.—One assay ton of the ore is placed in a beaker with sufficient 10 per cent nitric acid; it is covered with a clock glass and boiled for about one hour. It is then cooled (gold will be dissolved by the mixture of chloride and nitric acid unless quite cold), and about 1 ml. of hydrochloric acid or sodium chloride solution is added to precipitate the silver. The mixture is stirred and about 10 ml. (i.e., excess of) lead nitrate added, which forms a white precipitate of lead chloride with the excess of hydrochloric acid, and serves to collect the silver chloride precipitate.

The copper nitrate is filtered off and washed once with cold water. The filter paper with the undissolved ore is then placed in a crucible and assayed as a mine sample.

Sulphuric Acid Method.—One assay ton of the ore is placed in a porcelain dish, 25 ml. of strong sulphuric acid is added, an inverted glass funnel being used as a cover. The mixture is heated strongly for two hours in a fume chamber.

The mixture is cooled and diluted carefully with cold water and stirred thoroughly with a glass rod to dissolve the copper sulphate; allowed to cool, and hydrochloric acid and lead nitrate are added as before; it is then filtered, washed once with water and the sample is fluxed as above.

Arsenical and Antimonial Ores.

These are among the most refractory of the gold-bearing ores, and present great difficulty in the determination of the correct gold content.

Arsenical Ores.—A method for arsenical ores consists of a direct fusion with excess red lead; if a speiss forms, the assay must be repeated using more red lead.

The direct scorification method may be carried out as follows:—Mix half assay ton of the ore with 3 assay tons of granulated lead, place in a scorifier with not more than one gram of fused borax on top. The scorifier is placed at the entrance of the muffle, and the temperature gently raised by moving it farther in until the correct temperature has been attained. Scorification is continued until a malleable button of not less than 15 grams is obtained. The slag is crushed in a mortar and fused with sodium carbonate, fluorspar and a reducing agent. The resultant button is cupelled with the original one, and the assay completed in the usual way.

Method used at "Que Que Roasting Plant Assay Office" for arsenical concentrates:

Litharge	91 parts
Silica	9 ,,
Sodium carbonate	21 ,,
Borax	21 ,,
Fluorspar	8 ,,
Carbon	As necessary
Sample 0·5 A.T.	Flux 125 grams.

For a high percentage of arsenic up to 28 grams of extra soda may be added. The flux given above is suitable for arsenical concentrates containing up to 70 per cent arsenic.

Antimonial Ores.—In contrast to arsenical ores, these are usually, and probably best, assayed by direct fusion with nitre and an excess of sodium carbonate.

Although a preliminary roast will give good results, it is not recommended owing to the fusible nature of stibnite and the consequent liability towards caking.

If the button from the fusion is brittle it should be scorified and more lead should be added before cupellation. High temperatures should be avoided during the fusion of the ore.

The following is a suitable charge for both arsenical and antimonial ores:—

Ore	1·0 A.T.
Caustic Soda	2·0 A.T.
Red Lead	2·0 A.T.
Borax	0·7 A.T.
Silica	0·35 A.T.

In order to prevent undue corrosion of the crucible the silica should be placed at the bottom; 1 A.T. of the caustic soda is then placed on top of the silica, followed by the mixture of ore and red lead. The remainder of the caustic soda comes next, and finally the fused borax is added as a cover. When fusion is complete the assay is poured, the lead button detached and the slag retained. If the resultant button is too large or if

it is brittle, it is scorified. The slag from the scorification is added to the original slag which is then crushed and fused with a further portion of the above flux. The button from this fusion is cupelled with the original one.

Acid Treatment. A preliminary treatment with concentrated hydrochloric acid and dilution of the solution with a weak solution of tartaric acid (to prevent reprecipitation of the antimony) and final filtering, drying and scorification of the residue will give good results.

Telluride Ores.

Tellurium may be identified by heating a small piece of the telluride ore, or its concentrate, with concentrated sulphuric acid, until white fumes appear. On adding a small piece of tin foil to the solution, a carmine colour indicates the presence of tellurium. The colour disappears on cooling, but presents itself again on heating, and may appear before the tin is added. The presence of much iron will obscure the colour.

A more certain test, described by G. T. Holloway, consists in concentrating the telluride and conducting a fusion assay on the concentrate; a portion of the resultant lead button is dissolved in nitric acid, the solution diluted and brought into contact with lead foil. Any tellurium present is precipitated, and may be dried and tested with sulphuric acid as above. Also boiling the concentrate with very strong caustic potash and zinc shavings gives a violet colour.

The essential features governing the assay process for telluride ores are:—

(1) The charge should be fritted before fusion.

(2) The fusion should be conducted slowly and at a low heat until just before the end.

(3) The charge should contain a large excess of litharge for the two-fold purpose of inducing the tellurium to enter the slag and of producing a large-sized button.

(4) Excess of silver for parting purposes must be added to the fusion to prevent loss both during fusion and cupellation.

(5) The large lead button helps to remove tellurium during the early stages of cupellation. Too great a concentration of tellurium during the final stages of cupellation will produce heavy losses of gold and silver and tellurium should be removed BEFORE cupellation by "double scorification", i.e., it is necessary to scorify to about two-thirds or one-half size and pour, most of the tellurium being now in the slag. More lead is added and the scorification repeated, the pouring being done before the button is reduced to half size, since if scorification is taken too far, tellurium will come back from the slag into the lead. The reason for this is that tellurium is oxidised by the molten litharge formed during scorification and dissolves to a red glass in the slag. When the action of litharge to form silicates is completed, there is no longer any oxidising effect on the tellurium and it will combine with the lead instead of passing into the slag. Also molten metallic lead is a reducing agent and reduces some of the tellurium which has passed into the slag.

The following flux may be used for telluride ores:—

Ore	0·5 A.T.
Litharge	2·7 A.T.
Sodium carbonate ..	0·7 A.T.
Borax	0·7 A.T.

with sufficient reducing agent to give about a 40-gram button. The charge is fused at as low a temperature as possible. When fusion is complete the temperature is raised and the assay is completed at a high temperature (1,100—1,200°C.).

The slag is crushed, mixed with more flux and fused. The button is cupelled with that of the original assay.

MANGANESE.

When this metal is present as an oxide, an excess of reducing agent is added; probably about twice the amount required for the ordinary siliceous ore will be necessary.

ZINC.

Interference due to the presence of zinc may be overcome by increasing the proportion of sodium carbonate and by decreasing the amount of reducing agent.

TIN.

Tin may also be fluxed off with soda, less reducing agent being used.

Auriferous Tinstone.

Ore	1 A.T.
PbO	2·5 A.T.
Soda	1·5 A.T.
Borax	0·5 A.T.
Carbon	1·5 grams.

As only half the lead is reduced the reduction of the tin is prevented. When assaying ores containing over 1 oz. gold per ton the slag should be retained and re-assayed.

PYRITIC GOLD ORES.

The presence of pyrite (FeS_2) in a sample of gold ore complicates the assay. The sulphur from the pyrite combines with the lead button forming lead sulphide (PbS); makes the lead button very brittle and may cause appreciable loss of gold and silver during cupellation.

Samples containing more than 8 per cent of pyrite should, therefore, be treated by one of the following methods:—

1. Assay by roasting.
2. Direct fusion with excess litharge and little, or no reducing agent.
3. Direct fusion with metallic iron as a desulphurizer.
4. Preliminary treatment with nitric acid.

Assay by Roasting.—One assay ton of the ore is roasted at a low temperature as described earlier in this chapter.

The roasted product is fused with six assay tons of stock mine sample flux. The amount of reducing agent added must be sufficient, not only to reduce the ferric oxide formed by the oxidation of the pyrite to ferrous oxide, but also to produce a lead button of at least 30 grams. The ferrous oxide is readily fusible as ferrous silicate.

If the roast is carried out properly this method will give results at least as good as those obtained by any direct fusion method. But because of the time occupied in roasting, often an hour or more, and the risk of loss by "dusting", many assayers prefer the direct fusion.

Direct Fusion with Excess Litharge and little, or no Reducing Agent.—Metallic lead can be reduced from litharge by pyrites alone if this is present in sufficient quantity: the equation

$$FeS_2 + 7PbO + 2Na_2CO_3 = FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$

represents the action when carbon is not used as a reducer. Litharge equal to 13 times the pyrites is required. Hence if 30 grams of litharge is to be used and fully reduced, the corresponding amount of pyrites is 2·31 grams, which on 1 A.T. of ore equals 8 per cent. Carbon must, therefore, be used if the pyrites in the ore is much less than 8 per cent, whilst if the pyrites is much over 8 per cent, no carbon should be used, and an oxidant becomes necessary. Another reaction can take place when pyrites exerts its greatest reducing effect. This can occur if the soda and litharge of the flux are increased. The following equation will express this effect.

$$2FeS_2 + 15PbO + 4Na_2CO_3 \rightarrow Fe_2O_3 + 15Pb + 4Na_2SO_4 + 4CO_2$$

It will be seen that the sulphur and the iron have been fully oxidized during the reduction of the lead. The oxidation of these two elements during this reaction can be shown as follows:—

1. $2FeS_2 + 15PbO \rightarrow Fe_2O_3 + 15Pb + 4SO_3$.
2. $4SO_3 + 4Na_2CO_3 \rightarrow 4Na_2SO_4 + 4CO_2$.

The ore is fluxed as usual with stock mine sample flux and up to 30 grams of litharge is added in excess. The amount of reducing agent added is decreased as the percentage of pyrite increases and in some cases may even be omitted.

This method should not be used for very highly pyritic ores because the amount of litharge required to form an excess, yields very large lead buttons, which may have to be reduced in size by subsequent scorification.

Direct Fusion with Metallic Iron.—The object of this method is to convert the pyrite into ferrous sulphide according to the equation:

$$FeS_2 + Fe = 2FeS$$

The ferrous sulphide formed is dissolved in the excess sodium carbonate of the flux and passes into the slag, leaving the lead soft, malleable and free from the interfering substance.

To bring about the above reaction iron nails or pieces of hoop iron, bent in the form of a U, are pushed down into the charge before fusion. When fusion is complete and the slag is quite fluid the iron is grasped with a pair of tongs, tapped or shaken once or twice to detach any adhering lead or slag, and removed from the crucible. The fusion is then continued for a further five minutes before pouring.

This process requires considerable care and the nail or hoop iron is carefully examined to see that it carries no small shots of lead.

For this reason iron in the form of iron filings is often used as a desulphurizer and gives excellent results, particularly where the percentage of pyrite is high.

Iron filings can be more intimately mixed throughout the sample and consequently have greater opportunity of reacting with all the pyrite. Furthermore, an excess of iron in this form will, within limits, be absorbed by the slag. It has been found that up to twice the theoretical amount of iron may be added, in the form of filings, without any serious effects on the cupellation.

The use of iron nails has certain disadvantages when compared with the use of iron filings. If large nails are used they become coated with a film which prevents further reaction and this may happen before all the pyrite is decomposed. Moreover the nail must be washed in the slag, and removed, before pouring as already described; and where a large number of samples is being assayed this process takes up considerable time.

On the other hand, if small nails are used they must be added in approximately the correct numbers. If too few are added only a portion of the pyrite will be decomposed; while if too many are added the extra nails become embedded in the lead button from which they are removed with difficulty. If they are allowed to remain in the lead, the iron causes trouble during cupellation, because it is not readily absorbed by the cupel.

From the equation:

$$FeS_2 + Fe = 2FeS$$

We find that 120 gm. FeS_2 require 56 gm. Fe and thus where one assay ton of ore is taken for assay, 1·4 gm. of iron must be added for each 10 per cent of pyrite present.

For most pyritic samples a suitable flux consists of stock mine sample flux, with the addition of the required amount of iron, thus:

Ore	1 A.T.
Soda Ash	1·5 A.T.
Litharge	0·9 A.T.
Borax	0·6 A.T.
Iron filings	1·4 gm. for each 10 per cent FeS_2.
Maize meal	Sufficient to produce a 50 gm. button.

With a little experience the assayer is able to judge the approximate percentage of pyrite by the colour of the pulverized sample. The presence of pyrite imparts a black colour to the sample and in most cases the darker the colour of the sample, the higher the percentage of pyrite. The presence of much pyrite is also indicated by the "mineralization" of the sample.

This rule is not infallible, however, but in routine assaying a chemical determination is unnecessary and the pyritic content of the sample can be estimated by "panning" or by determining the specific gravity of the sample.

It should be remembered that the pyritic content of the ore need only be known to within about ten per cent because the stock mine flux can cope with up to ten per cent pyrite; and excess iron filings can be safely added for anything above that figure.

In practice, therefore, three measures holding respectively, 3 gm., 6 gm., and 12 gm. of iron filings are used. For samples containing ten per cent or less of pyrite, no iron is used. For samples containing between 10 and 25 per cent 3 gm. is added. For those containing between 25

and 50 per cent 6 gm. is added, while 12 gm. of the filings is added to samples containing over 50 per cent. These divisions are only approximate but will be found sufficiently accurate for routine work.

Preliminary Treatment with Nitric Acid.—In this method the requisite amount of ore is weighed out and placed in a beaker. Fifty per cent nitric acid is added and the beaker is gently warmed. When action has ceased a little more nitric acid is added. This is continued until the addition of more nitric acid produces no further reaction. The sample is then filtered through a fine filter paper and thoroughly washed with hot water.

Note.—Some of the gold particles may be extremely small and may pass through a medium or coarse filter paper.

The residue is then dried and assayed. The filter paper should be burned and the ashes added to the sample.

This method is not suitable for routine work.

Chapter XII.

AIR AND GAS ANALYSIS.

THE ESTIMATION OF UNDESIRABLE GASES IN MINE AIR.

Introduction.

Chemical methods are available for the detection and estimation of most of the harmful gases encountered in mine air, and the assayer is frequently called upon to determine the exact nature and percentage of these. Standard methods of qualitative and quantitative analysis have been evolved, which yield reliable and accurate results.

There is an unavoidable lapse of time before the results of these analyses are available, however, and instruments, which indicate the presence and measure the amount of harmful gases, are now being used to supplement the work of the assayer in this direction.

These instruments are usually small and easily portable and they can be used by unskilled persons, on the spot, to indicate whether the air is harmful or not.

It is essential that the accuracy and reliability of these instruments should be checked from time to time by comparison against proved chemical methods. For instance, although an instrument may appear to be functioning perfectly it may not be in exact adjustment and may, therefore, give inaccurate results. Again, certain instruments which are supposed to indicate the presence of one particular gas, have been proved to give positive results with other gases.

It can be seen, therefore, that in conjunction with chemical analyses these instruments have a very definite value. Since they indicate the presence of noxious gases almost immediately they can be used to give warning of the presence of these gases, and thus prevent unnecessary exposure to them. They can also be used to trace a gas to its source and, in this way, help in its elimination.

In this chapter the detection and estimation of the harmful gases, by chemical methods and by the use of instruments, will be covered.

Sampling of Mine Air.

Samples for the routine analysis of mine air should be taken in clean, dry bottles. Sampling by displacement of water is not advisable.

The use of a bellows is common practice on the Reef. The nozzle of a domestic bellows is fitted with a rubber tube long enough to reach the bottom of the sample bottle. Ten puffs of the bellows are generally sufficient to displace the original air of the sample bottle. If the sample is being taken for carbon dioxide determination, the sampler should turn his face aside when sampling to prevent any carbon dioxide from his breath entering the bellows. The bottle is then closed with a rubber stopper, which must be firmly tied down, since on taking the sample to the surface a considerable internal pressure often comes to bear on the stopper.

Another method of sampling is by the use of evacuated bottles. A bottle is fitted with a stopper through which passes one end of a precision ground glass stopcock. The bottle is evacuated in the assay office by means of a vacuum pump. The stopcock is then closed, the bottle is taken to the place of sampling, where the cock is opened, the sample of air is drawn in and and the cock is closed. It is, of course, essential that all joints be air-tight and the vacuum in the bottle should be checked with a vacuum gauge before sampling so that any loss of vacuum during transit from the assay office to the place of sampling may be detected.

The size of the sample depends on the accuracy required.

For carbon dioxide determinations one litre gives sufficient accuracy and quart bottles are suitable. For other gases a minimum sample of 2500 ml. is preferred and a "Winchester" quart bottle is often used.

CARBON DIOXIDE.

Introduction.

The Government regulation which fixes the maximum permissible amount of carbon dioxide in mine air at 0·2 per cent was introduced mainly because of the possibility that carbon monoxide might accompany high concentrations of carbon dioxide. By keeping the percentage of carbon dioxide at this figure, which is considerably lower than the figure allowed in most other countries, an adequate supply of fresh air is ensured.

The presence of a high concentration of carbon dioxide is not always an indication that carbon monoxide is present, nor can a low concentration of carbon dioxide be taken as proof that other gases are absent. It is obvious that under certain conditions abnormal amounts of other gases may be produced, which bear no relationship to the amount of carbon dioxide in the air.

The results obtained from the determination of carbon dioxide are used to supply information on the circulation of air in the mine, and are of importance for ventilation control.

The following is a formula which shows the connection between the percentage of carbon dioxide and the ventilation. It is based on the assumption that the carbon dioxide is produced mainly from the exhalation of men:

$$A = \frac{K}{CO_2\% - 0{\cdot}03} \times 100$$

where A is air in cubic feet per man per minute required to maintain a given concentration of carbon dioxide, and K is a factor representing the volume of carbon dioxide exhaled per man in cubic feet per minute, and may be taken as 0·025 when doing average work.

Occurrence.

The normal concentration of carbon dioxide in fresh air is 0·03 per cent. Additional amounts may be produced underground from the following sources:— Human exhalation, blasting operations, lamps, fires or burning of any description, the action of acid waters on carbonates and the decomposition of timber.

126·068 gm. oxalic ≡ 22·4 litres carbon dioxide at N.T.P.

$$1 \text{ ml. carbon dioxide} = \frac{126 \cdot 068}{22{,}400} = 0 \cdot 005628 \text{ gm. oxalic.}$$

∴ 1 ml. of the standard oxalic acid solution ≡ 1 ml. CO_2 (at N.T.P.)

A correction is required for temperature and pressure and this may be done by one of two methods.

In the first method the volume of the bottle is reduced to N.T.P. and the percentage calculated on this figure, while in the second method the carbon dioxide value of the acid is calculated to laboratory conditions of temperature and pressure.

The first method is commonly used on the Reef and is described below. A description of the second method will be found under the section headed Carbon Monoxide.

The volume is always calculated from the conditions of temperature and pressure prevailing in the assay office and not at the place of sampling. This is because the bottle is opened for analysis in the assay office, and the volume of the gas will be governed by the conditions prevailing in the office. Since the atmospheric pressure in the assay office is always less than that underground an internal pressure of several pounds may be set up in the bottle. Consequently, when the bottle is opened, air is expelled until the pressure inside the bottle is the same as that outside. The internal pressure makes it impossible for air to be drawn into the bottle and there is, therefore, no possibility of any dilution of the sample. Dilution of the sample could only take place in exceptional circumstances. For example, if the sample was taken in very shallow workings, under very hot conditions, then if the temperature in the assay office was low enough a partial vacuum inside the bottle could result.

The volume of the sample is reduced to N.T.P.—viz., the volume that the gas would occupy at a temperature of 0°C. and a pressure of 760 mm. of mercury, using the formula:

$$V_0 = V_1 \times \frac{273}{(t + 273)} \times \frac{P}{760}$$

$$= 0 \cdot 359 \times \frac{P}{(t + 273)} \times V_1$$

Where V_0 is the volume required at standard conditions; V_1 the observed volume; P the barometric pressure at the time of analysis; t the temperature in degrees Centigrade at the time of analysis.

EXAMPLE.—The volume of the mine air bottle was 1,100 ml. Atmospheric pressure was 623·5 mm. and the temperature 19·4°C.

25 ml. of the standard barium hydroxide required 25 ml. of the standard oxalic acid. 25 ml. barium hydroxide, after shaking with the mine air, required 23·7 ml. oxalic acid. Required the percentage by volume of carbon dioxide in the mine air.

$$V_0 = 1{,}100 \times 0 \cdot 36 \times \frac{623 \cdot 5}{(273 + 19 \cdot 4)}$$

$$= 844 \cdot 4 \text{ ml.}$$

In very accurate work the vapour pressure of water at the given temperature should be subtracted from the barometer reading, which

in mine air. This amount corresponds to a blood saturation of 10·5 per cent, and it is considered that the human organism can recover completely even after daily exposure to such a concentration.

OCCURRENCE.

Carbon monoxide is the product of incomplete combustion. It is produced underground during blasting, or through timber or refuse becoming ignited and burning in any place where there is no free circulation of air. It is also a constituent of the exhaust of Diesel engines. Fires occurring underground are the greatest source of carbon monoxide in mine air.

DETECTION.

1. Canaries are used to detect the presence of carbon monoxide in mine air. These warm blooded birds, with their rapid rate of respiration, quickly show symptoms of carbon monoxide poisoning and will succumb in concentrations of the gas which are still safe for human beings for a limited time.

On a number of the larger mines canaries are bred solely for this purpose.

The use of canaries is not a positive means of identifying carbon monoxide since other poisonous gases may also prove fatal to them.

2. Carbon monoxide can be detected in the air by means of properly prepared palladium chloride paper, which will detect 0·02 per cent. This method is now seldom used.

Filter paper is dipped in a five per cent solution of palladium chloride made by *boiling* the solid with water and filtering. The paper is then quickly dried in an atmosphere free from carbon monoxide. When dry, the paper is cut into strips about 1″ long by ½″ wide and immediately bottled in a dark bottle with a greased stopper. Paper dipped in unboiled palladium chloride solution is insensitive, and will probably not detect anything much less than 0·10 per cent.

For use, a strip of the prepared paper is moistened either in the centre with a drop of water, or at one end with an extremely small quantity of water, so as to leave three-quarters of the paper dry, and hung up in the suspected air for ten minutes. Traces of carbon monoxide cause a grey mark at the margin of the wet and dry portions; larger quantities give a black stain. This is metallic palladium, produced according to the equation:—

$$PdCl_2 + CO + H_2O = Pd + CO_2 + 2HCl.$$

DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE IN MINE AIR.

The reagent used for this determination is iodine pentoxide, I_2O_5. This reagent reacts with carbon monoxide at 135° C. liberating iodine according to the equation:—

$$I_2O_5 + 5CO = I_2 + 5CO_2.$$

The liberated iodine, which is evolved as a gas, is passed directly into a small quantity of ten per cent potassium iodide solution which absorbs it completely. The iodine solution is then washed out of the absorption tube and titrated with N/500 sodium thiosulphate. (NOTE: Some assayers prefer a stronger solution of thiosulphate.) Starch is used as an indicator.

The interfering gases most likely to be present in the air are hydrogen sulphide and unsaturated hydrocarbons. These must be removed before the air is passed through the iodine pentoxide.

All traces of moisture must also be removed from the air.

Hydrogen sulphide is removed by passing the air sample through pumice stone saturated with copper sulphate, or through a solution of lead acetate or other lead salt.

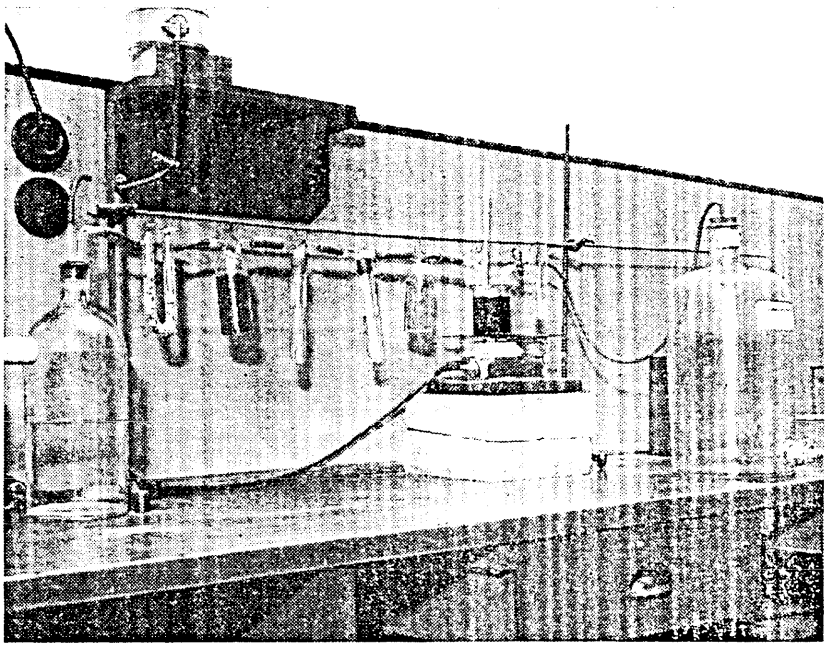


Fig. 62. Carbon Monoxide Train.
(With acknowledgment to East Geduld Mines Ltd.)

Unsaturated hydrocarbons may be removed or saturated and rendered harmless by passing the air sample through any one of the following:—

1. A mixture of concentrated sulphuric acid and chromic acid at room temperature.
2. Fuming sulphuric acid heated to a temperature of 165° C.
3. A ten per cent solution of bromine in potassium bromide. This reagent must be followed by an absorption tube filled with a saturated solution of potassium hydroxide in order to absorb the bromine vapour which is invariably given off.

Moisture is removed by passing the air sample through a concentrated sulphuric acid tube followed by a calcium chloride tube.

Other interfering gases that may be present are nitrous fumes and acetylene but these are also removed by one or other of the above reagents.

All these reagents may be placed in ordinary absorption tubes in the case of solutions or in U tubes in the case of solids.

The reagents are placed in their respective containers and are set up in the form of a train.

The sample is forced through the train by means of aspirator bottles connected to each end of the train. The first aspirator, which should be raised to a height of at least two feet above the remainder of the train, supplies water which displaces the air in the sample bottle and forces it through the train. The water in the end aspirator is allowed to run out, thus causing a suction and helping to draw the air through the train. The outlet from the second aspirator should dip into a water container below the surface of the water in order to prevent air bubbles entering the aspirator and so breaking its vacuum.

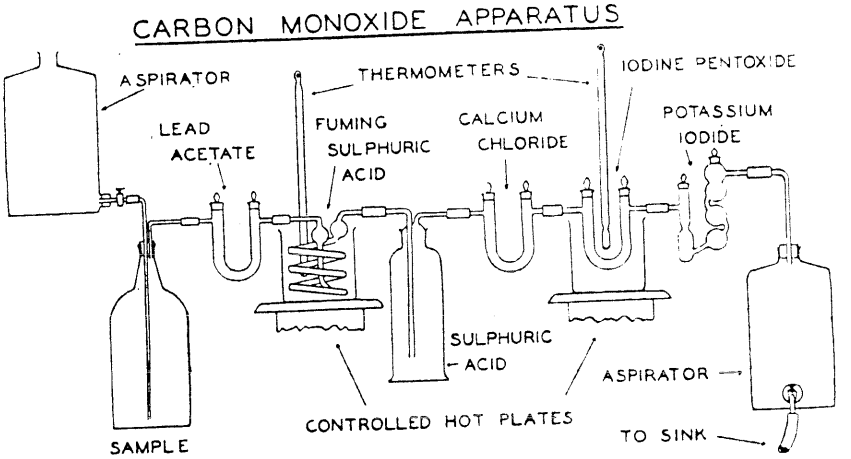


Fig. 63.

The tubes containing the reagents which require heating, are immersed in a beaker containing ordinary cylinder oil. The oil is heated either by means of a controlled bunsen burner or by means of a thermostatically controlled electric element.

The whole train should be hermetically sealed to ensure it does not leak.

The U tube containing the iodine pentoxide should have a plug of glass wool at the outlet end to prevent any of the reagent being carried over into the potassium iodide where it would liberate iodine according to the equation:—

$$3I_2O_5 + 5KI = 3I_2 + 5KIO_3.$$

The iodine pentoxide should have been previously heated at 185° C. for one hour to ensure that any iodic acid that may be present in the reagent is converted to the pentoxide. Before introducing the pentoxide into the tube it should be sieved and the finest dusty portion rejected, otherwise resistance to the passage of the air sample may be caused.

The tubes for removing the interfering gases are, of course, only necessary if these gases are present.

Hydrogen sulphide should always be guarded against but unsaturated hydrocarbons are not always present in gold mines, although they are generally found in coal mines. The hydrocarbons are absorbed in small

quantities by the sulphuric acid tower, and the extra control only becomes necessary if they are present in appreciable quantities.

Efficient drying towers are essential as the gas must be perfectly dry before entering the pentoxide tube.

The iodine pentoxide will last for a considerable time.

The sample can be run through the train at the rate of about one litre per hour.

Before the apparatus is used for the first time it must be run on relays of fresh air, until a nil result is obtained.

When all the air in the sample bottle has been displaced the determination is not yet finished as the train is still full of mine air. The connection from the bottle should be severed and a tube leading to fresh, carbon-monoxide-free air attached. The apparatus is run for ten minutes more to draw the mine air through the tubes.

The above method is extremely accurate for small quantities of carbon monoxide. When dealing with air containing more than 0·1 per cent carbon monoxide small samples of air should be used, and the air must be passed through the apparatus at a slower rate, otherwise the amount of iodine liberated will be so great as to cause condensation of iodine in the pentoxide tube. Should this happen the iodine so condensed may be volatilized by heating the pentoxide tube with a spirit lamp. This is not entirely satisfactory, however, and the assayer should endeavour to ascertain the source of the sample before passing it through the train. The exhaust gases of internal combustion engines, for example, may contain high percentages of carbon monoxide, and such a sample, if run through normally, may liberate sufficient iodine to block the tube permanently.

Since N/500 thiosulphate is unstable, this solution must be freshly prepared and is made by diluting 10 ml. of N/10 sodium thiosulphate to 500 ml. just before use. If little water is used in washing out the bulb-tube and the potassium iodide is too concentrated, the end-point with starch is brown purple, not blue. As the titration is done from blue to colourless an absolute minimum of very thin starch should be used, otherwise the end-point will be overshot.

Since 253·84 grams of iodine are liberated by 140·05 grams of carbon monoxide, and 253·84 grams of iodine require 1,000,000 ml. of N/500 thiosulphate, each ml. of N/500 thiosulphate equals 0·00014 gram of carbon monoxide, measuring *0·112* ml. as gas at N.T.P. At 630 mm. pressure and 25° C. (the average conditions in a Rand assay office) 1 ml. N/500 thiosulphate equals *0·147* ml. carbon monoxide.

Calculation.

This is done either by reducing the measured volume of the Winchester sample bottle to N.T.P. and using the factor:—1 ml. thiosulphate equals *0·112* ml. carbon monoxide, or by using the direct method given below. To avoid errors in reducing to N.T.P. note that *both* fractions are less than 1, since the temperature is always above zero and the barometric pressure below 760 mm.; e.g.:

Let V = volume of bottle and V_0 = the N.T.P. value.

$$V_0 = V \times \frac{273}{(273 + t)} \times \frac{P}{760}$$

Thus, if the bottle measures 2,950 ml. and the temperature was 28°C. and the barometer reading 630 mm. the volume at N.T.P. is:—

$$2{,}950 \times \frac{273}{301} \times \frac{630}{760} = 2{,}218 \text{ ml.}$$

As previously explained, it is the temperature and barometer readings of the laboratory, not of the place of sampling, that are used in the calculation.

The other method of calculation is to use the factor:—1 ml. N/500 thiosulphate equals 0·147 ml. carbon monoxide at 25°C. and 630 mm. barometer, together with the *actual* volume of the sample bottle. A correction can be made if the laboratory conditions differ greatly from those mentioned. The following is the calculation of the same analysis by the two methods:—

Volume of sample bottle 2,950 ml.; laboratory temperature 28°C.: barometric pressure 25·20 inches, equals 640 mm., *equals 630 mm.* when corrected for mercury and moisture. (See carbon dioxide.)

Suppose 1·55 ml. N/500 thiosulphate to have been used in the titration

Method (i).—Using N.T.P. values, the carbon monoxide found is 1·55 × 0·112 ml. (as gas at N.T.P.) = 0·174 ml. Now the N.T.P. volume of the bottle is, as shown above,

$$2{,}950 \times \frac{273}{301} \times \frac{630}{760} = 2{,}218 \text{ ml.}$$

Hence the percentage of carbon monoxide is $\frac{0{\cdot}174}{22{\cdot}18} = 0{\cdot}0078$

Method (ii).—Using standard, but not N.T.P. conditions, the carbon monoxide found is 1·55 × 0·147 = 0·228 ml. (as gas at 25°C. and 630 mm.). The volume of the bottle (measured without correction) is 2,950 ml. hence the percentage of carbon monoxide is $\frac{0{\cdot}228}{29{\cdot}5} = 0{\cdot}0078$

If necessary, since the bottle was at 28°C. instead of 25°C., a correction of $\frac{273 + 28}{273 + 25}$ to the sample volume may be made, but for practical purposes this refinement is not necessary.

Other Methods for the Detection and Determination of Carbon Monoxide.

Several other methods of detecting and determining carbon monoxide in mine air have been developed by the various companies specializing in this work. Some of these have been used on mines of the Witwatersrand to give approximate determinations on the spot but none of them have, as yet, been officially adopted. The iodine pentoxide method remains the standard method of determination.

The M.S.A. Carbon Monoxide Detector.—The M.S.A. detector is a small portable instrument which enables a sample of the air to be drawn through a detector tube. The tube contains a layer of silica gel impregnated with a silica-molybdate compound containing palladium sulphate as catalyst. The reagent changes from yellow to a green colour varying in shade according to the amount of carbon monoxide present. The colour is compared with a rotating colour scale mounted beside the tube, and graduated to read concentrations from 0·001 per cent to 0·10 per cent.

The instrument is operated by inserting a detector tube, after breaking off the tip, and squeezing the bulb according to the instructions on the instrument.

The P.S. Carbon Monoxide Detector.—This is an aspirator bulb to which is attached a glass tube containing silica-gel impregnated with a complex palladium salt (trade name pallado-sulphite-P.S.) in the centre and having pure silica-gel at each end.

The purpose of the silica-gel is to absorb water vapour, gasoline gas and other interfering substances. The carbon monoxide in the air causes the P.S. salt to turn brown and the length of the brown stain is an indication of the amount of carbon monoxide present.

As it is not the colour shade but the length of stain which is read, it can be used in any light or by persons who are colour blind. For example, a stain 2·5 millimetres long indicates 0·005 per cent carbon monoxide.

The M.S.A. Carbon Monoxide Indicator.—This instrument first removes moisture and then passes the air through a container filled with "hopcalite" (i.e., a mixture of metallic oxides). The "hopcalite" oxidizes the carbon monoxide to carbon dioxide with the evolution of heat. The heat evolved is a direct measure of the carbon monoxide present and is determined by differential thermocouples in series with a galvanometer which is calibrated to read percentage carbon monoxide.

The sensitivity of this instrument is about 10 parts per million—i.e., 0·001 per cent.

NITROUS FUMES.

The term "nitrous fumes" refers to the mixture of oxides of nitrogen which are produced during blasting. These oxides consist generally of nitric oxide NO, nitrogen dioxide NO_2 and nitrogen tetroxide N_2O_4, and possibly nitrogen trioxide N_2O_3.

Occurrence.

Nitrous fumes are produced by the detonation of explosives. The amount produced is greatly increased if the detonation is incomplete, i.e., by a "soft shot". Large quantities of nitrous fumes are produced when an explosive burns without exploding and fatal "gassing" often results. In this case the presence of the gas is so obvious to the smell that testing is unnecessary.

Both NO and NO_2 are produced in blasting, and although the NO is finally oxidised to NO_2, the oxidation is by no means immediate.

The Government regulation requires that there should be no practically detectable trace of the oxides of nitrogen in the air.

Effects.

Nitrous fumes attack the mucous membranes of the eyes, nose and throat, causing irritation in the nose, smarting of the eyes, pains in the chest and coughing.

The action of the gas is insidious and dangerous amounts may be inhaled before warning symptoms are obvious to the breather. Again, the initial effects of the "gassing" may pass off and the patient considers he has recovered, but acute symptoms develop several hours later, because of the

irritant action of the gas on the lungs. The lungs may become water-logged and this condition invariably proves fatal.

A concentration of nitrous fumes of 0·1 per cent as NO_2 is dangerous to life if inhaled only for a few minutes, and 0·01 per cent may be fatal in half-an-hour to an hour.

In the mines of the Witwatersrand complete elimination is aimed at because of the possibility that smaller concentrations than those usually regarded as immediately dangerous may affect the bronchial system and, in association with dust, may accelerate the development of silicosis.

Detection.

Nearly all the methods for detecting nitrous fumes depend upon the detection of the NO_2 in the mixture since there is no easy method of detecting NO.

1. *Detection by Starch-Iodide Paper.*

Test papers are prepared as follows:—

A dipping solution containing 6 grams of soluble starch and 2 grams of potassium iodide per litre of boiling water is made. When cool, circles of filter paper (Whatman No. 1) are dipped in the solution, drained and hung up to dry in an atmosphere free from oxides of nitrogen. When dry, the paper is cut into strips about 1½ inches long by ¾ inch wide, and stored in a well-stoppered bottle.

For use, the lower end of the test paper is moistened with pure water to a length of 2 to 3 mm., and suspended or waved in the air to be tested. The presence of NO_2 is detected by the appearance of a brown line at the margin of the wet and dry parts. Some persons prefer to use a small drop of distilled water from a glass rod to make a wet spot about ½ inch diameter in the centre of the paper, and watch for a brown line to appear round the circumference of this spot.

If the proportion of NO_2 in the air approximates 0·01 per cent, the brown line will appear within about three seconds; if the proportion is about 0·005 per cent the brown line will appear in about 20 seconds; at 0·0025 per cent the line appears in about one minute. Air may be considered sufficiently free of nitrous fumes if no brown line appears after two or three minutes exposure of the test paper.

It should be borne in mind that the starch-iodide test paper is sensitive only to NO_2, and that invariably NO is present as well as NO_2, but will not affect starch-iodide paper.

It should also be remembered that oxidizing agents such as ozone will give a positive reaction with potassium iodide paper. Therefore in the neighbourhood of electrical gear, particularly electrostatic precipitators, this point should be borne in mind.

Determination of Nitrous Fumes.

For the quantitative determinations of nitrous fumes the most satisfactory method appears to be the phenoldisulphonic acid method for total nitrogen oxides (except N_2O) which is used extensively by the Chamber of Mines. In this method the gases are sampled by means of evacuated bottles which contain a dilute acid solution as absorbing medium with hydrogen peroxide to oxidise all the absorbed fumes to the nitrate. By treatment with phenoldisulphonic acid a yellow colour is produced

which is compared with a standard solution of nitrate similarly treated. The method is specific for nitrates.

PHENOLDISULPHONIC ACID METHOD FOR THE ESTIMATION OF TOTAL NITROGEN OXIDES IN MINE AIR.

Solutions Required.

Phenoldisulphonic Acid Reagent.—25 grams of pure phenol (carbolic acid) crystals dissolved in 150 ml. concentrated sulphuric acid. Add the phenol slowly to the acid to prevent charring. Add 75 ml. fuming sulphuric acid (15% excess SO_3). Heat at 100°C. for four hours.

Hydrogen Peroxide.—Six per cent solution. Keep in a dark glass stoppered bottle.

Sodium Carbonate.—N/2 (approx.). 26·5 grams anhydrous Na_2CO_3, or equivalent, per litre of distilled water.

Standard Nitrate Solution.—0·4510 gram potassium nitrate per litre of distilled water.

For use, dilute 10 ml. to 100 ml. then—

1 ml. = 0·0451 mgm. KNO_3 = 0·02052 mgm. NO_2
= 0·0100 ml. NO_2 at N.T.P.
= 0·0133 ml. at average Rand conditions (630 mm. and 25° C.).

Procedure.

Sampling for nitrogen oxides is best accomplished by the use of evacuated quart bottles.

Introduce into the sampling bottle 25 ml. of distilled water containing 2·5 ml. N/2 sulphuric acid (or 25 ml. of N/20 H_2SO_4) and add 0·5 ml. of six per cent hydrogen peroxide.

Evacuate the bottle as far as possible using a water jet pump or other vacuum pump.

The sample is obtained underground by opening the stop cock and allowing the air to be drawn in. The vacuum should be checked by means of a gauge before sampling. In the laboratory the bottle and contents are allowed to stand overnight to ensure oxidation of all NO to NO_2 and thus complete the absorption of the fumes and the oxidation of nitrite to nitrate.

Transfer the solution from the bottle to a 100 ml. evaporating basin rinsing two or three times with small quantities of water. Neutralize by adding N/2 sodium carbonate solution carefully from a burette and testing externally with litmus paper and then add 0·5 ml. in excess. A titre of about 3·0 ml. is required.

Evaporate to dryness on the steam bath.

Allow the basin to cool thoroughly, then measure out 2·0 ml. of phenoldisulphonic acid reagent into the basin, rotate the basin and stir with a glass rod to ensure complete contact with the residue. Allow to stand for ten minutes with intermittent stirring. Then dilute the acid with about 50 ml. distilled water and mix well. Now render the solution alkaline by adding 10 ml. of concentrated ammonium hydroxide (12N)—this should be added slowly with gentle stirring so as not to overheat the

liquid. When the yellow colour has developed, the solution is made up to 100 ml. in a flask, well mixed and filtered if necessary.

Prepare a standard by taking 10 ml. of the diluted 1 : 10 standard potassium nitrate solution, add 2·5 ml. of N/2 sulphuric acid (or 25 ml. of N/20 H_2SO_4) render alkaline in excess with N/2 sodium carbonate as described, and evaporate to dryness. Cool, add 2·0 ml. phenoldisulphonic acid reagent, stand ten minutes, dilute with 50 ml. distilled water, add 10 ml. concentrated ammonium hydroxide. Dilute to 100 ml.

$$1 \text{ ml.} = \frac{10 \times 0{\cdot}0100}{100} = 0{\cdot}001 \text{ ml. } NO_2 \text{ at N.T.P.}$$

After not less than 20 minutes compare the colour of the test solution with the standard. Using a colorimeter is the most convenient method of obtaining a comparison. Allowance should also be made for a blank, particularly at low concentrations. Alternatively a set of standards may be made by diluting 1, 2, 4, 6, 8 ml. of the coloured standard to 10 ml. in 10 ml. comparison tubes. For more accurate work it is necessary to add sufficient ammonium hydroxide to each tube to maintain the same concentration of alkali as in the test solution.

Since the colour is stable the standard coloured solution may be retained for subsequent tests.

For accurate determinations a photo-electric photometer should be used.

Photo-electric photometer.—Calibration curves are prepared by treating a series of standards in exactly the same way as the test and measuring the transmittancy of the final coloured solutions at an appropriate wavelength and with the most suitable cell thickness.

For the range 0·0001 to 0·001 ml. NO_2 at N.T.P. per ml. final solution:—

Make standards with the following amounts of the *diluted 1 : 10* standard nitrate solution:—

Mls.	0	1	2	4	6	8	10
Final Conc...	(Blank)	0·0001	0·0002	0·0004	0·0006	0·0008	0·0010

Wavelength: 425 mμ
Cell: 30 or 50 mm.

For the range 0·001 to 0·01 ml. NO_2 at N.T.P. per ml. final solution:—

Make standards with the following amounts of *undiluted* standard nitrate solution:—

Mls.	0	1	2	4	6	8	10
Final Conc...	(Blank)	0·001	0·002	0·004	0·006	0·008	0·010

Wavelength: 480 mμ
Cell: 10 mm.

The transmittancy of the final solutions is measured in comparison with distilled water and plotted against the concentration on semi-logarithmic paper. These curves are then used to enable the concentration of the test solution to be read off from the transmittancy measurement.

It is necessary to check the calibration curves when a new supply of phenol-disulphonic acid is started. Since the curves are straight lines, a blank and two concentrations (say 0·0005 or 0·005 and 0·001 or 0·01) should be sufficient to indicate any change.

EXAMPLE.

Conditions at sampling point: 30″ mercury and 27° C.
Vacuum tested at sampling point: 27″ mercury.
Bottle: 1150 ml.

$$\text{Therefore sample} = \frac{27}{30} \times (1{,}150 - 25)$$
$$= 1{,}012 \text{ ml.}$$

Test solution (100 ml.) is found to equal standard.

Therefore, test = 0·001 ml. NO_2 per ml. final solution.

Therefore fumes (as NO_2) in sample = 100 × 0·0010
= 0·100 ml. at N.T.P.
= 0·110 at underground conditions.

NOTE.—This standard method measures the total concentration of toxic nitrogen oxides (except N_2O) and is considered the most satisfactory method to use. Most other methods, e.g. the sulphanilic-naphthylamine or Greiss-Ilosvay methods measure the nitrite-fixed portion only of the absorbed fumes and it has been shown that the ratio of nitrite to nitrate is by no means constant.

An acid absorbent and oxidizing solution is used since it has been found that in an alkaline solution the oxidation of nitrite to nitrate by hydrogen peroxide is not complete.

PRECAUTIONS.

The phenoldisulphonic acid must be prepared as directed to ensure correct composition, and departure may lead to production of monosulphonic acid which would increase any green or murky tints produced in the final solution. If a pure fuming sulphuric is not available replace with pure sulphuric acid. This results in a slight decrease in colour, but gives a more satisfactory blank. The volume of reagent added must be accurately measured, as different volumes affect the final colour.

The residue, after evaporation, must be thoroughly cooled before adding the phenoldisulphonic acid reagent, for a variable heating effect may produce green tints—this tendency is reduced if the reagent is wholly disulphonic acid.

The reagent and residue must remain in contact not less than the stated ten minutes.

The ammonium hydroxide added for neutralizing should be approximately measured to give similar final concentrations, as the colour increases somewhat with increasing concentrations of excess ammonium hydroxide. An excess of 5 ml. of 12N ammonium hydroxide is allowed for in the directions given. (12N potassium hydroxide gives a somewhat

deeper colour than ammonium hydroxide, and the colour varies less with different alkali concentrations.)

The solution should be well diluted before introducing the ammonium hydroxide, which should be added slowly to prevent heating and thus a possible loss of ammonia, upsetting the concentration and also tending to produce green or murky tints.

Any organic matter present results in a brown coloration on the addition of sulphuric acid, and therefore should be removed, e.g. by alumina cream or activated charcoal.

The use of sodium carbonate for neutralization has been found preferable to caustic soda or potash as previously used. A slight excess as described is important as loss of nitrates may occur on evaporating an insufficiently alkaline solution.

Chlorides also interfere, e.g. 1 mgm. chlorine produces a ten per cent reduction in colour. For accurate results halogens, if present, should be removed by silver sulphate.

DETERMINATION OF NITROUS FUMES BY MODIFIED GRIESS-ILOSVAY METHOD.

1. Introduction.

Although the phenol-disulphonic acid method described above is the most precise method it is time consuming and requires strict attention to detail.

On mines using nitrous fume absorption plants, it is desirable that the operation of the plants be checked by periodical analysis of the air for nitrous fumes. While the method given below, namely, a modification of the Griess-Ilosvay method, is less exact than the phenol-disulphonic acid method it is suitable for purposes of control of nitrous fume absorption plants as it is reasonably accurate, relatively quick and simpler to use than the disulphonic acid method.

A colorimeter or spectrophotometer can be used but a fair degree of accuracy can be obtained by simple colour comparison in Nessler tubes.

The procedure embodies sampling of the air into evacuated bottles containing an alkaline absorbing medium, allowing the sample sufficient time for nitrogen dioxide and trioxide to be absorbed in the solution and for the nitric oxide to be oxidized and also absorbed.

The nitrate content of this solution is then estimated by the Griess-Ilosvay method.

The standard method recommended by the Transvaal and Orange Free State Chamber of Mines is as follows:—

2. Sampling.

The same type of sampling bottle as used in the Phenol-disulphonic acid method is used, i.e. a quart sized bottle of oval cross-section provided with a rubber stopper through which fits a precision-ground glass stopcock. All bottles should be tested for strength under vacuum. Taps and stoppers should be tested for leakage under vacuum.

2.01 *Preparation of Sample Bottles.*

The absorbing solution consisting of 25 mls. of 0·5% sodium carbonate solution is introduced into the bottle by pipette before evacuation.

The stopper with stopcock is placed firmly in position and the bottle is evacuated to as high a degree of vacuum as can be obtained either with mechanical pump or a good water jet pump.

Sample bottles should be prepared as near as practical to the time of test and should not be kept longer than 24 hours before sampling.

2.02 *Sampling.*

The sample is taken by opening the stopcock when the air will be drawn into the bottle to fill the vacuum.

Before sampling, the state of the vacuum in the bottle is checked with a small vacuum gauge of the dial type to ensure that there has been no leakage during transit to the sampling point. The reading of the gauge should be noted for correction of the volume sampled. It is necessary also to know the barometric pressure and the temperature at the sampling point.

The position at which samples are taken depends on the purpose in mind. General samples of the atmosphere should be taken near head height. Samples of air in a pipe may be taken by connecting the upper limb of the stopcock with a short rubber tube to a narrow-bore glass tube projecting into the pipe.

3. Method of Analysis.

3.01 *Solutions Required.*

(*a*) Sodium Carbonate.

Dissolve 5 gms. of A.R. anhydrous sodium carbonate or an equivalent weight of hydrated salt in a litre of distilled water.

(*b*) Sulphuric Acid N/10 (approx.).

Add 2·7 ml. pure C.P. concentrated (98%) H_2SO_4 to a litre of distilled water.

(*c*) Griess-Ilosvay Reagent.

(1) *Sulphanilic Acid Solution.*—Add 50 ml. of C.P. glacial acetic acid to 50 ml. of distilled water. Add 1·0 gm. of C.P. sulphanilic acid in small portions to the mixture which may be warmed slightly to facilitate solution (not over 70° C. otherwise charring may occur forming a brown discoloured solution). When solution is complete dilute with distilled water to a final volume of 300 ml.

(2)*α-Naphthylamine Solution.*—Dissolve 0·2 gram of α-naphthylamine in 50 ml. of C.P. glacial acetic acid and dilute with distilled water to a final volume of 300 ml.

The α-naphthylamine crystals used should not be more than slightly discoloured. It is recommended that small 25 or 50 gm. packings of this material should be used and the crystals should at all times be stored in an air-tight amber glass bottle.

For use: Mix equal quantities of (1) and (2).

(20 ml. of mixed Griess-Ilosvay reagent are to be added to every 80 mls. of solution under test.)

Note.—The sulphanilic acid solution keeps well for a period of thirty days or more and may be prepared in bulk, but the α-naphthylamine solution must be prepared fresh just before use.

(*d*) Standard Nitrite Solution.

Stock Solution: Dissolve 0·380 gm. of pure potassium nitrite crystals (KNO_2) per litre of distilled water. Standardize the solution by permanganate titration.

0·380 gm. KNO_2 per litre = 0·2054 mg. NO_2 per ml.
= 0·1 ml. NO_2 per ml. solution (at N.T.P.)

For use: Dilute 10 ml. of stock solution to 100 ml. in a standard flask.

Then 1 ml. working soln. = 0·02054 mg. NO_2
= 0·010 ml. NO_2 @ N.T.P.
= 0·0133 ml. NO_2 @ average Rand laboratory conditions (25° C. and 630 mm. Hg.).

3.02 *Analysis.*

After sampling allow the bottle and contents to stand overnight or at least 12 hours to ensure complete oxidation and absorption of the fumes.

Transfer the absorbing solution quantitatively from the bottle into a 100 ml. standard flask, rinsing the walls of the bottle three or four times with small amounts of distilled water.

Make up to the mark.

Make up a blank solution by diluting 25 ml. of 0·5 per cent sodium carbonate to 100 ml. in a similar fashion

(*a*) Visual Comparison.

Pipette out 10 mls. aliquot of the made-up sample solution into a Nessler tube.

(10 mls. is usually a suitable aliquot but 5 or 25 mls. may be taken for very high or very low concentrations.)

Place suitable aliquots of the working standard solution into a row of 100 ml. Nessler tubes to give final concentrations covering the expected sample range. A suitable scale is suggested below:—

Mls. working solution ..	0	0·2	0·5	1·0	2·0	5	7·5	10
Final conc. as mls. NO_2 per ml. final solution (at N.T.P.) ..	Blank	·00002	·00005	·0001	·0002	·0005	·00075	·001

To each comparison tube:—

(1) Add one drop of a 0·1 per cent phenolphthalein in alcohol indicator solution.

(2) Add deci-normal sulphuric acid drop-wise from a burette until solution just becomes colourless (approximately 2·5 ml. of acid will be required per 10 ml. aliquot of sample and one drop for the standards).

(3) Dilute to a volume of 60 to 70 mls. approximately.

(4) Add 20 mls. of mixed Griess-Ilosvay reagent and mix.

(5) Make up to 100 ml. mark with distilled water

(6) Allow to stand for ten minutes.

(7) Match colour of sample with standards.

The above procedure is applicable for Nessler tube comparison and for simple visual comparators. For colorimeters of the variable depth type only two standards (·0001 and .001) need be made up.

(*b*) Photo-electric Spectrophotometer.

The usual method is applied of preparing calibration curves from a series of standards treated in the same way as the test sample, the transmittance of the final coloured solutions being measured at suitable wavelength in a cell with suitable optical path. The analytical procedure is identical to that described in the previous section but the coloured solutions are developed in 100 ml. stoppered standard flasks instead of Nessler tubes. As the colour complex formed is not very stable, it is essential that the transmittance of the solutions should be measured after 10 and before 30 minutes of developing the colour.

It is advantageous to make two calibration curves, one for low concentrations and the second for higher ones, from suitable aliquots of the standard nitrite solution. The following two ranges are suggested:—

(1) *Diluted.*

Mls. working solution ..	0	0·1	0·2	0·5	1·0
Final Conc. as mls. NO_2 per ml. final solution (at N.T.P.)	Blank	·00001	·00002	·00005	·00010
Wavelength 560 m μ.	Optical path of cell 50 mm.				

(2) *Concentrated.*

Mls. working solution ..	0	1·0	2·0	5·0	10
Final conc. as mls. NO_2 per ml. final solution (at N.T.P.)	Blank	·0001	·0002	·0005	·0010
Wavelength 560 m μ.	Optical path of cell 10 mm.				

Above concentrations of 0·001 mls. NO_2 per ml. of final solution, the colour formation does not follow Beer's law and it is advisable to take a smaller aliquot.

The transmittance of the final solutions is measured in comparison with distilled water, which is taken as having 100 per cent transmittance, and plotted against concentration values on semi-logarithmic paper. These curves are then used to estimate from the transmittance value the concentration in the unknown solution.

Calibration curves should be checked whenever a new bottle of α-naphthylamine is put into use or if the instrument adjustments are in any way altered (e.g. when a new lamp is fitted) and are preferably checked as a routine say once every three months.

4. Calculation of Results.

The oxides of nitrogen dissolve in alkaline solution in the following manner.

NO_2/N_2O_4 dissolves to form equal quantities of nitrite and nitrate:—

$$2NO_2 + Na_2CO_3 — NaNO_2 + NaNO_3 + CO_2 \quad .. \quad .. \quad .. \quad (1)$$

N_2O_3 dissolves to form wholly nitrite:

$$N_2O_3 + Na_2CO_3 — 2NaNO_2 + CO_2 .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

NO oxidizes mainly to N_2O_3 but also to NO_2 in proportions depending on the circumstances, and these then dissolve as above.

Hence to convert the nitrite measured in the solution to the equivalent oxides of nitrogen in the air (calculated as NO_2) it is necessary to multiply the nitrite by 2 if it is derived from NO_2/N_2O_4 (equation 1) or by 1 if it is derived from N_2O_3 (equation 2) or by a figure nearer 1 than 2 if it is derived from NO (equations 1 and 2). Since a mixture of the oxides may be present in the air after blasting, the factor to be used will lie between 1 and 2 and may vary from sample to sample.

In actual experiments on samples taken underground, it was established that the factor to be used in the method as described can fairly consistently be taken as 1. In other words, in samples taken underground after blasting, in the manner described, the amount of nitrite in solution can be taken as equivalent to the oxides of nitrogen in the air calculated as NO_2. It must be emphasized that this factor is correct only if the sampling is carried out as described in a bottle containing the alkaline absorbent and does not apply for sampling in a bottle with acid or neutral absorbent or in a dry bottle with absorbent added subsequently.

5. EXAMPLE.

$$\begin{aligned} \text{Capacity of bottle} &= 1150 \text{ ml.} \\ \text{Vacuum} &= 685 \text{ mm. Hg.} \\ \text{Barometer} &= 735 \text{ mm. Hg.} \\ \text{Temp.} &= 27^\circ \text{ C.} \\ \therefore \text{Sample volume} &= \frac{685}{735} \times (1{,}150 - 25) \\ &= 1{,}047 \text{ ml.} \end{aligned}$$

After sampling, etc., the absorbing solution is transferred and diluted to 100 ml., of which an aliquot of 10 mls. is treated with G.I. reagent and made up to 100 mls.

The colour intensity of the final solution (100 mls.) is found to equal that of the standard solution (100 mls.) containing 0·00010 ml. NO_2 per ml. of final solution.

$\therefore$ Nitrite in final solution (as NO_2)
$= 100 \times 0{\cdot}00010$ ml. (at N.T.P.)

$\therefore$ Nitrite in total absorbing solution

$$\begin{aligned} &= \frac{100}{10} \times 100 \times 0{\cdot}00010 \\ &= 0{\cdot}10 \text{ ml. at N.T.P.} \\ &= 0{\cdot}10 \times \frac{290}{273} \times \frac{760}{735} \text{ at } 27^\circ\text{C. and } 735 \text{ mm. Hg.} \\ &= 0{\cdot}1135 \text{ ml.} \end{aligned}$$

$\therefore$ Nitrous fumes in air corresponding to this nitrite value
$= 0{\cdot}1135$ ml. (as NO_2)

$\therefore$ Nitrous fumes (as NO_2) in air (using factor 1 established in practice)

$$\begin{aligned} &= \frac{0{\cdot}1135}{1{,}047} \times 100 \\ &= 0{\cdot}0108\% \text{ (or 108 ppm)} \end{aligned}$$

6. Remarks and Precautions.

As stated, a method measuring total nitrite and nitrate in solution, as by the phenoldisulphonic acid method, is superior to one which measures either the nitrite or the nitrate, since the ratio of nitrite to nitrate in solution may not be constant. The factor of 1 has been established by practical sampling underground but caution is required in using it, particularly in circumstances where conditions may not be usual. It must therefore be realized that the results obtained by this method are an indication of the order of the concentrations of nitrous fumes rather than the exact concentrations. If precise information is required then samples should be analysed by the phenoldisulphonic acid method.

It is advisable to use the purest A.R. grade chemicals obtainable.

For reproducible results it is advisable to carry out the procedure meticulously as described. The quantities of reagents given should be adhered to as the full stable colour will only be developed if the amounts specified are present. This applies particularly to the amount of mixed Griess-Ilosvay reagent added to develop the colour. In no case should this be less than 20 per cent v/v of the final solution and the solution should be neutralized to the acid side of phenolphthalein before adding the reagent.

When a photo-electric spectrophotometer is used, it is desirable that the same salts as are in the sample should also be present in the standard solutions used for deriving the calibration curves, as salts affect the transmittance to a certain extent.

DETERMINATION OF NITROUS FUMES BY POTASSIUM IODIDE METHOD.

If the phenoldisulphonic acid method cannot be applied due to lack of reagent, or other cause, assay offices may find the potassium iodide method sufficiently satisfactory if great accuracy is not required, and the presence of comparatively large quantities of nitrous fumes is suspected, and where oxidizing agents such as ozone are known to be absent.

The sample may be taken in an evacuated bottle containing 10 ml. of ten per cent potassium iodide solution. Alternatively, the sample may be taken in a dry bottle using bellows, and the solution added immediately after sampling. A Winchester quart is advisable. The addition of reagent is best done before evacuation or otherwise immediately after sampling because of possible disintegration of fumes during transport to the laboratory.

In the laboratory, the bottle should be agitated intermittently for several hours, and preferably left overnight. The liquid becomes brownish due to the liberation of iodine. The liquid is washed into a beaker, and the iodine titrated with freshly diluted, N/500 sodium thiosulphate. 1 ml. N/500 thiosulphate equals 0·000092 grams NO_2 or 0·059 ml. NO_2 at average Rand laboratory conditions of pressure and temperature.

If the quantity of liberated iodine is too small to be satisfactorily titrated, the amount may be determined colorimetrically by adding a measured quantity of starch solution, and comparing the blue colour with standards prepared by adding starch to known solutions of iodine in potassium iodide.

CALCULATIONS.

The reaction of nitrous fumes on potassium iodide solution may be summarised as follows:

$$2KI + 2NO_2 + O_2 \rightarrow I_2 + 2KNO_3$$
$$(2 \times 46{\cdot}008)$$
$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$
$$(2 \times 248{\cdot}206)$$

Hence: $(2 \times 46{\cdot}008)NO_2 \equiv (2 \times 248{\cdot}206)Na_2S_2O_3$

Now:

1 litre of N/10 thiosulphate contains 24·8206 grams $Na_2S_2O_3.5H_2O$
$\therefore$ 1 ,, ,, N/10 ,, $\equiv$ 4·6008 grams nitrous fumes as NO_2
$\therefore$ 1 ,, ,, N/500 ,, $\equiv$ 0·9202 grams nitrous fumes as NO_2
or 1 ml. ,, N/500 ,, $\equiv$ 0·000092 grams nitrous fumes as NO_2
(0·000092 grams NO_2 at average Rand conditions, i.e., 25°C. and 630 mm. Hg = 0·059 ml.)

ANALYSIS OF FUMES FROM CHEESA STICKS (FUSE IGNITERS).

Since the exact composition of these sticks is usually a trade secret, it may be necessary to apply tests to ensure that they comply with the Government regulation. This states that, in burning, a cheesa stick shall not give off more than $\frac{1}{2}$ of 1 per cent of its weight of nitrous fumes.

A sample of the fumes is obtained by burning 1 gram of the cheesa stick in a dry bottle of about 10 litres capacity. In order to duplicate working conditions, the burning stick is inserted into the inverted bottle for the number of seconds previously ascertained to be required to burn 1 gram (usually about 11 seconds). The ash should be shaken on to the cork and rejected.

The gases in the bottle are then analysed for nitrous fumes by one of the methods previously described. See also "Polarographic Analysis".

HYDROGEN SULPHIDE.

INTRODUCTION.

Hydrogen sulphide (H_2S), is intensely poisonous and acts as an acute lung irritant. It acts also on the nerve centre controlling the sense of smell so that after breathing air contaminated with high percentages of hydrogen sulphide for a short time, the strong odour of the gas apparently disappears, thus misleading the miner. Sense of smell may be affected when there is 0·01 per cent or more of the gas present. An important warning symptom is the irritation of the eyes, which can be regarded as distinctly dangerous; 0·02 per cent can be sufficient to give warning within 5 minutes. 0·05 per cent will kill a canary in 30 seconds while 0·2 per cent is fatal to human beings in a few minutes.

OCCURRENCE.

The main source is when old workings, containing stagnant water are opened up.

It may be liberated under pressure if such water is encountered during drilling operations.

Underground fires and the heating of coal are further sources of this dangerous gas, and it is often found associated with methane in mine air.

DETECTION.

Test Paper.—A test paper for detection of hydrogen sulphide may be made by dipping paper in a solution of lead acetate and then drying. Quantities of hydrogen sulphide as small as 0·005 per cent by volume may be detected by wetting and exposing this paper to the atmosphere. The brown colour of lead sulphide becomes apparent on the paper at this concentration, deepening to black at higher percentages.

D.S.I.R. Method.—A refinement of the above method developed by the Department of Scientific and Industrial Research in Great Britain draws the air to be tested through test papers by means of a suction pump. The inlet of the pump has a test paper holder attached. The test paper is clamped in this holder and the air is drawn through the paper.

A chart is used which carries stains of definite concentrations of hydrogen sulphide.

A measured amount of the air, determined by the number of strokes of the pump, is drawn through the paper.

The concentration is measured in one of two ways; either by matching the colour produced by a fixed quantity of air or by measuring the amount of air required to produce a certain intensity of colour.

The test papers are made by dipping Whatman's No. 1 filter papers in the following solution:

Lead acetate	10 grams.
Glacial Acetic Acid	5 ml.
Distilled water	100 ml.

The paper is said to be sufficiently sensitive to detect 1 part of hydrogen sulphide in 20,000 parts of air (·005%).

M.S.A. Hydrogen Sulphide Detector.—This is a portable apparatus consisting of an aspirator bulb by means of which the air is drawn through a detector tube. The tube contains a layer of a specially prepared chemical, consisting of silver cyanide on activated alumina. The granules react with hydrogen sulphide and turn grey in colour, and the length of travel of the discoloration through the layer is proportional to the percentage of the gas in the atmosphere tested. A graduated scale is provided, which is calibrated to show concentration with ten squeezes of the bulb. The instrument indicates a range from 0·0025 per cent to 0·04 per cent. A special supersensitive detector is also available indicating concentrations from 0 to 0·0050 per cent.

DETERMINATION.

Hydrogen sulphide in mine air or mine water may be accurately determined by adding a known volume of iodine and titrating the excess with sodium thiosulphate.

Since the hydrogen sulphide is likely to oxidize to sulphate during transit it is necessary to add the excess iodine at the place of sampling. The bottle may then be taken to the assay office for determination.

The determination of hydrogen sulphide in mine air is carried out by adding 100 ml. of water and a known excess of N/10 iodine to the Winchester quart bottle. (This is done at the place of sampling, immediately

the sample is taken.) On receipt at the assay office, the bottle is well shaken and, to ensure complete absorption of all hydrogen sulphide present, the residual air is tested with lead acetate paper. If no coloration is shown, the excess iodine is estimated by titration with N/10 sodium thiosulphate using starch as indicator.

In mine water the hydrogen sulphide is determined in a similar manner. 100 ml. of the water, or such quantity that, on dilution to 100 ml., will yield less than 0·04 per cent H_2S, is placed in a Winchester quart bottle and agitated with a known volume of N/10 iodine. After reaction, the excess iodine is estimated by titration with N/10 sodium thiosulphate.

The amount of iodine which reacts with the hydrogen sulphide is obtained by difference and the percentage hydrogen sulphide is calculated as shown below.

Calculation.

Since 1 ml. N/10 thiosulphate equals 1 ml. N/10 iodine, the amount of thiosulphate used subtracted from the number of ml. N/10 iodine added, will give the number of ml. N/10 iodine which has reacted with the hydrogen sulphide.

From the equation:

$$H_2S + I_2 = 2HI + S$$

$$34{\cdot}082 \text{ grams } H_2S \equiv 2 \times 126{\cdot}92 \text{ gm. } I_2$$

Since an N/10 solution of iodine contains 12·692 grams I_2

$$1 \text{ litre N/10 iodine} \equiv 1{\cdot}7041 \text{ grams } H_2S$$

Since 34·082 grams H_2S occupy 22,400 ml. at N.T.P.

$$1 \text{ litre N/10 iodine} \equiv 1{\cdot}12 \text{ litres } H_2S \text{ at N.T.P.}$$

$$1 \text{ ml. N/10 iodine} \equiv 1{\cdot}12 \text{ ml. } H_2S \text{ at N.T.P.}$$

$$\therefore \text{ per cent hydrogen sulphide} = \frac{\text{No. of ml. } I_2 \times 1{\cdot}12}{\text{Vol. of bottle at N.T.P.}} \times 100$$

When converting the volume of the bottle to N.T.P. it must be remembered that, since the charging of the reagent has been done underground, the conditions of temperature and pressure at the place of charging must be used in the calculation.

METHANE.

Introduction.

Methane (or Marsh Gas, CH_4) is not a poisonous gas, but, like carbon dioxide, large quantities may cause a deficiency of oxygen in the air, with resultant dulling of the senses, headache, etc. The danger of methane lies in its explosive properties when mixed in certain proportions with air. The presence of 5 to 15 per cent of methane in air produces a mixture which is explosive either by compression or ignition. Methane is the main constituent of the so-called "Fire Damp", usually associated with coal mining but also to a lesser extent in gold mines.

Occurrence.

Methane is produced when vegetable matter decomposes in the absence of oxygen. It is often encountered in coal mines and is also found in layers

of shale or dolomite, and not infrequently occurs in gold mines. Mining Regulations require that no person shall be allowed to work in any part of a mine where there is sufficient inflammable gas to show a distinct cap on the reduced flame of the safety lamps ordinarily in use in the mine.

DETECTION.

Although methane is usually the only explosive gas which is likely to be encountered in dangerous quantities it is always accompanied by hydrogen and other hydrocarbons. In the routine testing of mine air for explosive gases methods are used which will generally cause all explosive gases present to react.

Thus the first two methods given, merely indicate the percentage of combustible gas. The analyst may report such gases as methane but it is unlikely that the result is *all* due to methane.

Method 1.—*Safety Lamps.*—The standard method of testing the air in mines is by using an oil burning safety lamp. The presence of methane is shown by a blue cap burning on top of the flame. The height of the cap will depend on the percentage of methane. Colza oil is generally used in test lamps as illuminant.

The table below shows how the height of the cap with a lowered flame indicates the percentage methane, with the safety lamps used on the Witwatersrand.

Height of Cap.	*Percentage Methane.*
$\frac{1}{4}$ inch	2%
$\frac{1}{2}$,,	3%
$\frac{3}{4}$,,	$3\frac{1}{2}$%
$1\frac{1}{4}$ inches	4%
$1\frac{3}{4}$,,	$4\frac{1}{2}$%

Method 2.—*The M.S.A. Methane Detector.*—This is an electrically operated instrument used in conjunction with an Edison Caplamp cell and will give direct readings from nil to 5 per cent methane. The scale is graduated to read to 0·1 per cent, thus enabling the user to obtain accurate results.

The principle is to draw the air to be tested through two cells, in each of which there is a heated platinum wire filament, the current being supplied by the Edison battery.

In the first cell the detector filament is catalytically activated to cause combustion of any methane present. The second cell is a compensating cell, so designed that external influences, which would affect the accuracy of the reading are eliminated. The air then passes out through a flash-back arrestor and exhaust valve to the aspirator bulb.

The electrical circuit is a Wheatstone bridge. The burning of methane on the activated filament increases its temperature and thus alters its resistance. This unbalances the circuit to a degree proportional to the amount of methane. This is measured on a galvanometer graduated to show percentages of methane.

ESTIMATION.

Method 1.—*The Orsat Apparatus.*—Methane may be estimated by means of an Orsat apparatus. The procedure is fully described in the section

dealing with fuel gases. This method gives very good results, being especially useful when other gases are present. The application of the Orsat apparatus is limited to concentrations of methane not lower than about 0·5 per cent; since it is accurate to about 0·2 per cent.

Method 2.—Two samples of about 2½ litres are required.

The sample in the first bottle is displaced by water and caught in a conical flask over a beehive shelf, also by the displacement of water. From 10 to 20 ml. of water should be left in the flask. The flask is then sealed with a rubber bung which has been fitted with two electrodes connected to a heating element. The flask is removed and placed in a water bath. The electrodes are connected to a battery and the amperage regulated to 7 or 8 amps.

The methane present in the sample will ignite and form carbon dioxide.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

The reason for placing the flask in a water bath is that the mixture may be within the explosive range.

When combustion is complete, the carbon dioxide present in the bottle is estimated, using Pettenkofer's method.

Also by means of Pettenkofer's method the carbon dioxide in the second bottle is estimated. This figure is subtracted from that obtained from the first bottle and the result gives the amount of carbon dioxide resulting from the combustion of the methane.

Since one volume of methane produces one volume of carbon dioxide, the percentage by volume of carbon dioxide is a direct measure of the percentage methane.

This method gives very accurate results even when small quantities are present.

It must be remembered that each volume of methane requires two volumes of oxygen for complete combustion. Thus when the air contains 9 per cent methane there is just sufficient oxygen present for complete combustion, and at higher percentages of methane extra air must be added.

HYDROCYANIC ACID GAS.

Introduction.

The presence of this gas underground is very rare and nowadays poisoning cases are seldom encountered. It is a highly poisonous gas, and 0·01 per cent or more present in the air is considered to be highly dangerous.

The gas has a peculiar smell of bitter almond oil.

It is also encountered in the Reduction Works where large quantities of cyanide are dissolved in water.

Occurrence.

The source of this gas is the sand tailings used for sand filling underground. Fresh dump sand usually contains a small proportion of residual cyanide and when this comes in contact with sulphuric or other acids which are present underground the reaction is as follows:—

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN$$

The Mining Regulation states that when tailings are used for filling worked-out areas underground the moisture contained in such tailings

and the liquid draining from such areas shall not have a higher cyanide content than 0·005 per cent expressed as cyanide of potassium.

Detection.

A sensitive test paper may be made by dipping filter paper in a solution made by boiling 2 grams of commercial tolidine and 3 grams of copper acetate in 200 ml. of 0·5 per cent acetic acid, the solution being finally cooled and filtered. A strip of filter paper is dipped at one end in a few drops of this reagent and exposed in the suspected air. A light blue colour develops within a minute if one part of hydrocyanic acid gas per million parts of air is present (0·0001 per cent). The higher the proportion of hydrocyanic acid the more rapid and intense the colour. At high concentrations the stain has a copper-like lustre.

Determination.

The determination of hydrocyanic acid in mine air may be carried out in the following manner. The sample of air is taken in a Winchester quart which is then sealed with a rubber bung. To the bottle 25 ml. of strong potassium hydroxide is added, and the whole shaken to convert all hydrocyanic acid to potassium cyanide, according to the equation:

$$HCN + KOH = KCN + H_2O$$

The contents are washed into a beaker (for clarity of end-point). A few drops of potassium iodide solution are added to sharpen the end-point, and the potassium cyanide titrated with N/100 silver nitrate. As the drops fall into the liquid, a turbidity is produced (AgCN) which almost immediately redissolves.

The overall reaction is as follows:—

$$\underset{169\cdot888}{AgNO_3} + \underset{130\cdot228}{2KCN} = KAg(CN)_2 + KNO_3$$

When all the cyanogen has been converted to potassium silver cyanide, the next drop produces a permanent turbidity of AgCN, intensified by the presence of silver iodide and a few ml. ammonium hydroxide.

Since N/100 silver nitrate contains 1·69888 grams/litre,

1 litre N/100 silver nitrate ≡ 1·30228 grams potassium cyanide.
1 ml. N/100 ,, ,, ≡ 0·0013 ,, ,, ,,
≡ 0·448 ml. hydrogen cyanide at N.T.P.

Determination in Water.

The determination of potassium cyanide in the water contained in tailings used for sand filling cannot be done by direct titration as the amount present is so small. Thus it is necessary to concentrate the solution. This is best done by taking a large sample of the water to be tested, adding sulphuric acid and distilling over until about a tenth of the volume has evaporated. The cyanide is converted to hydrocyanic acid gas and this passes over with the water vapour. The distillate is caught in 20 ml. of 5 per cent potassium hydroxide solution so that the hydrocyanic acid is converted to potassium cyanide.

$$HCN + KOH = KCN + H_2O$$

This may then be titrated directly with N/100 silver nitrate.

Method.—To a conical flask add 1,000 ml. of the water to be tested. Connect the flask to a Liebig condenser, the end of which dips into a solution of 5 per cent potassium hydroxide. By means of a separating funnel, the stem of which also passes through the stopper of the flask, add 10 ml. of sulphuric acid. Distil over about 100 ml. of the water. Titrate the distillate with N/100 silver nitrate and calculate the potassium cyanide present. This is, of course, the amount present in 1,000 ml. of water sample.

The percentage is calculated as follows:—

$$\frac{\text{Amount of KCN}}{1{,}000} \times 100 = \text{percentage KCN.}$$

SULPHUR DIOXIDE.

In mine air this gas is not likely to be found in dangerous quantities. A dangerous local concentration may, however, be built up by leakage from underground refrigeration plants which use sulphur dioxide as refrigerant, although Freon is almost invariably used nowadays. It may possibly be produced to a very small extent from the fumes of fires or after an explosion. It is easily recognisable by its peculiar pungent odour of burning sulphur. Like hydrogen sulphide it is a powerful irritant, respiratory poison.

Detection.

Its detection may be made chemically by soaking filter paper in potassium iodate solution and a little starch solution, and then hanging the paper in the suspected air for a few minutes. Any sulphur dioxide present will liberate iodine and cause a blue colour to appear. On further exposure this colour may disappear. The sulphur dioxide first liberates the iodine and then in turn reduces it so that the colour disappears, the equation being:—

$$5SO_2 + 2KIO_3 + 4H_2O = I_2 + 2KHSO_4 + 3H_2SO_4$$

Determination.

Iodine Method.—The method given below is the same as that used for the determination of hydrogen sulphide, but these two gases cannot both be present except in absolutely dry air which is impossible under normal conditions. Hydrogen sulphide reacts with sulphur dioxide in moist air according to the equation:—

$$2H_2S + SO_2 = 2H_2O + 3S$$

Lead acetate paper gives no reaction with sulphur dioxide and it may, therefore, be used to distinguish between the two gases.

To the samples, received in Winchester quarts, a known volume of N/10 iodine solution is added. The bottle is then well shaken and the excess iodine is titrated with standard sodium thiosulphate using starch indicator.

The reaction is as follows:—

$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI$$

64·066 grams (22,400 ml.) $SO_2 \equiv 2 \times 126{\cdot}92$ grams I_2

Since N/10 iodine contains 12·692 grams/litre.

1 litre N/10 iodine ≡ 3·2033 grams (1,120 ml.) sulphur dioxide.

1 ml. N/10 iodine ≡ 0·003203 grams (1·12 ml.) sulphur dioxide.

≡ 1·12 ml. sulphur dioxide at N.T.P.

EXAMPLE:

The observed volume of the mine air sample was 2,880 ml. when the temperature was 19·4°C. and the atmospheric pressure was 623·5 mm.

10 ml. of N/10 iodine was added to the bottle and after agitation the amount of N/10 sodium thiosulphate required for titration was 9·6 ml.

The volume of the air sample at N.T.P. is 2,206 ml. (for calculation see the example given under carbon dioxide).

Now since 1 ml. N/10 thiosulphate = 1 ml. N/10 iodine it follows that the excess iodine = 9·6 ml.

Therefore the amount of iodine reacted on by the sulphur dioxide = 0·4 ml.

1 ml. N/10 iodine ≡ 1·12 ml. sulphur dioxide.

0·4 ml. N/10 iodine ≡ 0·448 ml. sulphur dioxide.

This is $\frac{0{\cdot}448}{2{,}206} \times 100 = 0{\cdot}0202$ per cent sulphur dioxide.

D.S.I.R. METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY.

The Department of Scientific and Industrial Research, of Great Britain, has devised methods for the detection of toxic gases by means of simple apparatus, which can be used by non-technical operators.

A known volume of the air or gas under examination is drawn through filter paper impregnated with a suitable reagent and the depth of colour change is used as a measure of the concentration of the toxic gas. In some cases a solution is used. The apparatus employed for the purpose is either a hand operated exhaust pump, fitted with a special test paper holder, or an aspirator fitted with a similar holder. The concentration of the toxic gas is determined by comparison of the colour of the stain on the filter paper or solution either with standard colour charts issued with the explanatory booklets, or with standard coloured solutions.

The gases colorimetrically dealt with are:—Aniline, Arsine, Benzene, Carbon Bisulphide, Chlorine, Hydrogen Cyanide, Hydrogen Sulphide, Nitrous fumes, Phosgene and Sulphur Dioxide.

The complete outfit consisting of an exhaust pump, test paper holder, All Purposes Lovibond Comparator and colour standards is available in one case, weighing approximately 11 pounds.

The use of colour glasses has been approved as a method of comparison alternative to the colour standard charts, the former having the advantage of greater permanence with age and continued handling. In cases where the official standards consist of coloured solutions permanence of colour is also claimed.

The D.S.I.R. outfit simplifies conditions for the operator, and makes for compactness and ease of storage, and where tests have to be carried out at different points, the portability of the complete set is a great advantage.

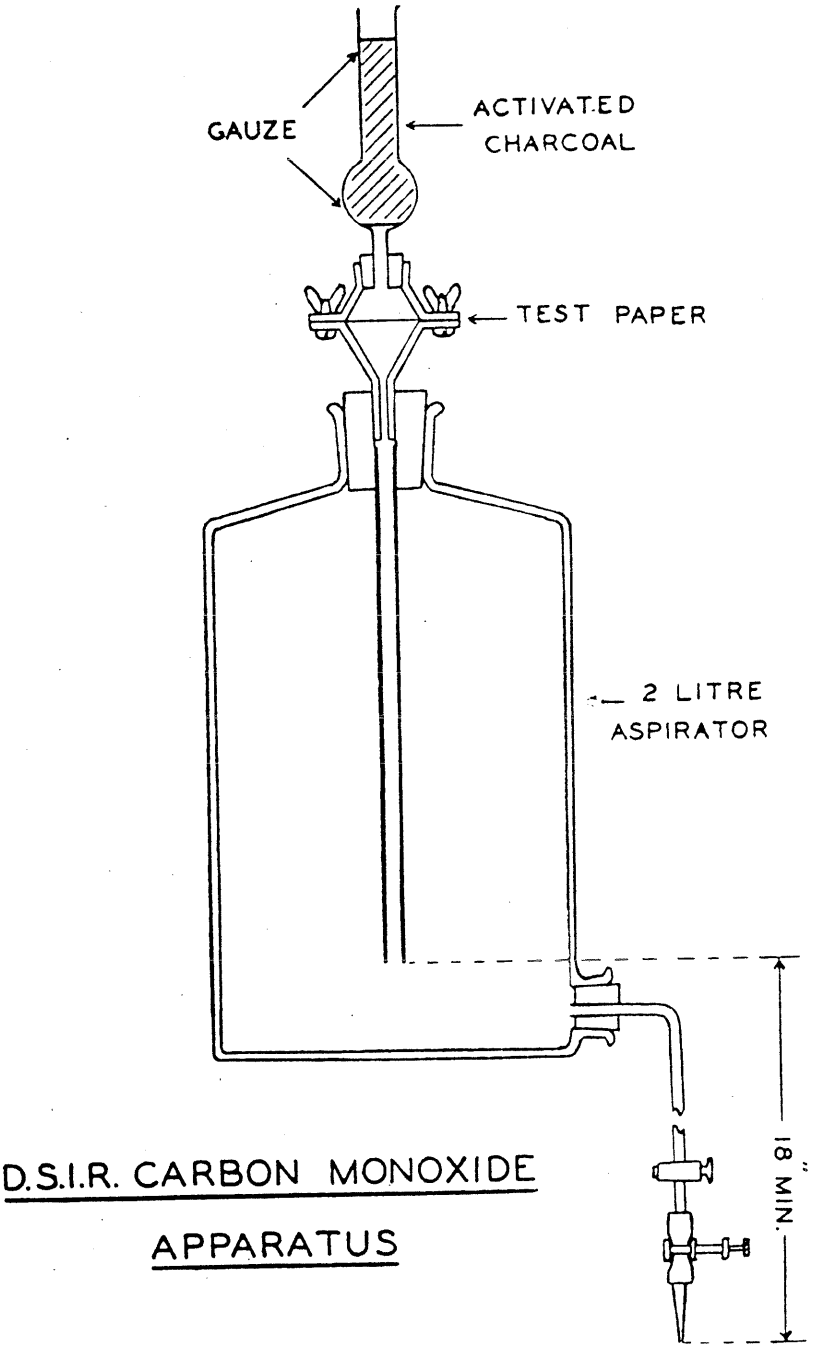

GAUZE
ACTIVATED CHARCOAL
TEST PAPER
2 LITRE ASPIRATOR
18 MIN.
D.S.I.R. CARBON MONOXIDE APPARATUS

Fig. 64.

ANALYSIS OF FLUE AND FUEL GASES.

General.

The examination of flue gases is of great importance in connection with the most economical use of fuels in engines, boilers and furnaces. In the correct use of solid, liquid or gaseous fuels for industrial purposes, the object is to supply an amount of air which will give as nearly complete combustion of the fuel as possible.

This means that the carbon of the fuel should be found in the exhaust or flue gases only as carbon dioxide. In practice it is usually found necessary to admit from one and a half to twice the theoretical amount of air in order to secure good combustion, but the greater the excess of air used, the larger will be the amount of heat carried away by the flue gases.

It is generally required to estimate only the carbon dioxide and the oxygen in such gaseous mixtures. Occasionally, the carbon monoxide may be required; in the waste gases from blast furnaces, for instance, a considerable amount of carbon monoxide is present. Strictly speaking, however, blast furnace gases should be considered to be *fuel* gases rather than flue gases, since they are used again to heat the incoming air blast. The complete analysis of gases used for fuel, such as coal gas, producer gas, etc., requires considerable manipulative skill and experience, and for details of the method and apparatus used, works devoted to gas analysis should be consulted. In the present article only the simple Orsat apparatus, which is widely used in technical work, will be described.

The Orsat can also be used for the examination of fuel gas, in this case being used in conjunction with the Hempel explosion pipette.

In this way the following constituents may be estimated:—carbon dioxide, carbon monoxide, oxygen, heavy hydrocarbons, methane, hydrogen and nitrogen.

The first four are determined by the Orsat alone and the last three by means of the Hempel explosion pipette used in conjunction with the Orsat.

Sampling the Gas.

The usual method is to make a connection from the flue or pipe, conveying the gases, to a bottle filled with brine which acts as an aspirator; the brine is allowed to drip out at a suitable rate, and its place is taken by the gas sample.

The connecting tubes should be swept free of air by running the aspirator for a few minutes and re-filling it before actually connecting up with the sample.

Again, carbon dioxide is appreciably soluble in water, and the brine should, therefore, be acidified with hydrochloric acid. A little methyl orange added serves as a reminder and also aids in the readings.

For accurate work it is necessary to use mercury instead of water as the confining liquid. In this case smaller sample tubes may be used; a convenient form of these is fitted with a three-way ground-glass stopcock at each end so that an outlet to the air is provided as well as to the tube. In this way the connecting tubes from the flue can be filled with gas before connection with the sample tube is made.

ANALYSIS.

The method used to estimate most of the constituents of a gaseous mixture is to absorb the constituents successively by means of suitable reagents and, after each gas has been absorbed, to measure the volume of gas remaining. In the case of the gases carbon dioxide, carbon monoxide and oxygen, the absorption method is available. For certain gases (e.g., methane) suitable absorbents are not known, and other methods are used, depending on the combustion of the gas with oxygen.

The Orsat apparatus designed for this purpose consists of a gas burette of capacity 100 ml., with its lower end, of small diameter, accurately graduated.

The lower end of the burette is connected by means of "pressure" tubing to the levelling bottle filled with acidulated brine solution. The top end of the gas burette is connected by capillary tubing to absorption pipettes through stopcocks.

The absorption pipettes contain short glass tubes to provide a larger absorbing surface, and each pipette is connected by a U-tube at the bottom to a glass reservoir at the back, into which the absorbing reagent is forced when gas enters the pipette. A three-way stopcock controls the entrance of the gas sample into the burette and also a lower tube, which can be connected to a filter pump for freeing the capillary tubes of air.

MANIPULATION.

The burette is filled with acidulated brine solution up to the capillary by opening the stopcock and raising the levelling bottle. Then it is connected to the sample bottle through the capillary, and the sample of gas drawn in by lowering the levelling bottle. By manipulating the levelling bottle and the stopcock exactly 100 ml. of gas at atmospheric pressure can be obtained in the burette.

The analysis is now carried out by passing the gas successively into the three pipettes. Sufficient time must be given for each absorption, and it is essential to pass the gas backwards and forwards between the burette and the pipette being used at the moment until constant readings of the remaining volume of gas are obtained. At the end of each absorption the remaining volume is noted, after the pressure has been adjusted to the original value (atmospheric). The volume of gas absorbed is given by the decrease in volume.

The details of the different absorbing solutions are given below.

Errors in analysis with the Orsat apparatus arise from the fact that it does not permit of sufficiently intimate contact of the oxygen and the carbon monoxide with their respective reagents, so that complete absorption is not always obtained. Changes in temperature during the analysis also affect the accuracy. Modifications of the original Orsat apparatus have been designed, with a view to providing better contact of gas and reagent and elimination of temperature errors.

Reagents Required:—The following reagents are required for the absorption of the four gases:—

Carbon dioxide.—A solution of 50 grams potassium hydroxide in 100 ml. water.

Heavy hydrocarbons.—Saturated bromine water.

Oxygen.—To a solution of potassium hydroxide containing 25 grams of the solid to 25 ml. of water a solution of 5 grams of pyrogallol in 5 ml. of water is added.

Carbon monoxide.—Either an acid or an ammoniacal solution of cuprous chloride is used.

For the ammoniacal solution 1,200 ml. of the acid solution should be taken and poured into 4 litres of water. The resulting precipitate is transferred to a graduated stoppered cylinder of 250 ml. capacity. After two hours the supernatant liquid is siphoned off and 7·5 per cent ammonia is added to the 250 ml. mark.

Copper wire or foil should be placed in the pipette containing the reagent in order to preserve it in the reduced or cuprous condition.

Methane and hydrogen are determined by explosion with oxygen. Nitrogen is obtained finally by difference.

It is important to absorb the gases in the order given above as some of the reagents absorb more than one gas. Thus the oxygen absorbent will also absorb carbon dioxide and the cuprous chloride absorbs oxygen as well as carbon monoxide.

EXAMPLE.

100 ml. of coal gas were taken for analysis. The volume after absorption in potassium hydroxide was 97·8 ml., after the bromine water 93·0 ml., after the pyrogallol solution 92·2 ml., and after the cuprous chloride 75·0 ml.

The percentages were therefore:—

Carbon dioxide	100 —97·8 =	2·2%
Heavy hydrocarbons	97·8—93·0 =	4·8%
Oxygen	93·0—92·2 =	0·8%
Carbon monoxide	92·2—75·0 =	17·2%

Thus we have a residue of 75·0 ml.

For the determination of methane and hydrogen by explosion a certain volume, say 12·8 ml. of the residual gas is measured off from the burette and mixed with 83 ml. of air, so that the volume for explosion is brought up to 95·8 ml.

This is passed over into an explosion pipette and an electric spark passed between the terminals.

The reactions occurring are an oxidation of methane to carbon dioxide and water and of hydrogen to water.

$$\underset{1\text{ vol.}}{CH_4} + \underset{2\text{ vol.}}{2O_2} = \underset{1\text{ vol.}}{CO_2} + \underset{\text{Nil.}}{2H_2O}$$

$$\underset{2\text{ vol.}}{2H_2} + \underset{1\text{ vol.}}{O_2} = \underset{\text{Nil.}}{2H_2O}$$

In both equations the water is condensed to liquid.

From the equation one volume methane equals one volume carbon dioxide. Thus the carbon dioxide present is a direct measure of the methane present. In this equation the actual volumes reacting are: 1 volume methane reacts with two volumes oxygen to produce 1 volume carbon dioxide. That is, three volumes of the reacting gases are contracted to one volume of carbon dioxide.

Likewise with the hydrogen two volumes hydrogen and one volume oxygen are completely contracted to liquid.

After the explosion, return the residual gas to the Orsat and measure the contraction, and then measure the carbon dioxide by absorption in potassium hydroxide.

The gas measured 78 ml. after explosion, and 74·2 ml. after absorption in the potassium hydroxide.

Let x be the volume of methane present.

Then $2x$ is the volume of oxygen required for the combustion of the methane.

Let y be the volume of hydrogen present.

Then $\frac{y}{2}$ is the volume of oxygen required for the combustion of the hydrogen.

Therefore the total oxygen required for the combustion of the methane and the hydrogen is $2x + \frac{y}{2}$. In the actual determination the contraction is measured and then the carbon dioxide is measured. These two represent the total contraction.

Thus, including the absorption of carbon dioxide, the contraction due to methane is:—One volume of methane plus two volumes of oxygen is reduced to zero. As we have x volumes of methane and $2x$ volumes of oxygen this contraction is $3x$.

Likewise in oxidation of hydrogen we have y volumes of hydrogen and $\frac{y}{2}$ volumes of oxygen reduced to zero. Therefore the contraction due to hydrogen is $y + \frac{y}{2}$.

We have established: oxygen $O_2 = 2x + \frac{y}{2}$ (1)

We have to evaluate: $2x + \frac{y}{2}$

Total contraction $C = 3x + \frac{3y}{2}$ (2)

Solve by multiplying (1) by 3 and (2) by 2.

$$3O_2 = 6x + \frac{3y}{2} \quad (3)$$

$$2C = 6x + 3y \quad (4)$$

Subtract (3) from (4)

$$2C = 3O_2 + 3y - \frac{3y}{2}$$

$$\frac{3y}{2} = 2C - 3O_2$$

$$y = \frac{4}{3}C - 2O_2$$

i.e., hydrogen equals $\frac{4}{3}$ total contraction minus oxygen.

To solve for the value of x, substitute this value for y in (2).

$$C = 3x + \frac{3}{2}\left(\frac{4}{3}C - 2O_2\right)$$

$$C = 3x + 2C - 3O_2$$

$$3x = 3O_2 - C$$

$$x = O_2 - \frac{C}{3}$$

i.e., volume of methane = total oxygen minus one-third total contraction.

From this last equation we have the amount of oxygen used in the combustion as the methane is known from the amount of carbon dioxide found.

Applying these values to our example:—

Contraction before absorption in potassium hydroxide:

$$95{\cdot}8 - 78{\cdot}0 = 17{\cdot}8$$

After absorption in potassium hydroxide:

$$78{\cdot}0 - 74{\cdot}2 = 3{\cdot}8$$

Therefore the methane is 3·8 ml. and the total contraction is:

$$17{\cdot}8 + \ 3{\cdot}8 = 21{\cdot}6 \text{ ml.}$$

In the equation methane $= O_2 - \frac{1}{3}C$

Substitute for methane and total contraction:

$$3{\cdot}8 = O_2 - \left(\frac{1}{3} \times 21{\cdot}6\right)$$

i.e., $O_2 = 11$ ml.

From the equation $H = \frac{4}{3}C - 2O_2$ and substituting the values for oxygen and total contraction:

$$H = \left(\frac{4}{3} \times 21{\cdot}6\right) - (2 \times 11)$$
$$= 6{\cdot}8 \text{ ml.}$$

Or, to put it another way:—

Let C be the contraction after the explosion.

Let M be the contraction due to the absorption of the CO_2 formed.

Let X be the volume of hydrogen present.

We have seen that M = Volume of methane present .. .. (1)

Now M volumes methane have combined with 2M volumes of oxygen, therefore 2M volumes of the contraction is due to the combination of methane and oxygen.

The remainder of C, i.e. C — 2M, is due to the combination of hydrogen and oxygen.

Since 2 volumes of hydrogen combine with 1 volume of oxygen to form water, then:—

$$X = \frac{2}{3}(C - 2M) \quad .. \quad .. \quad .. \quad (2)$$

In the example, then:—

From (1) M = 78 — 74·2 = 3·8 ml. methane.

From (2) $X = \frac{2}{3}[(95{\cdot}8 - 78) - 2 \times 3{\cdot}8] = 6{\cdot}8$ ml. hydrogen.

As these volumes were obtained from 12·8 ml., the—

percentage methane is: $\frac{3{\cdot}8 \times 75{\cdot}0}{12{\cdot}8} = 22{\cdot}3\%$

and hydrogen is: $\frac{6{\cdot}8 \times 75{\cdot}0}{12{\cdot}8} = 39{\cdot}8\%$

(*a*) *Composition of the Dust.*

Several constituents occur in air-borne mine dust:—

(i) Carbon—from acetylene lamps.
(ii) Oil—from lubrication of drills.
(iii) Steel—from the wearing of drill steels.
(iv) Rust—from rusty compressed air pipes.
(v) Soluble salts—from atomisation of mine water containing calcium sulphate and other salts.
(vi) Rock particles—from pulverization of rock.

Since it is the concentration of the particles derived from the rock that is generally required in dust estimation, the sample must be treated by suitable methods for removal of the extraneous matter, viz., ignition to remove the carbonaceous matter and oil, and acid treatment to remove the soluble salts and other acid-soluble matter.

The composition of the particles derived from the rock is of interest. For simplicity from the silicosis point of view the rock material may be regarded as consisting of three constituents: Quartz or free silica, silicates and pyrites.

On the Witwatersrand the parent rocks from which the dust is derived are the gold-bearing reefs which generally contain over 80 per cent of quartz; the strata under and over them, also very high in quartz, except in certain regions where shale is encountered which contains some 30 per cent of quartz. In general, the composition of the rocks may be given roughly as:

Quartz	80 per cent.
Silicates	20 per cent
Pyrites	1—5 per cent.

In the dust produced from these rocks, it is found that the proportions of the constituents have changed considerably, the quartz contents being generally much lower than in the rock, a fact ascribed to the greater ease of breaking the silicates into fine particles.

A typical composition for the rock matter in an air-borne dust may be as follows:—

Quartz	50 per cent.
Silicates	45 per cent.
Iron oxide	5 per cent (oxidised pyrites).

(*b*) *Size of Particles.*

The size of particles is measured in microns:

$$1 \text{ micron } (\mu) = \tfrac{1}{1000} \text{ millimetre.}$$

Samples of air-borne mine dust show that particles up to 50 microns may be present, but the greater proportion of dust is under 5 microns in size. The lower limit of the particles is not known, but it is found that particles down to the finest visible under the highest power microscope, i.e, about $\frac{1}{10}$ micron, are always present and the possibility is, therefore, that still finer particles may occur.

Dust particles as small as these are seldom found in nature, the mineral dust present in the air of towns or deserts being generally much coarser than the above sizes.

For comparison with these fine sizes it may be stated that the finest sieve used on the Witwatersrand, viz., 325 mesh. has an average aperture of 44 microns.

(*c*) *Quantity of Dust in Mine Air.*

The concentration of dust in air may be measured by weight or by number.

In Witwatersrand mines the dust concentrations generally occurring are low. By weight the average amount of rock dust in the air is of the order of $\frac{1}{2}$ milligram per cubic metre. What this means from a sampling point of view may be realised from the fact that to collect a sample of only 1 milligram with an instrument sampling at the rate of 1 cubic foot per minute would take over one hour.

In determinations of the dust by number, the usual method is to report the dust concentration in terms of the number of particles per cubic centimetre (p.p.c.c.). Typical concentrations are between 100 and 200 particles per cubic centimetre as measured by the Konimeter (ignition first technique) corresponding to about 300 particles per cubic centimetre measured by the Thermal Precipitator (this refers to rock particles as measured after acid treatment).

It is generally considered that gravimetric results of over 1 mg. per cubic metre or konimeter counts of over 300 particles per c.c. indicate that some improvement in conditions is required.

NOTE.—Owing to the fact that the term "cubic centimetre" is generally used by Ventilation Officers it has been used throughout this section instead of the more usual "millilitres".

DUST SAMPLING INSTRUMENTS.

Dust sampling instruments may be of two main types:

(*a*) Gravimetric.

(*b*) Number determination.

In South Africa the standard method at present is number determination, the Konimeter being used for routine sampling and the Thermal Precipitator for special investigations.

Gravimetric samples are to-day taken only for special purposes, the sugar tube being sometimes used for weight concentrations, and the filter paper or electrostatic method for collecting bulk samples for chemical analysis.

The following is a tabulation of the most common instruments in actual use for dust sampling in various parts of the world.

(*a*) Gravimetric Instruments.

1. Sugar tube.
2. Filter paper and Soxhlet thimble.
3. Solubie and volatile filters (salicylic, anthracene).
4. Electrostatic sampler.

(*b*) Number Determination.

1. Konimeter.
2. Thermal precipitator.
3. Midget Impinger.

Recently other instruments have come into use such as the P.R.U. handpump, usually assessed by a densitometric method and the Tyndallometer, using photo-electric means of estimation.

DESCRIPTION OF THE MORE COMMON INSTRUMENTS.

Sugar Tube.—The sugar tube method was one of the first to be used for sampling mine dust. By this method the weight of dust in the air is determined. Owing to the very small amount of dust by weight in mines at present, it is no longer used as a routine method on the Witwatersrand, but is sometimes used for special tests.

The sugar tube consists of a thick-walled glass tube 5″ long and 1¼″ in diameter. At the lower end a rubber stopper is provided through which passes a piece of ½″ glass tubing. A wad of cotton wool is placed at the bottom of the tube to cover the opening in the tubing, and on this is placed 40 grams of sugar. The sugar used is Tates' Mineral Water C or Coffee Crystals, sieved to pass ten mesh and remain on 20 mesh. The top of the tube is closed with a solid rubber stopper, which is removed for sampling.

The tube is connected by rubber tubing to a double-acting suction pump, and air drawn through the sugar at the rate of approximately one cubic foot per minute. The volume of air usually sampled is ⅓ cubic metre, which requires 100 double strokes of the pump. This takes about ten minutes. During sampling the tube is held at head height. After sampling, the tube is closed with the stopper, and transferred to the surface for analysis.

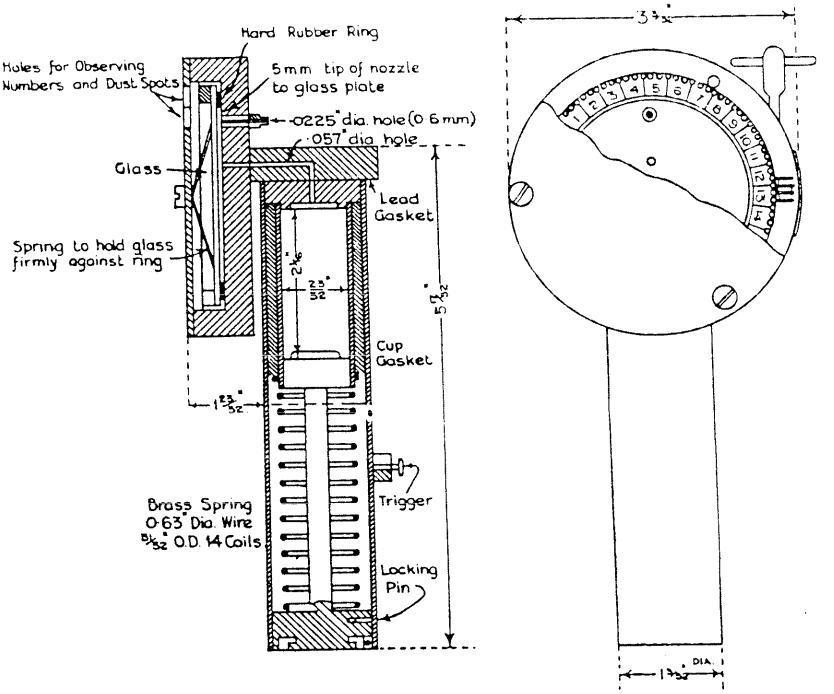
The tubes are wiped with a damp cloth, and the sugar shaken out into a metal screen which consists of an inverted truncated cone, the narrow end of which is covered with 350 mesh gauze. The screen rests in a glass funnel fitted with a close-textured filter paper. The sugar is washed through the screen with hot water, and the washing continued until all the sugar has dissolved and passed through the filter paper. The dust is caught on the filter paper. The paper is then burnt in a silica crucible over a Bunsen burner, the crucible is allowed to cool, and then weighed. The dust is brushed out and the crucible weighed again. The difference in weight is the weight of dust plus filter ash and contamination in the sugar. The sum of the latter is determined periodically from blank samples and is usually of the order of 0·5 milligram. This is subtracted from the gross weight of dust found, to give the weight of dust in ⅓ cubic metre. This is multiplied by three to give milligrams per cubic metre.

The Konimeter.—The Konimeter is an instrument used to collect a sample of the dust in the air by causing a measured volume to impinge through a jet on to a glass slide coated with a thin film of adhesive. The dust particles are deposited on the slide in the form of a spot suitable for subsequent counting under a microscope.

Two types of Konimeters have been in general use on the Witwatersrand. The Kotze Konimeter was used by the Government Mines' Department, and the Circular Konimeter by the Chamber of Mines and by the

officials on the mines. The main difference between the two types was that the Kotze uses a 1″ by 1½″ rectangular slide on which nine to twelve spots may be taken, whereas the Circular collects the samples on a circular slide 2¼″ in diameter which can be rotated after each spot has been taken, enabling up to 58 spots to be taken in a circle round the slide. The instruments differ, too, in certain constructional details.

A new type of Konimeter known as the "Witwatersrand Konimeter" has recently been designed and is now replacing the above mentioned types (see later).



THE CIRCULAR KONIMETER.

Fig. 65. Sketch of Circular Konimeter.

Circular Konimeter.—The Konimeter is essentially a small suction pump with a capacity of 5 c.c. It consists of a barrel 5¼″ long and 1⅛″ in diameter, which is attached to a circular head, in which the slide is placed. In the barrel at the top end is a cylinder ½″ inside diameter. A leather plunger acts as a piston in the cylinder, and is attached by a piston rod to a guide which slides along inside the barrel at its lower end. The operator pushes the piston up into the cylinder by pressing his finger on the guide and forcing it up against the pressure of a coiled brass spring. The piston is kept in position by the engagement of a locking-pin in the trigger. When the trigger is depressed, the coiled spring forces the piston to the end of its stroke, thereby causing a vacuum in the cylinder and drawing in 5 c.c. of air.

The circular glass slide in the head rests on a rubber ring against which it is pressed by a spring on the cover closing the head. An air-tight chamber is thus formed under the slide, and this space is in communication with the top of the cylinder. When the piston is displaced, the vacuum in the cylinder is communicated to the space under the slide, and 5 c.c. of air is drawn in from the outside air at a rapid rate through a nozzle or jet. The air impinges at high velocity on the glass slide, which has been treated by applying to it a thin film of vaseline, and the dust particles adhere firmly to the slide in the form of a spot.

The jet is 0·6 mm. in internal diameter and is placed at a distance of 0·5 to 0·6 mm. from the slide.

The strength of the spring is sufficient to allow the stroke to be completed in about $\frac{1}{3}$ second, and produce a calculated average velocity of impingement at the jet of about 70 to 100 metres per second.

The glass slide is held in a toothed brass ring which engages with a pinion in the head of the Konimeter, by means of which the slide can be advanced in a circle after taking each spot. Three half-turns of the winding-handle are generally given between spots, and this enables up to 58 spots to be taken on a slide.

Recently a new method of applying the adhesive has been adopted. A solution is used consisting of yellow petroleum jelly (vaseline is very suitable) in xylol with a concentration of one gram per 100 c.c. The slide is removed from its metal ring, cleaned in the usual way and then held face upwards while about $\frac{1}{2}$ c.c. of the solution is squeezed on to the surface by means of a dropper similar to a fountain pen filler. By rocking the slide gently, the solution is made to flow over the whole surface, after which the excess solution is tipped off. The slide is then drained by leaning it face downwards against a perpendicular surface at an angle of about 30° from the vertical, and with the bottom edge resting on a few thicknesses of blotting or filter paper. A small box is used for the purpose. The xylol quickly dries off and the slide is then ready for use.

By this technique a jelly film of uniform thickness is obtained, giving good even dust spots.

As soon as prepared, the slide should be placed in the Konimeter to prevent contamination. It is not advisable to keep prepared slides unused for more than a few days.

Treatment of Slide.—Before counting the spots the slides are treated by ignition and acid-immersion to remove carbon and water-borne salts respectively. The procedure now followed by the Government Mines Department and the Chamber of Mines is ignition of the slide, then acid treatment followed by a final ignition.

After sampling, therefore, the slide is removed from the brass ring and heated on a hot plate or in a muffle to a low red heat (about 550° C. or 1050° F.) in order to burn off the carbon. It is then placed in a specially designed immersion cell for the acid treatment.

The immersion cell measures 4″ by $3\frac{1}{2}$″ by $1\frac{1}{2}$″ externally and is made of three vulcanite blocks screwed together, the middle block being cut away to form a cell $\frac{1}{2}$″ wide, $1\frac{3}{4}$″ long and $2\frac{1}{2}$″ deep. The ends of the cell are slotted to take the Konimeter slide. A funnel is provided at one end of the cell through which the cell is filled with boiling 50 per cent hydrochloric acid. When the cell is full, excess acid overflows into an overflow launder. The acid is then displaced through the overflow by pouring two or three times its volume of boiling distilled water through

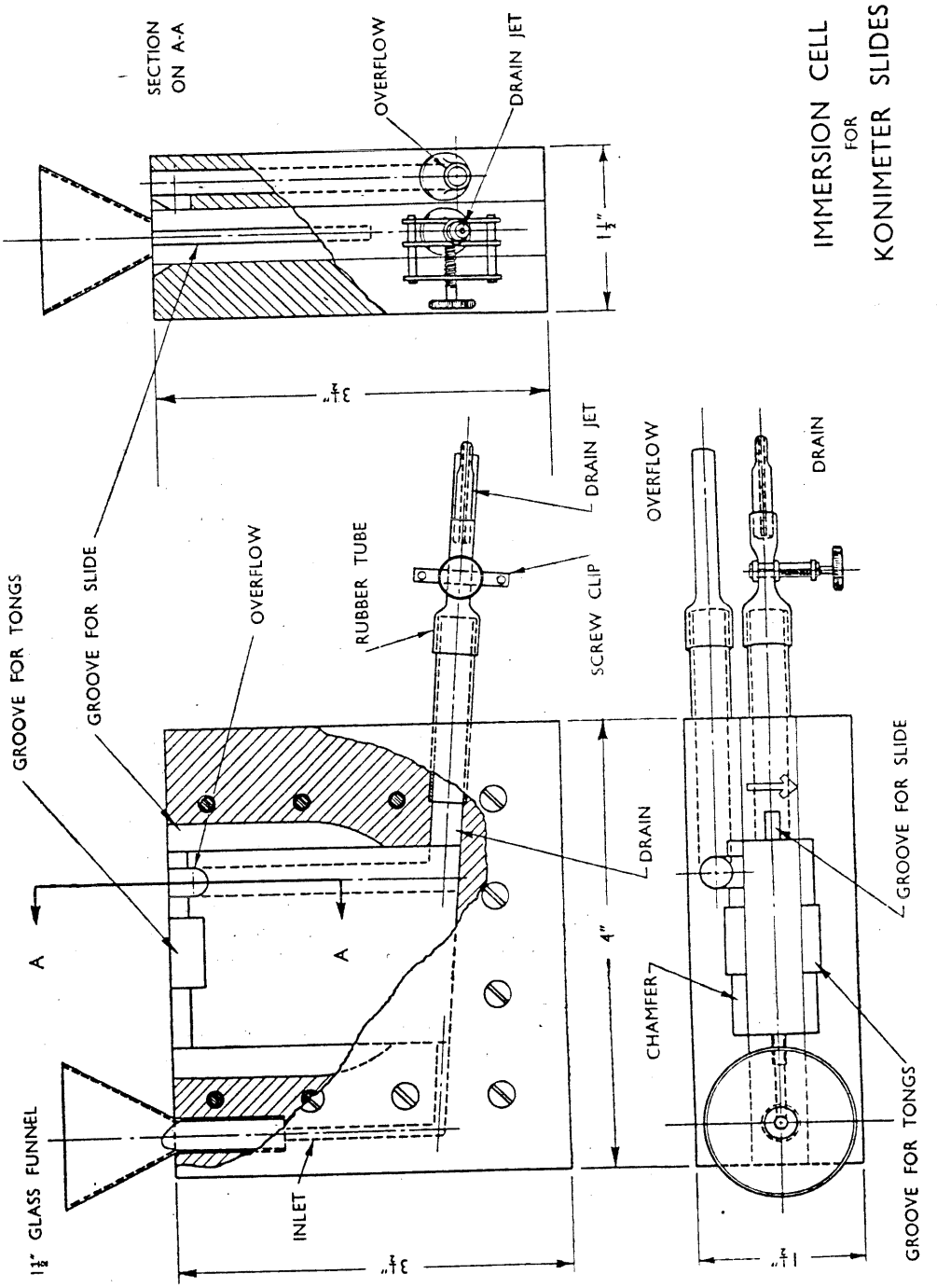


FIG. 66. (*By courtesy of the Transvaal Chamber of Mines.*)

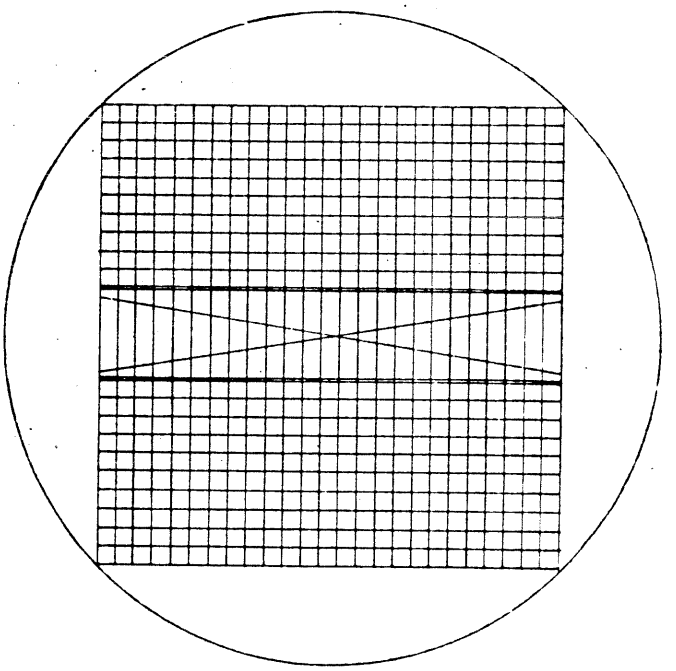
the funnel, after which the liquid in the cell is slowly run out by opening a draining tube connected to the bottom of the cell.

After immersion the slide is removed from the cell and again heated on the hot plate or in the muffle. The purpose of the final ignition is to remove water residue marks which sometimes occur on the slide after the acid treatment.

When cool, the slide is replaced in its brass ring and is then ready for counting.

Microscope Technique.—The slide is transferred to the stage of a microscope and the spots examined at a magnification of 150 using a 16 mm. objective and a × 15 eyepiece. Dark-field illumination is used to increase the visibility of the fine particles. This is obtained by placing an opaque disc or "stop" below the condenser in the path of the light, and results in the particles showing up as bright specks on a dark background.

It is estimated that particles down to nearly 0·2 micron may be visible with this illumination.



- GRATICULE -
USED IN KONIMETER WORK

Fig. 67.

(*By courtesy of the Transvaal Chamber of Mines.*)

The particles are counted by means of a sector graticule placed in the eyepiece of the microscope. The spot is centred and the graticule turned to cover an average position. All the particles appearing within the intersecting lines of the graticule, which cut each other at 18°, are then counted. To obtain particles per c.c. the count in the two 18° sectors is multiplied by 10 (360° for full circle divided by 36 for two 18° sectors) and divided by 5 (number of c.c. sampled).

i.e., Particles per c.c. = (count in 18° sectors) × 2.

Efficiency of the Konimeter.—It has been found that the count obtained with the Konimeter is about two-thirds or 60 to 70 per cent of that obtained with the Thermal Precipitator; using the ignition-immersion-ignition method in each case.

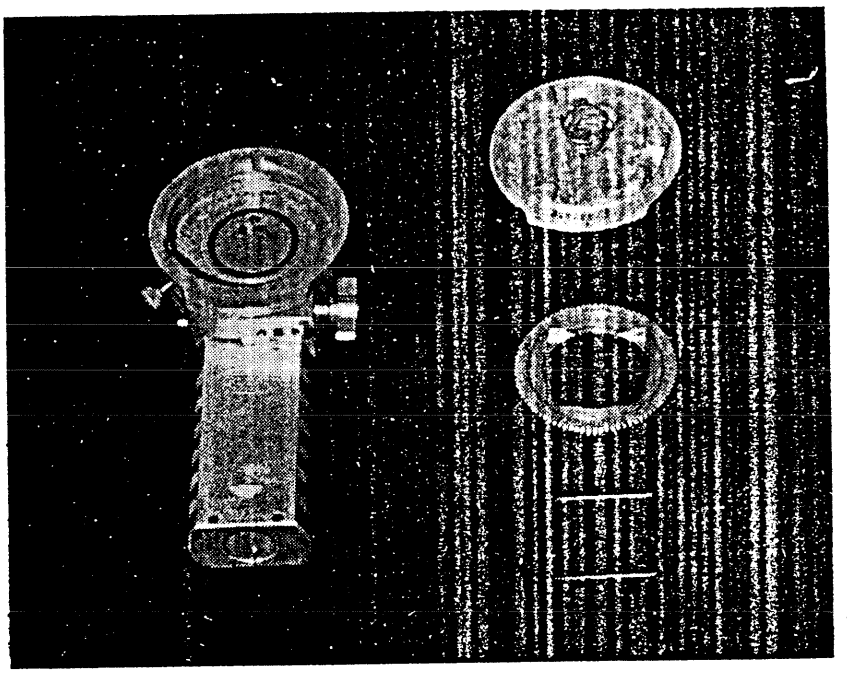


Fig. 68. Rand Konimeter.

Witwatersrand Konimeter.

This is an improved type of Konimeter, operating on the same principles as the previously mentioned types. The body is made of a light aluminium alloy, and is partially streamlined. Special features of the instrument include ease of handling and the fact that it uses a square slide 1½″ × 1½″ on which a circle of up to 58 dust spots can be taken.

A tapered jet is used, and the exhaust is around the jet. The piston is made of steel.

The square glass slide is held in position in a recess cut in a toothed brass ring, into which it fits without the need of screws. The ring is rotated by a winding handle provided with a notch to give accurate spacing.

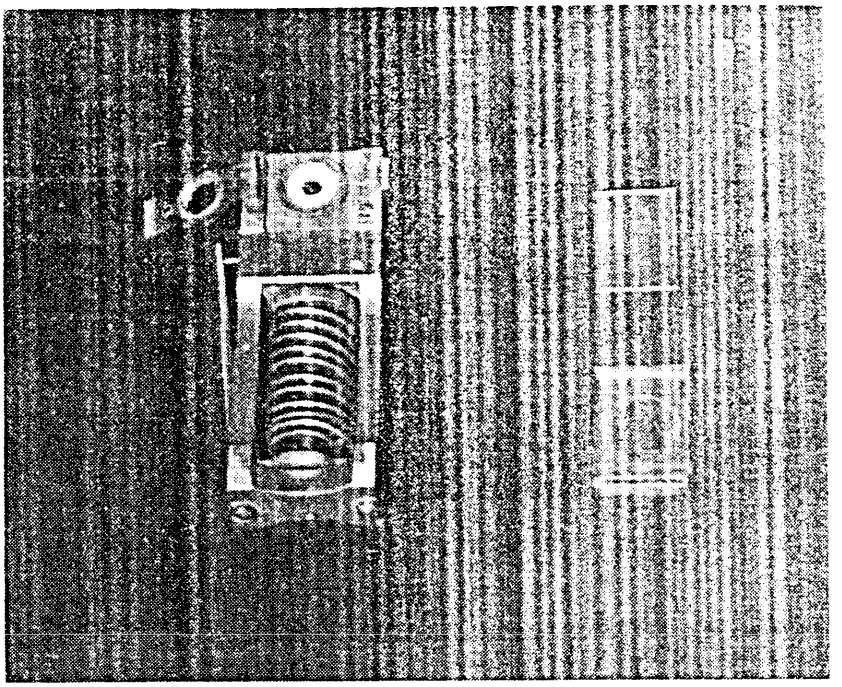


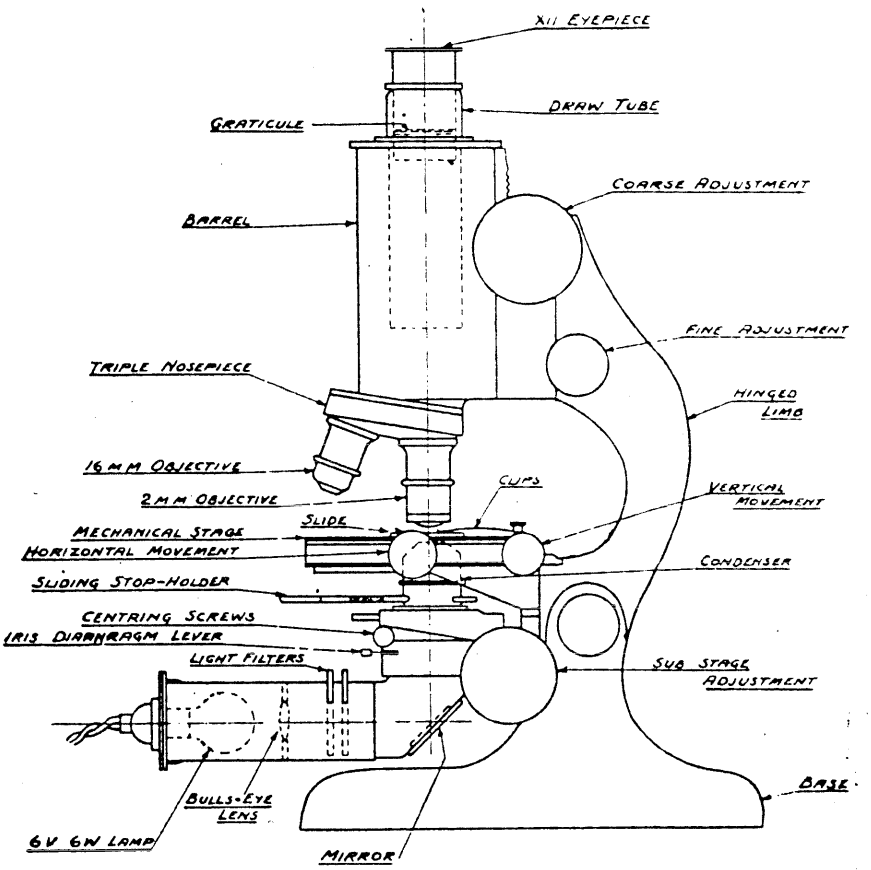
Fig. 69. Konze Konimeter

Thermal Precipitator.

The Thermal Precipitator is claimed to be one of the most accurate dust sampling instruments. With this instrument particles from 7 microns down to the finest visible with the best available microscope technique are collected on a slide. It enables the particles to be sized, as well as counted. It is, however, cumbersome to use underground and can only be handled by trained personnel. At the most, only three or four places can be sampled in a morning. The counting is time-consuming and requires skill and continual practice.

The sampling action of the instrument depends on the fact that a hot body appears to be surrounded by a dust-free space, and if air is drawn past such a body, in this case a hot wire, the dust in the air will be deflected and precipitated on cold surfaces in the vicinity.

The Thermal Precipitator head consists of two nickel plated brass blocks. These are screwed together to form a cube of approximately $1\frac{1}{2}$". Between the brass blocks, thin bakelite spacers are clamped to form a narrow vertical channel, 10 mm. wide and 0·51 mm. across, through which the sample of air is drawn. A wire 0·254 mm. thick is stretched horizontally across the width of the channel. The wire is electrically heated to a temperature of about 100°C., by passing a current of 1·5 amperes through it from a 2-volt battery, carried in a separate case with a miniature ammeter and resistance. In the sides of the Thermal Precipitator head, directly opposite the wire, cylindrical holes are provided, through which are inserted circular cover



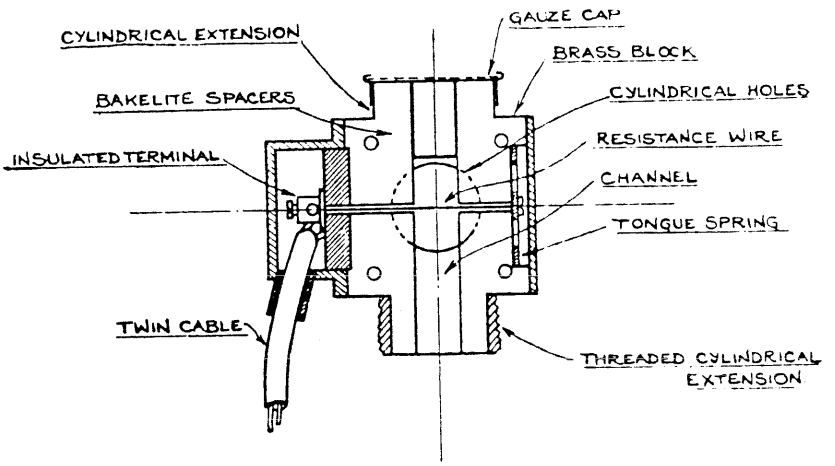
MICROSCOPE

Fig. 71.

(*By courtesy of the Transvaal Chamber of Mines.*)

glasses $\frac{3}{4}$" in diameter and about 0·16 mm. thick. These are kept in place by cylindrical plugs inserted in the holes, and are kept at a distance of 0·127 mm. from the hot wire on each side of it by the bakelite spacers.

A gauze cover made of 60-mesh brass screening was originally used to cover the inlet channel but as this reduced the efficiency it is no longer used. A hood may be used over the instrument to protect it from sludge, etc.



SECTION THROUGH
—THERMAL PRECIPITATOR HEAD —

Fig. 70.

(*By courtesy of the Transvaal Chamber of Mines.*)

The cover glasses are boiled in hydrochloric acid, washed in alcohol, wiped clean and examined under the microscope before use. No adhesive is used.

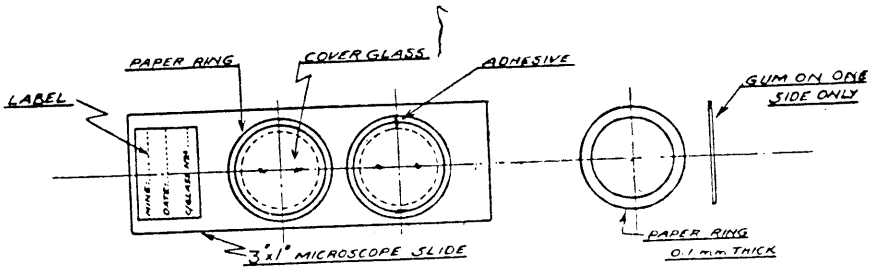
The Thermal Precipitator head is mounted on an aspirator of about 1 litre capacity filled with water or it may be connected to it by means of rubber tubing. The aspirator is supported on a tripod. Water is run out of the aspirator through a tap into a measuring cylinder at a rate not exceeding 7 ml. per minute (about 2 drops per second). Air is thus drawn through the channel in the Thermal Precipitator head past the hot wire, and the dust particles are deflected and deposited on the cover-glasses in the form of two strips, one on each glass, about 1 cm. in length opposite the wire and parallel to it.

At the end of the sampling period the aspirator tap is closed and the current switched off. The cover-glasses are removed and placed in a special container. The volume of the water run out, which is equal to the volume of air aspirated, is noted.

Samples are generally about 200 ml. (half-hour sampling) but may vary from 100 ml. or less to 600 ml. or more, depending on dust conditions.

The cover-glasses are ignited on a hot-plate at 550°C. (dull red heat) to remove carbon, cooled and then acid-treated with hot 50 per cent hydrochloric acid in a special immersion cell to remove water-borne salts. After acid treatment they are again ignited to ensure absence of water residue marks, and allowed to cool.

The two cover-glasses representing the one sample are mounted face downwards on paper rings gummed to a 3" × 1" microscope slide, the glasses being pegged down with a suitable cellulose adhesive. A special metal holder may also be used, which is provided with light clips to hold the cover-glasses down.



METHOD OF MOUNTING ON GLASS SLIDE USING PAPER RINGS.

Fig. 72.

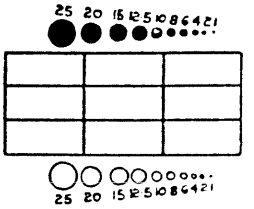
(By courtesy of the Transvaal Chamber of Mines.)

The slide is placed under the microscope and the records examined at a magnification of 1,000 with light-field illumination. A 2 mm. oil immersion objective is used with a × 11 eyepiece. Great care is needed to adjust the illumination, centre the condenser and to make all the necessary adjustments of the microscope.

The particles are counted by means of a rectangular graticule placed in the eyepiece. The slide is moved across the field so that a traverse is made across the width of the dust strip, and all the particles passing through a section of the graticule are counted. By comparison with a series of numbered dots and circles of increasing size on the graticule, the sizes of the particles are estimated. The smallest dot on the graticule corresponds to a size of 0·2 micron and sizing is made to a size smaller than this. The finest particles visible have been estimated to be about 0·13 micron in size.

Two or three traverses across the strip are generally made on each cover-glass, and the average for the two glasses added together. The number of particles per c.c. in the sample is then calculated as follows:—

The length of the dust strip for each instrument is known by previous measurement of a strip with the stage verniers of the microscope, and is usually 9·5 mm. The width of a traverse across it with the graticule is calibrated with a stage micrometer and is usually 0·0085 mm. Suppose the average of three counts across the one glass was 60 and the average of three counts across the other was 50 particles, the sum over 0·0085 mm., of the record is therefore 60 + 50 = 110 particles.



GRATICULE

Fig. 73.

(By courtesy of the Transvaal Chamber of Mines.)

Therefore the number of particles sampled over the whole record, i.e., 9·5 mm. is $110 \times \frac{9 \cdot 5}{\cdot 0085}$ particles.

Suppose volume sampled 200 c.c.

Then particles per c.c. $= \frac{110}{200} \times \frac{9 \cdot 5}{\cdot 0085} = 615$

It is customary to make a count of the record before acid treatment, i.e., immediately after the first ignition. This gives the total number of particles including water-borne salts and is carried out because these salts include some soluble silica. When this count is completed the cover-glasses are removed from the paper rings, acid-treated, ignited and counted for rock particles. Counts before acid treatment are of course much higher than after acid treatment owing to the large amount of salt particles chiefly calcium sulphate from atomisation of mine water, and may be of the order of 1,000 to 5,000 particles per c.c. during drilling.

In order to facilitate the taking of samples with the Thermal Precipitator under mining conditions, carriers have been devised in which all the component parts of the instrument are compactly assembled in one box.

Modified Thermal Precipitator.

Several modifications of the standard form of the thermal precipitator described above have been developed. In these forms the principle of thermal precipitation has been retained, but the instrument has been altered in design to make it more convenient to use or to enable it to collect samples for special purposes, such as for the electron microscope.

The Chamber of Mines Research Laboratories have designed an instrument known as the "Modified Thermal Precipitator" which is more convenient than the standard instrument for taking samples underground. The samples are taken on a 3″ × 1″ slide, only one record being taken for each sample, and twelve samples may be taken on a slide. The water aspirator is replaced by a mechanical bellows operated by a small electric motor which is run off the same battery used to supply the heating current for the wire. Samples may be counted with a 4 mm. objective or assessed in a photo-electric counter designed for the purpose at the Chamber of Mines Research Laboratories. A photo-electric assessment gives a measure based on the surface area of the particles in the samples.

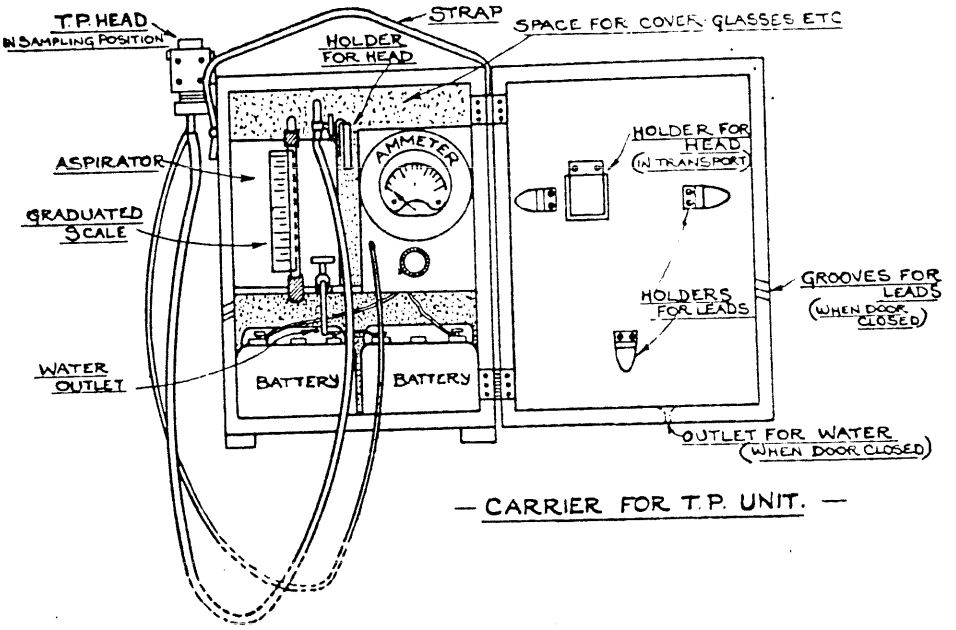


Fig. 74.

(By courtesy of the Transvaal Chamber of Mines.)

Midget Impinger.

The impinger is a dust-sampling instrument largely used in the U.S.A. It is an apparatus in which the dust is collected by bubbling the dust-laden air through a flask containing water.

In its original form, known as the Greenburg-Smith Impinger, the flask consisted of a 500 c.c. bottle containing 200 c.c. of distilled water. The air was drawn through the flask at the rate of 1 cubic foot per minute by means of an ejector or a rotary hand pump. The air entered the bottle through a glass jet below the level of the water, and the stream was broken up into bubbles by a metal plate placed just below the jet.

In its most recent form, the Midget Impinger consists of a flask or tube of about 50 c.c. capacity about 5 inches high and 1 inch in diameter, containing from 10 to 30 c.c. water. The jet fits through a rubber or ground-in glass stopper and reaches to just above the bottom of the flask. Air is drawn from the flask through another tube in the stopper, by means of a small hand pump, at the rate of $\frac{1}{10}$ cubic foot per minute, and entering through the jet, impinges on the bottom of the flask and bubbles through the water.

The dust is collected in the water, and after sampling, a portion of the water is run into a Deep Cell (see under "Deep Cell Method for Mine Water") and the particles counted under the microscope. In the U.S.A. the practice is to count the particles with light-field illumination, whereby fewer particles are visible than by the dark-field technique used on the Witwatersrand. Knowing the dust content of the water and the volume of air sampled from which it was obtained, the concentration of the dust

in the air can be calculated. In the U.S.A. the dust concentrations are generally expressed as "million particles per cubic foot", and the counting is often done by "microprojection", i.e., the field in the microscope is projected on to a screen, greatly enlarged, and the particles counted on the screen.

The dust collected in the water in the flask may also be filtered through a filter paper, ignited and weighed. In this way a gravimetric result can be obtained.

DUST IN MINE WATER.

Deep Cell Method of Counting Particles in Water.

Water is extensively used underground to prevent the formation of dust. It is important to ensure that the water itself is clean and does not contain excessive quantities of siliceous matter in suspension, which might contaminate the air when the water is atomised. The method used for estimating the amount of dust in mine water is to examine a sample of the water under the microscope in a so-called "Deep Cell", i.e., a glass cell measuring 50 mm. by 20 mm. in area, and 1 mm. deep.

The sample of water is shaken up in the sample bottle, and 95 c.c. is transferred to a 100 c.c. measuring cylinder, 5 c.c. of concentrated hydrochloric acid is added, the contents shaken up, and allowed to stand for about quarter-of-an-hour to enable acid-soluble matter to dissolve. The solution is again shaken up to mix the dust, and a quantity just sufficient to fill the cell is poured into the Deep Cell. A glass cover slide is placed over the cell, displacing any excess liquid. The cell is wiped, and set aside for half-an-hour to allow as many particles as possible to settle on the floor of the cell.

The cell is placed on the stage of the microscope and the dust particles counted. The same type of microscope is used as for Konimeter work, magnification 150 and dark-field illumination. The same eye-piece graticule is used, but the count is made in the square rulings just above the sector lines. These squares are 40 microns in size. The microscope is focused on the particles on the floor of the cell, and all the particles visible in 4 squares are counted. Then the microscope is racked up, and the particles in suspension in the same area are added as they come into focus, until the bottom of the cover slide is reached.

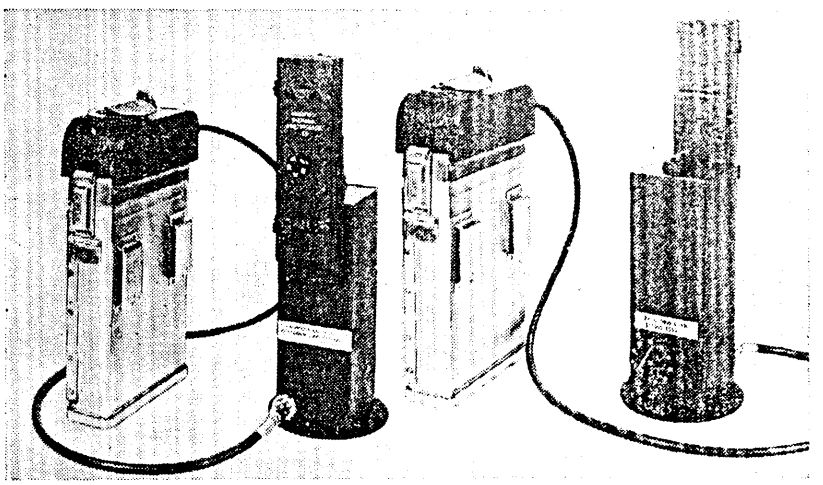


Fig. 75. Modified Thermal Precipitator. Front and rear view.

Chapter XIII.

pH AND ELECTROMETRIC TITRATIONS.

Hydrogen Ion Concentration and Determination of pH Values.

For many purposes, in both applied and pure chemistry, reliable and useful information regarding the acidity or alkalinity of a solution, can only be obtained by measuring the intensity, or strength, as well as the amount of acid or base present.

According to the electrolytic theory of ionic dissociation, acidic properties are imparted to a solution by the presence of the H^+ ion, e.g. $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$. Likewise the property of alkalinity is due to the presence of the OH^- ion; $NaOH \rightleftharpoons Na^+ + OH^-$.

The intensity factor of the solution is thus dependent upon the degree of dissociation of the acid or base present, i.e. upon the concentration of free hydrogen or hydroxyl ions present in the solution. Strong acids and bases such as hydrochloric acid and sodium hydroxide are dissociated to an extent of over 90 per cent in normal solutions, in fact the evidence is in favour of complete dissociation, the association effect being considered due to attraction between the charged ions. Weak acids and bases, on the other hand, are comparatively slightly dissociated, and consequently supply relatively few ions to their solutions. Thus it will be readily appreciated, that although two different acids or bases may have the same strength in terms of quantitative normality their chemical and physical properties may vary greatly owing to different degrees of dissociation.

Pure distilled water is dissociated to a very slight extent into H^+ and OH^- ions; $H_2O \rightleftharpoons H^+ + OH^-$.

From the equation it is evident that the acidity is equal to the alkalinity, and consequently pure water is adopted as the standard of neutrality.

The concentration of H^+ ion formed as the result of the dissociation of water has been found by electrical conductivity measurement to be very nearly one ten millionth of a gram ion per litre; i.e.

$$[H^+] = [OH^-] = \frac{1}{10{,}000{,}000} = 10^{-7}.$$

(square brackets about a symbol indicate concentration expressed in gram moles or gram ions per litre).

If we consider an aqueous solution of a compound which undergoes partial dissociation into its constituent ions, and further if we imagine the system to be in equilibrium, i.e. the reaction in one direction proceeds no faster than that in the other, we may write the equation; $AC \rightleftharpoons A^+ + C^-$ where A represents the anion, C the cation, and the arrows indicate the reversibility of the reaction.

Assuming an ideally simple system and a constant environment, the velocity with which the concentration of AC is decreasing at any instant is proportional to the concentration of [AC] at that instant, thus we

The cell is moved to another position, and the count repeated similarly in 4 squares on the floor and in suspension. This is repeated until 5 positions over the area of the cell have been examined. The sum of the counts over the 5 positions is divided by *32* and this gives the dust content in "millions of particles per c.c.". The figure thus obtained must be corrected for the addition of the acid by multiplying by $\frac{100}{95}$.

The factor 32 is derived from the dimensions of the graticule area counted, and the depth of the cell (see below).

EXAMPLE.

Counts obtained: 20, 26, 22, 18, 19. Total *105*

$$\text{Deep Cell Count} = \frac{105}{32} \times \frac{100}{95} = 3{\cdot}5 \text{ million particles per c.c.}$$

If the sample of water is very dirty, it is necessary to dilute the sample with a measured volume of distilled water before introducing it into the cell, otherwise the layer of particles settled on the floor of the cell will be too thick for satisfactory counting under the microscope. For example, 20 c.c. of sample may be taken, 5 c.c. of acid added and diluted to 100 c.c. with distilled water. The dilution is then 20 in 100 or 1 in 5 and the count obtained must be multiplied by 5 to give the final result.

Typical Counts.—A count of 2 million particles per c.c. or less is regarded as very good. Most waters are between 2 and 5 million particles per c.c. Counts over 10 million are unsatisfactory and indicate that treatment of the water is necessary.

Rand Water Board water averages 2 to 3 million particles per c.c.

Derivation of Factor 32:

$$\text{Area counted per position} = 4 \text{ squares each } 40 \text{ microns} = \frac{4 \times 40 \times 40}{10{,}000 \times 10{,}000} \text{ sq. cm.}$$

(1 cm. = 10,000 microns.)

$$\text{For 5 positions} = \frac{5 \times 4 \times 40 \times 40}{10{,}000 \times 10{,}000} \text{ sq. cm.}$$

$$\text{Depth of cell} = 1 \text{ mm. or } \frac{1}{10} \text{ cm.}$$

$$\therefore \text{ Volume counted} = \frac{5 \times 4 \times 40 \times 40}{10{,}000 \times 10{,}000 \times 10} \text{ c.c.}$$

Suppose sum of counts in 5 positions = C

$$\text{Then particles per c.c.} = \frac{C}{\left(\frac{5 \times 4 \times 40 \times 40}{10{,}000 \times 10{,}000 \times 10}\right)} = C \times \frac{1{,}000{,}000}{32}$$

To report results in "Millions", divide by 1,000,000,

$$\text{i.e., Million particles per c.c.} = C \times \frac{1{,}000{,}000}{32} \times \frac{1}{1{,}000{,}000} = \frac{C}{32}$$

have $V_1 = k_1[AC]$, where V_1 represents the velocity and k_1 is a velocity coefficient constant. The velocity of the reverse reaction is dependent upon the concentrations of $[A^+]$ and $[C^-]$ and is proportional to the product of these concentrations; i.e. $V_2 = k_2[A^+][C^-]$. But since V_1 is equal to V_2, we have $k_1[AC] = k_2[A^+][C^-]$

$$\therefore \frac{k_1}{k_2} = \frac{[A^+][C^-]}{[AC]} = Kc$$

The constant Kc is known as the dissociation constant of the compound.

If we apply this law of mass action to the dissociation of water we have

$$\frac{[H^+][OH^-]}{[HOH]} = \text{a constant.}$$

Since no serious error will be introduced by assuming [HOH] to be equal to the total quantity of water present we may write the equation; $[H^+][OH^-] = Kw$. The constant Kw is known as the ionic product and is constant over a limited range of dilute solutions.

We have already seen that—

$$[H^+] = [OH^-] = 10^{-7}$$
$$\therefore \quad [H^+][OH^-] = 10^{-14}$$
$$\text{i.e.} \quad Kw = 10^{-14}.$$

Taking the case of an N/10 acid solution and assuming complete dissociation we have—

$$[H^+] = 0{\cdot}1 = 10^{-1}$$
$$\therefore \quad [OH^-] = 10^{-13}$$

Likewise if we consider the case of an N/100 alkali solution we have—

$$[OH^-] = {\cdot}01 = 10^{-2}$$
$$\therefore \quad [H^+] = 10^{-12}$$

From the above it will be seen that it is only necessary to determine the $[H^+]$ concentration of a solution the $[OH^-]$ concentration being readily determined from the simple formula—

$$[OH^-] = 10^{(-14-x)}$$

where the concentration of $[H^+]$ is expressed as 10^x.

For many purposes, expression of the H^+ concentration as a fraction or decimal is both cumbersome and inconvenient, and it was proposed by Sorenson that a logarithmic function of H^+ related to the potential of the hydrogen electrode be used in place of the former methods. This function, known as the hydrogen ion exponent, and denoted by the symbol pH is equivalent to the negative logarithm of the H^+ concentration, i.e.—

$$pH = -\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]} \text{ or } [H^+] = 10^{-pH}.$$

Thus referring again to the above examples, an N/10 acid solution has an H^+ concentration of 10^{-1}, therefore pH = 1 and pOH = 13. In the case of the N/100 alkali, pH=12 and pOH=2, and in general pH+pOH=14.

Determination of pH by Colorimetric Methods.

It is a well known fact that certain substances, generally weak organic acids or bases act as indicators of hydrogen ion concentration. Each

indicator, either by tautomeric change, or by the formation of coloured ions, exhibits colour change within a characteristic zone of pH. The zone covered by each indicator has been determined by electrometric methods and the following table summarizes the pH range and colour change of a number of the better known indicators.

Indicator.	Colour Change.		pH Range.		A.
	Acid.	Alkaline.			
Brilliant cresyl blue ..	Red-orange	Blue	0·2	1·0	—
Meta cresol purple ..	Red	Yellow	1·2	2·8	26·2
Bromophenol blue ..	Yellow	Blue	3·0	4·6	14·9
Methyl Orange	Red	Yellow	3·1	4·4	—
Bromo-cresol green ..	Yellow	Blue	3·8	5·4	14·3
Methyl red	Red	Yellow	4·2	6·3	—
Bromo-cresol purple ..	Yellow	Purple	5·2	6·8	18·5
Bromothymol blue ..	Yellow	Blue	6·0	7·6	16·0
Phenol red	Yellow	Red	6·8	8·4	28·2
Cresol red	Yellow	Red	7·2	8·8	26·2
Thymol blue	Yellow	Blue	8·0	9·6	21·5
Phenolphthalein ..	Colourless	Red	8·3	10·0	—
Thymol phthalein ..	Colourless	Blue	9·3	10·5	—
Eosin B.N.	Purple	Yellow	10·5	14·0	—

Column A gives the number of ml. of N/100 sodium hydroxide required per 0·1 gram indicator to make an aqueous solution of the mono-sodium salt. This solution when diluted with water to 250 ml. gives a 0·04 per cent solution, five drops of which will be found suitable for 10 ml. of sample. Solutions of the mono-sodium salt should be employed when the use of alcohol is inadmissible or when the greatest possible accuracy is desired. For most ordinary purposes, however, a 0·04 per cent alcoholic solution will give sufficiently accurate results.

It will be seen by referring to the table, that given a selection of appropriate indicators, a rough estimation of the pH value of colourless solutions may be easily made. Normally, however, a more exact determination of the pH value will be required and colorimetric methods can, under suitable conditions, be used for the estimation of pH correct to the nearest 0·1 of a unit.

For this purpose it will be necessary to make up a range of solutions of known pH, covering the zone in which the indicator shows the pH of the unknown to lie.

Estimation of the pH of the sample is then simply carried out by treating equal volumes of the standard solutions and sample with equal quantities of the indicator and matching the colours.

Solutions which offer resistance to change in hydrogen ion concentration upon the addition of small quantities of acid or alkali are known as Buffer solutions, and it is solutions of this type which must be employed as standards in the colorimetric determination of pH. Buffer solutions consist generally of a mixture of an acid and its alkali salt. The following tables summarize the composition of mixtures suitable for the production of buffer solutions in steps of 0·2 units covering the pH range between 2·2 and 11·0.

McILVAINES STANDARDS.
18°C.

pH	0·2M Na_2HPO_4	0·1M Citric Acid	pH	0·2M Na_2HPO_4	0·1M Citric Acid.
	ml.	ml.		ml.	ml.
2·2	0·40	19·60	5·2	10·72	9·28
2·4	1·24	18·76	5·4	11·15	8·85
2·6	2·18	17·82	5·6	11·60	8·40
2·8	3·17	16·83	5·8	12·09	7·91
3·0	4·11	15·89	6·0	12·63	7·37
3·2	4·94	15·06	6·2	13·22	6·78
3·4	5·70	14·30	6·4	13·85	6·15
3·6	6·44	13·56	6·6	14·55	5·45
3·8	7·10	12·90	6·8	15·45	4·55
4·0	7·71	12·29	7·0	16·47	3·53
4·2	8·28	11·72	7·2	17·39	2·61
4·4	8·82	11·18	7·4	18·17	1·83
4·6	9·35	10·65	7·6	18·73	1·27
4·8	9·86	10·14	7·8	19·15	0·85
5·0	10·30	9·70	8·0	19·45	0·55

KOLTHOFF AND VLESSCHHOUWER.
18°C.

ml. A.	ml. B.	pH
0	100	9·2
35·7	64·3	9·4
55·5	44·5	9·6
66·7	33·3	9·8
75·4	24·6	10·0
82·15	17·85	10·2
86·9	13·1	10·4
91·5	8·5	10·6
94·75	5·25	10·8
97·3	2·7	11·0

Solution A: 5·30 grams Na_2CO_3 per litre.
Solution B: 19·10 grams $Na_2B_4O_7.10H_2O$ per litre.

CLARK AND LUBS'.
20°C.

M/5 H_3BO_3, M/5 KCl	M/5 NaOH	pH
ml.	ml.	
50	4·00	8·0
50	5·90	8·2
50	8·55	8·4
50	12·00	8·6
50	16·40	8·8
50	21·40	9·0

In each case dilute to 200 ml.

If the determination of pH is to be a routine procedure and if the type of solution to be operated upon is suited to colorimetric methods, i.e. is free from any pronounced inherent colour or turbidity, the assayer would be well advised to consider the acquisition of one of the several excellent colour comparators commercially available. These instruments can be supplied with sealed tubes of standard buffer solutions to cover any desired range, and are so designed and operated that any slight degree of colour or turbidity in the sample is compensated for.

ELECTROMETRIC METHODS.

If a metal is placed in a solution containing its ions, a difference of potential will exist between the metal and the solution and this difference of potential will vary with the concentration of the metal ions.

The electrode potential E can be expressed as—

$$E = \frac{RT}{nF} \log_e \frac{p}{Z}$$

R = gas constant expressed in electrical units.
T = absolute temperature.
n = valency of the ion.
F = one Faraday (Electrical charge carried by one gram equivalent).
p = the osmotic pressure.
Z = the electrolytic solution pressure (The tendency of the metal to dissolve ionically).

The single electrode potential (E) cannot be measured directly, but if connected by means of a suitable liquid junction to another electrode of known potential (E_1), the two electrodes form a complete cell from which current can be drawn. The voltage of the complete cell (E_2) will then be the algebraic sum of the known and unknown electrode potentials.

$$\text{We then have } E = E_2 - E_1 = \frac{RT}{nF} \log_e \frac{p_2}{Z} - \frac{RT}{nF} \log_e \frac{p_1}{Z}$$

$$= \frac{RT}{nF} \log_e \frac{p_2}{p_1}$$

and since the osmotic pressure is proportional to the concentration:

$$E = \frac{RT}{nF} \log_e \frac{C_2}{C_1}$$

Assuming a temperature of 18° C. and changing to common logarithms the expression reduces to—

$$E = \frac{\cdot 058}{n} \log \frac{C_2}{C_1}$$

If platinum metal coated with platinum black be immersed in a solution saturated with hydrogen gas, the platinum black will absorb hydrogen, and the unit will behave as if it consisted of pure hydrogen only. If now this hydrogen electrode is placed in a solution, molar with respect to hydrogen ions, i.e. of unit concentration, and the half cell so formed be connected by means of a liquid junction to another similar half cell containing a solution of unknown hydrion concentration, the electromotive force developed between the two electrodes will be given by:

$$E = \cdot 058 \log \frac{1}{[H^+]} \text{ and since } \log \frac{1}{[H^+]} = pH.$$

$$E = \cdot 058\ pH.$$

The value of E is of course determined by suitable potentiometric equipment, the standard reference half cell, known as the molar hydrogen electrode, being considered as having zero potential.

Hydrogen electrodes are not, however, used to any great extent in the practical application of electrolytic methods for the determination of pH. The reasons for this are:— (1) the hydrogen electrode is easily "poisoned" by impurities in the solution, and (2) the technique of operation is difficult and requires a fair amount of experience on the part of the operator. As reference electrode, the molar hydrogen electrode is usually replaced by a calomel half cell, the potential of which, relative to the standard hydrogen electrode, is known. The other hydrogen electrode is usually replaced by one of the following:—

(*a*) Metal—metal oxide systems, e.g. the antimony electrode.

(*b*) The quinhydrone electrode.

(*c*) The glass electrode.

A detailed discussion of the above electrode systems is rather beyond the scope of the present work. It may however, be said that the glass electrode is superior to the other two and gives results which are comparable with those produced by the hydrogen electrode under ideal conditions.

Commercial electrometers fitted with sealed glass electrodes are available and these instruments are ideally suited to the determination of pH where rapid and accurate results are required.

Advantages of the electrometric determination of pH by means of the glass electrode are:

(1) May be easily carried out by comparatively inexperienced operators.

(2) Accuracy unaffected by colour or turbidity of solution.

(3) Completely immune to all known poisons.

High concentrations of alkali salts in the solution may introduce errors when using the glass electrode. These errors, however, may be easily compensated for by standardizing the instrument on a buffer solution having similar cation characteristics.

When titrating coloured solutions, or solutions such as highly acid mine waters which throw down precipitates on addition of the alkali, the electrometer may be substituted for the indicator, titration to any desired pH can then be carried out.

Electrometric Titrations.

The employment of electrometric means for determining the end point in volumetric estimations offer the advantages of a greater degree of accuracy than the use of chemical indicators in several instances, and in replacing many of the more tedious gravimetric methods of analysis.

In the present chapter only a very brief outline of the subject will be undertaken. Fuller information must be sought in textbooks on Physical Chemistry and works dealing specifically with this branch of chemical analysis.

Electrometric methods are divided into two distinct classes:

(*a*) Potentiometric, i.e. the measurement of electromotive force (voltage).

(*b*) Conductometric, i.e. measurement of conductivity, or its reciprocal, i.e. resistance.

Oxidation-Reduction Reactions.

Referring to the section on the determination of pH values, it will be seen that the concentration of the H^+ ion is directly related to the voltage developed by the hydrogen half-cell, and in a similar manner, if the hydrogen electrode or its equivalent be replaced by a noble metal, e.g. gold or platinum, and this electrode immersed in a solution containing a substance in different states of oxidation, a voltage will be developed according to the equation:

$$E = P - \frac{0{\cdot}058}{N} \log 10 \frac{C_1}{C_2}$$

E Electromotive force developed in volts.

P A constant which is equal to E when $C_1 = C_2$.

N The change in valency.

C_1 The concentration of the substance in the lower state of oxidation.

C_2 The concentration of the substance in the higher state of oxidation.

It should be noted that the equation is not dependent upon the absolute concentrations but only upon the ratio of these concentrations. The equation also shows that the value of E decreases very rapidly as a substance approaches complete oxidation, and the end point is thus obtained by noting the point at which an abrupt change occurs in the electromotive force developed by the cell.

As a few examples of the many oxidation-reduction estimations which may be carried out by potentiometric means the following may be mentioned:—

Iron by dichromate or permanganate.

Zinc by ferrocyanide.

Chromium by ferrous sulphate etc.

The commercial electrometers available for the determination of pH values are usually supplied with a noble metal electrode for this type of work.

The Measurement of Solution Conductivity.

For this purpose a conductivity cell and some form of Wheatstone bridge will be required. The conductivity cell consists essentially of a glass vessel, usually cylindrical in shape with openings at sides and bottom, and containing two platinum electrodes coated with platinum black. The electrodes are fixed in the vessel in such a manner as will ensure that their relative positions will remain undisturbed.

For solution conductivity measurement it is essential that the bridge current output be alternating, since direct current would effect chemical decomposition of the electrolyte.

Various forms of the Wheatstone bridge are obtainable commercially, some of the more modern types incorporate electronic circuits with visual indication of bridge balance.

Conductometric Reactions.

Conductometric titrations of acids and alkalis in coloured solutions may prove useful if potentiometric equipment is not available. Consider the titration of hydrochloric acid by sodium hydroxide;

$$[Na^{+}(OH^{-})] + [H^{+}Cl^{-}] \rightarrow [Na^{+}Cl^{-}] + [H^{-}(OH^{-})]$$

As the alkali is added the rapidly moving H^{+} ion is replaced by the less mobile sodium ion, the conductivity of the solution will, therefore, gradually decrease until the neutral point is reached; thereafter, the addition of sodium hydroxide will cause the conductivity of the solution to increase owing to the presence of the highly mobile hydroxyl ion.

In order to obtain a sharp end-point the alkali should be at least 50 times more concentrated than the acid, since if a dilute solution of alkali is used the titrated solution will be so diluted as to cause conductivity changes apart from the effect of the chemical reaction.

Reactions which result in the formation of precipitates also cause a sharp change in the conductivity of the solution in which the reaction is taking place. The following examples illustrate useful practical applications of conductometric titrations to this type of reaction;
Estimation of Barium by lithium sulphate:

$$[Ba^{++}(Cl^{-})_2] + [(Li^{+})_2SO_4^{--}] \rightarrow [Ba^{--}SO_4^{--}]\downarrow + 2[Li^{+}Cl^{-}]$$

The lithium ion has one of the lowest and the sulphate ion one of the highest mobilities, consequently the replacement of barium ions by lithium ions, and at the end-point, the addition of sulphate ions results in a sharp change in conductivity. An accurate determination is thus made possible.

Estimation of magnesium sulphate by barium hydroxide:

$$[Mg^{++}SO_4^{--}] + [Ba^{++}(OH^{-})_2] \rightarrow [Mg^{++}(OH^{-})_2]\downarrow + [Ba^{++}SO_4^{--}]\downarrow$$

In this case double precipitation takes place and the end point is marked by a sharp rise in conductivity due to the presence of highly mobile hydroxyl ions. Magnesium sulphate may be determined in the presence of calcium by this method.

Chapter XIV.

THE ANALYSIS AND TREATMENT OF WATERS.

Introduction.

With increasing industrial development, this subject is assuming ever greater importance. It is becoming more and more necessary for adequate data to be available regarding the quality of the supply and the nature of the harmful constituents of the waste liquors.

Water for boilers, cooling dams and drinking purposes usually requires specific routine analyses, but it is advisable to have a full chemical knowledge of the nature of the water from the main source of supply. To obtain this information a full analysis should be carried out at various seasons of the year.

In modern practice the system of reporting results of analysis in parts per million (p.p.m.) is generally used. It offers a ready means of interpretation by both analyst and engineer of connective data from the analysis.

1 milligram per litre = 1 part per million.
1 p.p.m. = 10 lb. per million gallons.

Sampling.

This is preferably done by using clean glass-stoppered bottles. Care should be taken that the sample is as representative as possible and also large enough to duplicate any particular determination. Winchester quart bottles are ideally suited to this purpose.

THE ANALYSIS OF WATER.

For general technical purposes, the methods given under "Routine Analysis for Technological Purposes" given later in this chapter should be followed. A full detailed analysis is rarely called for but if this is required the following methods are generally employed.

Suspended Matter.

If the water is not quite clear, filter a measured quantity containing about 0·1 gram of suspended matter through a prepared Gooch crucible. Rinse container and crucible with distilled water, dry at 105°C., and weigh.

$$\frac{\text{Weight of suspended matter (grams)} \times 1{,}000{,}000}{\text{ml. of sample}} = \text{p.p.m. total suspended matter.}$$

If the quantity of mineral matter in suspension is required, ignite the crucible at a full red heat for 30 minutes. Cool. Recarbonate by adding a few drops of ammonium carbonate solution. Heat at a temperature of about 300°C. in order to expel ammonium salts. Cool and weigh.

$$\frac{\text{Weight of mineral matter (grams)} \times 1{,}000{,}000}{\text{ml. of sample}} = \text{p.p.m. mineral matter.}$$

The difference between total suspended matter and mineral matter is taken to represent the organic matter.

DISSOLVED SOLIDS.

Take 100—1,000 ml. of the filtered water and evaporate to dryness in a platinum dish on a water bath. Transfer the dish to an oven and dry for two hours at 105°C. Cool in a desiccator, and weigh as rapidly as possible. Return the dish to the oven and weigh again after one hour. Repeat until weight is constant to within 1 milligram.

$$\frac{\text{Weight of solids (grams)} \times 1{,}000{,}000}{\text{ml. of sample}} = \text{p.p.m. dissolved solids.}$$

It must be remembered that $CaSO_4.2H_2O$ when dried at 105°C. is converted to $(CaSO_4)_2.H_2O$. A temperature of over 200°C. is required to expel the remaining water. Also the compound $MgSO_4.7H_2O$ loses 6 molecules of H_2O at 120°C.—130°C. A temperature of between 200° and 230°C. is required to expel the remaining molecule.

It will, therefore, be evident that the analyst must at all times state on the certificate the temperature at which the estimation was carried out.

To obtain the volatile and organic matter, heat the sample, dried at 105°C., gradually to redness. Note any changes taking place, such as smell, darkening or blackening, which indicates the presence of organic matter. Maintain at a red heat for about 30 minutes, cool in a desiccator and weigh. Report loss in weight as volatile and organic matter.

$$\frac{\text{Loss in weight} \times 1{,}000{,}000}{\text{ml. of sample}} = \text{p.p.m. volatile and organic.}$$

ANALYSIS OF DISSOLVED SOLIDS.

Silica.

250 ml. of the filtered sample is acidified with hydrochloric acid and evaporated to dryness on a water bath in a platinum or porcelain dish, baked on a hotplate at about 125°C. for 20 minutes to fix any silica, and digested with hot water and hydrochloric acid. The silica is filtered off, ignited at a red heat, cooled in a desiccator and weighed.

$$\frac{\text{Weight of silica (grams)} \times 1{,}000{,}000}{250} = \text{p.p.m. silica } (SiO_2).$$

Iron Oxide and Alumina.

To the filtrate from the silica determination add a few drops of concentrated nitric acid and boil in order to oxidize any iron present. Add three grams of ammonium chloride and when this is dissolved make alkaline with ammonia. Boil off nearly the whole of any excess ammonia and filter. Wash thoroughly, dry the precipitate, ignite, cool in a desiccator and weigh. The ignited precipitate consists of ferric oxide and alumina.

$$\frac{\text{Weight of residue (grams)} \times 1{,}000{,}000}{250} = \text{p.p.m. ferric oxide and alumina.}$$

If the respective amounts of these are required, grind the ignited precipitate carefully in an agate mortar and digest with aqua regia till dissolved. Dilute and re-precipitate with ammonia. Filter and wash the

Magnesium.

Take the filtrate from the calcium determination to dryness and ignite gently till all ammonium salts are destroyed. Take up the residue with hydrochloric acid, filter if necessary, and make faintly alkaline with ammonia. Add sufficient ammonium phosphate, stir vigorously for some time, and allow to stand in a cool place overnight. Filter and thoroughly wash the precipitate with 1 : 10 ammonia. Dry and ignite, first at a red heat, and finally at a high temperature till the precipitate shows perfectly white. It is weighed as $Mg_2P_2O_7$.

$$\text{Weight of } Mg_2P_2O_7 \text{ (grams)} \times \frac{1{,}000{,}000}{250} \times \frac{48{\cdot}64}{222{\cdot}60} = \text{p.p.m. magnesium (Mg.).}$$

Sodium and Potassium.

Concentrate the filtrate from the magnesium determination to about 100 ml., transfer to a weighed porcelain or platinum dish, and evaporate to dryness with a small quantity of sulphuric acid. Ignite to expel ammonium salts, cool in a desiccator and weigh as the sulphates of sodium and potassium. This method gives high results since some metaphosphoric acid tends to remain unvolatilized.

Preferably a fresh quantity of 250 ml. of the sample should be taken and the alkalis determined as follows:—

Concentrate by evaporation to about 50 ml. Add barium chloride to precipitate the sulphates and filter. Add a little milk of lime, and boil, precipitating iron and magnesium, filter. Precipitate calcium and barium in filtrate with excess ammonia and ammonium carbonate and a little ammonium oxalate. Filter, take filtrate to dryness and ignite residue to drive off all ammonium salts. Take up residue with water, test with one drop of ammonium oxalate solution and filter if necessary. Acidify with hydrochloric acid, take to dryness, ignite and weigh alkalis as chlorides.

Separation of Sodium and Potassium.—Dissolve the mixed chlorides in a small quantity of distilled water acidified with a few drops of hydrochloric acid. Add a sufficient quantity of a solution of platinic chloride to combine with all the sodium and potassium present. Take to dryness on a water bath and extract the sodium salt by digesting with alcohol. Filter through a weighed Gooch crucible, wash with alcohol and dry. Heat at 140°C. till weight is constant. It is essential to carry out blank determinations for alkalis in the reagents, using as far as possible the same quantities as in the analysis of the sample.

Calculation (Sodium and Potassium).

Since Na = 22·997, Cl = 35·457 and NaCl = 58·454

$$\text{Weight of NaCl} + \text{KCL in grams} \times \frac{1{,}000{,}000}{250} \times \frac{22{\cdot}997}{58{\cdot}454} = \text{p.p.m. sodium and potassium expressed in terms of Na.}$$

Potassium.

Weight of $K_2PtCl_6 \times 0{\cdot}3067$ = weight of KCl.

Weight of combined NaCl and KCl minus weight of KCl = Weight of NaCl.

Since K = 39·096, Cl = 35·457 and KCl = 74·553

$$\text{Weight of KCl (grams)} \times \frac{1{,}000{,}000}{250} \times \frac{39{\cdot}096}{74{\cdot}553} = \text{p.p.m. potassium (K).}$$

$$\text{Weight of NaCl (grams)} \times \frac{1{,}000{,}000}{250} \times \frac{22{\cdot}997}{58{\cdot}454} = \text{p.p.m. sodium (Na)}$$

Sulphates.

Take 250 or 500 ml. (according to quality of the filtered water), acidify with hydrochloric acid, and evaporate to about 70 ml. While boiling add 10 per cent barium chloride drop by drop until in slight excess. Boil for ten minutes, remove and allow to cool before filtering. Wash free from chlorides, testing with silver nitrate. Dry, ignite and weigh.

Calculations: (Sulphates). If 250 ml. were taken:—

$$\text{Weight of } BaSO_4 \times \frac{1{,}000{,}000}{250} \times \frac{96{\cdot}06\ (SO_4)}{233{\cdot}42\ (BaSO_4)} = \text{p.p.m. sulphate } (SO_4)$$

Weight of $BaSO_4$ × 1,646·1 = p.p.m. sulphate (SO_4).

Chlorides (Cl).

To 25 ml. in a porcelain dish add 2 drops of phenolphthalein indicator and neutralize with approximately N/50 sulphuric acid; add a few drops of potassium chromate indicator and titrate with N/50 silver nitrate, stirring well all the time until the precipitated silver chromate is no longer decomposed by the chloride and the solution becomes, therefore, tinged with reddish-brown. The chloride content is calculated as below. A correction of 0·2 ml. of N/50 silver nitrate is made for the excess required to produce a noticeable amount of red precipitate.

Chlorides as NaCl in p.p.m. =

$$\frac{1{,}000 \times \text{No. of ml. N/50 silver nitrate} - 0{\cdot}2\text{ ml.}}{\text{volume of sample in ml.}} \times 1{\cdot}1691$$

Equations of reactions:—

$$NaCl + AgNO_3 = NaNO_3 + AgCl.$$
$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3.$$

ROUTINE ANALYSIS FOR TECHNOLOGICAL PURPOSES.

Acidity.

The acidity of water is due to the presence in solution of carbon dioxide, mineral or organic acids or hydrolized salts.

Free carbon dioxide in waters may be determined by titration with standard sodium carbonate using phenolphthalein as indicator. It is important that this determination be made immediately upon opening the sample bottle.

100 ml. are titrated with N/10 sodium carbonate in a small stoppered bottle of about 150 ml. capacity with about 5 drops of phenolphthalein indicator, stoppering and gently agitating between each addition of sodium carbonate until the end point is obtained.

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

1 ml. N/10 sodium carbonate = 22 p.p.m. carbon dioxide.

Free Mineral Acid.—Free mineral acid is determined by titrating with standard sodium hydroxide using methyl orange as indicator.

1 ml. N/10 sodium hydroxide = 0·0049 gram H_2SO_4.

Total Acidity.—Total acidity, which includes that imparted by certain hydrolized salts, is determined by titration with standard sodium hydroxide using bromothymol-blue, (which is almost fully changed at pH 7·0), as indicator. Owing to the precipitation of coloured hydroxides it is preferable to use the indicator externally.

More accurate results are obtained by electrometric titration. For a description of this method see Chapter XIII.

ALKALINITY.

This condition is normally imparted to water by the presence of one or more of the following:—

(*a*) Hydroxides (OH)
(*b*) Normal carbonates (CO_3)
(*c*) Bicarbonates (HCO_3)

In view of this, there are five alkalinity conditions possible in a sample of water:—

(1) Hydroxides alone.
(2) Hydroxides and normal carbonates.
(3) Normal carbonates alone.
(4) Normal carbonates and bicarbonates.
(5) Bicarbonates alone.

Hydroxides and bicarbonates cannot exist together in the same solution. These five conditions may be distinguished, and the quantities determined from the results obtained by titration with standard acids.

A titration is made with a standard acid using two indicators successively. The indicators used are phenolphthalein and methyl orange. Phenolphthalein gives a pink colour only in the presence of hydroxide or normal carbonate. The change from pink to colourless occurs at a pH value of 8·3 or under. Methyl orange is yellow in the presence of hydroxide, normal carbonate, and bicarbonate, and red in the presence of acid. The colour change occurs at a pH of approximately 4·4. The phenolphthalein is added to the water sample first, and titrated to the end point with standard acid. The reading is taken, then methyl orange is added and the titration continued to the second end point. From these two readings the data of alkalinity of the water can be calculated thus:—

Let P = the ml. of standard acid used for the titration with phenolphthalein.

Let T = the ml. of acid used for the total titration (phenolphthalein and methyl orange).

This "T" figure is known as the "total alkalinity" or the "methyl orange alkalinity".

If the results of the titration of a 100 ml. sample with N/50 sulphuric acid are substituted for P and T, and these results multiplied by 10 as below, the values obtained will be in parts per million of the specific alkalinity in terms of $CaCO_3$.

(Alkalinities are usually expressed in terms of $CaCO_3$.) The factor 10 is used because 1 ml. of N/50 sulphuric acid is equal to 1 mg. of $CaCO_3$.

(1) $P = T$
Hydroxide $= P \times 10$ p.p.m.

(2) $P > \frac{1}{2}T$
Hydroxide $= (2P - T) \times 10$ p.p.m.
Normal carbonate $= 2(T - P) \times 10$ p.p.m.

(3) $P = \frac{1}{2}T$
Normal carbonate $= T \times 10$ p.p.m.

(4) $P < \frac{1}{2}T$
Normal carbonate $= 2P \times 10$ p.p.m.
Bicarbonate $= (T - 2P) \times 10$ p.p.m.

(5) $P = 0$ (Nil)
Bicarbonate $= T \times 10$ p.p.m.

Water Hardness.

Water acquires its hardness from contact with mineral-bearing materials in the earth's surface. Rainfall, after reaching the earth, takes up carbon dioxide and organic acids from the soil and loses some or all of its dissolved oxygen. Limestone is dissolved by water containing carbon dioxide, resulting in the formation of calcium bicarbonate, a soluble compound.

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

The sulphates and chlorides of calcium and magnesium are comparatively soluble; and the sulphates, in particular, are found in appreciable quantities in many water supplies. It is therefore seen that the hardness of water is caused principally by calcium and magnesium as bicarbonates, sulphates and sometimes as chlorides and nitrates. These salts are deposited as scale in boilers and water heating systems. Hardness again is classified into "temporary hardness" and "permanent hardness". "Temporary hardness" is caused by the bicarbonates of calcium and magnesium, and can be removed by boiling the water or by treating it with lime. "Permanent hardness" is mainly due to calcium sulphate, which is precipitated at temperatures above 300°F. Compounds causing permanent hardness are often termed "incrustants".

Hardness-producing substances react with soaps, forming insoluble compounds before a lather is produced. They are thus a measure of the soap-consuming power of a water. Several methods for the determination of hardness are in use.

Clarke's standard soap method is not very accurate in the presence of a large quantity of magnesium salts, but is a useful test for the routine work of water-softening.

For more accurate determinations the palmitate method (Blacher's) should be used or alternatively the hardness may be calculated from the results of a detailed analysis of the water, the calcium and magnesium salts being determined by gravimetric methods.

Hardness is always expressed in terms of calcium carbonate ($CaCO_3$).

Clarke's Method for the Determination of Hardness.

This method consists of agitating 50 ml. of the water with a standard soap solution in a 250 ml. rubber-stoppered bottle till a lather is obtained which will stand unbroken for 5 minutes when the bottle is laid on its side.

Solutions Required.

Standard Solution of Calcium Chloride:—This is prepared by dissolving 0·2 gram of pure calcium carbonate in dilute hydrochloric acid and evaporating several times with water on a water bath, dissolving the residue in distilled water and making up to a litre. This solution contains calcium chloride equivalent to 200 parts calcium carbonate per million.

Alternatively dissolve 0·4886 gram of pure barium chloride ($BaCl_2.2H_2O$) in a litre of distilled water. This solution also contains the equivalent of 200 parts calcium carbonate per million.

Standard Soap Solution.—Weigh out about 17 grams of B.P. standard soft soap (Sapo Mollis) and dissolve in a litre of a mixture of 60 per cent rectified spirits of wine and 40 per cent distilled water. Neutralize to bromothymol blue with N/10 sodium hydroxide and allow the solution to stand for 24 hours and filter.

Standardize by titrating 50 ml. of the standard calcium or barium chloride solution and dilute with the mixture of spirits and water till a permanent lather is produced by 10·5 ml. The lather factor for this solution is 0·5 ml. and must be deducted from all titrations. The soap solution should be added in quantities not exceeding 0·5 ml., the sample being vigorously shaken after each addition until the end point is reached. Since 50 ml. of the standard calcium chloride solution requires 10 ml. of soap solution,

1 ml. of soap solution = 20 p.p.m. calcium carbonate.

Total Hardness.

Measure out 50 ml. of the water into a stoppered bottle of about 250 ml. capacity. Shake well and draw out the air in the upper portion of the bottle with a pipette in order to remove any carbon dioxide which may have been given off. Proceed with the titration as for the standardization of the soap solution.

If magnesium salts are present in large quantities a false end point is often obtained, a good lather forming and suddenly disappearing. The end point, too, is often difficult to ascertain, and it is then better to dilute the sample so that a smaller quantity of soap solution gives a good lather. If more than 10 ml. of the soap solution are required, it is advisable to take a smaller measured quantity and dilute to 50 ml. with freshly boiled, cold distilled water.

ml. soap solution × 20 = p.p.m. calcium carbonate.

Permanent Hardness.

1. Take about 250 ml. of the water in a flask and weigh flask and water.
2. Boil for half an hour, adding distilled water from time to time.
3. Cool and make up to original weight with freshly boiled cold distilled water.
4. Filter and titrate 50 ml. with standard soap solution as before.

ml. soap solution × 20 = p.p.m. calcium carbonate.

Temporary Hardness.—The difference between the total and the permanent hardness gives the temporary hardness of the water.

The above method for determining permanent and temporary hardness is not favoured by some authorities and in practice these figures are usually obtained from the total hardness and the total alkalinity figure (i.e. the "T" figure obtained in the alkalinity titration) in the following manner.

Permanent Hardness.—When the total hardness is greater than the alkalinity, the difference is a direct measure of the permanent hardness. When the alkalinity is greater than the total hardness no permanent hardness is present.

Temporary Hardness.—When the alkalinity is either equal to or less than the total hardness then the alkalinity figure is all temporary hardness. When the alkalinity is greater than the total hardness then the total hardness is all temporary hardness and the difference between the total hardness and the alkalinity is due to sodium carbonate and sodium bicarbonate. This difference is termed the "soda alkalinity".

Blacher's Method for Total Hardness.

Take 100 ml. of the water sample and add a few drops methyl orange indicator, then neutralize with N/10 nitric acid, and add four drops in excess. Boil off any carbon dioxide, cool, add phenolphthalein indicator and then N/10 sodium hydroxide until a pink colour just appears. Discharge this colour with a drop of acid and titrate the solution with a standard solution of potassium palmitate until a faint pink colour reappears.

The equation of the reaction is:—

$$2K(CO_2C_{15}H_{31}) + CaX_2 = Ca(CO_2C_{15}H_{31}) + 2KX_2$$
$$\text{and/or} \qquad \text{and/or}$$
$$(Mg) \qquad (Mg)$$

X_2 representing either SO_4, Cl_2 or $(NO_3)_2$.

Standardize the potassium palmitate solution against a standard solution of calcium so that 1 ml. = 0·005 gram calcium carbonate.

By taking 100 ml. water sample, every ml. potassium palmitate solution used in the titration is therefore equivalent to 50 p.p.m. calcium carbonate. (Total Hardness.)

Potassium palmitate solution is made up by dissolving 25·63 grams of pure palmitic acid in a mixture of 250 grams glycerol and 400 ml. of 90 per cent alcohol, and then titrating to neutrality (phenolphthalein) with a 3·5 per cent alcoholic potash (KOH) solution. Make up to one litre with 90 per cent alcohol.

Hehner's Method.

Estimation of Hardness by Standard Acid.—The following solutions are required:—

(*a*) Decinormal sulphuric acid.

(*b*) Decinormal sodium carbonate.

(*c*) Methyl orange indicator.

Temporary Hardness. (Bicarbonate of lime and magnesia.)—100 ml. of the water is titrated with N/10 acid, using methyl orange as indicator. 1 ml. N/10 acid = 0·0050 gram calcium carbonate (magnesium carbonate

and calcium bicarbonate being reported as calcium carbonate). The number of ml. acid required multiplied by 50 gives parts calcium carbonate per million.

Permanent Hardness.—To 100 ml. of the water add 20 ml. N/10 sodium carbonate; place in a platinum dish and take to dryness on a water bath. Extract the residue with hot distilled water, filter and wash thoroughly with hot distilled water. Cool and titrate with N/10 acid using methyl orange indicator. The difference between the number of ml. N/10 acid used and the number of ml. N/10 sodium carbonate added, in this case 20, gives the number of ml. N/10 sodium carbonate which has reacted. This difference multiplied by 50 gives the permanent hardness.

If magnesium salts are present use 10 ml. N/10 sodium hydroxide and 10 ml. N/10 sodium carbonate in place of the 20 ml. sodium carbonate.

Total Hardness.—The total hardness is obtained by adding together the temporary and permanent hardness.

Hehner's method is a good practical method for control work on a softening plant, both for unsoftened and softened waters, as it gives results for soda consumption on a small scale, corresponding exactly with what should take place in a softening plant, and also shows if any undue quantity of soda is being used.

The determination of hardness may be complicated by the presence of the carbonates or bicarbonates of the alkalis. Consider the case of a dolomitic water containing the bicarbonates of calcium, magnesium, and the alkalis. Hehner's method for temporary hardness and Clarke's method for total hardness would give fictitious results; since the bicarbonates of the alkalis, although reacting with the reagents used, are not scale-forming salts. Hehner's method for permanent hardness would give a negative result, since, on boiling the water, the calcium and magnesium bicarbonates would revert to the normal carbonates, and be precipitated. The alkali carbonates on the other hand would be redissolved, and be estimated together with the alkalis added as reagents.

Clarke's soap solution method for permanent hardness would, in a water of this type, give a zero hardness. It is therefore evident that the scale-forming salts, i.e. salts of calcium and magnesium, would have to be determined by the analytical methods previously described.

To estimate the alkalis present, boil down a measured quantity to about half its volume. Filter if necessary, wash, and make up to the original volume with distilled water. Titrate with N/10 sulphuric acid using methyl orange as indicator.

1 ml. N/10 sulphuric acid = 0·0053 gram sodium carbonate.

Acidity of Mine Waters and the Problem of the Corrosion of Metals.

Although this is still to some extent a controversial subject, there can be no doubt nowadays that the only measure of acidity is hydrion-concentration (or proportion of hydrogen-ions present). There is only one source of the acidity, viz., oxidation of pyrites, e.g.:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

and the difficulties of the analysis arise from the fact that some of the bases from the rock which have in course of time partly neutralized the sulphuric acid are "weak bases"; the salts of "weak bases" are not neutral,

but acid. Magnesia, lime, ferrous oxide and manganous oxide are strong bases, but alumina and ferric oxide are weak bases.

Now, for the purpose of preventing corrosion of iron and other metals underground, it is not necessary to render the water markedly alkaline (e.g., alkaline to phenolphthalein). This would require a hydrion concentration of pH 9, whereas pH 7 is sufficient, and in practice it is found that, before this stage is reached, precipitation of ferric hydrate and alumina takes place, and it is quite unnecessary (and leads to considerable waste of neutralizing lime) to remove the other bases. All that is required is to destroy the "free acid" and the larger proportion of the aluminium and ferric sulphates without attacking ferrous and magnesium sulphates. Technically speaking, this is the same as saying that the pH of the water must be reduced from (say) three to seven.

The analytical method, therefore, consists in titrating the mine water with standard sodium hydroxide and an appropriate indicator, used externally. The indicator must be such as to be almost fully changed at pH 7. Thus methyl orange, which changes at about pH 4·4 gives totally incorrect (low) results; similarly phenolphthalein, which changes at pH 8·3, gives results which are too high. "Bromothymol-blue" is the correct indicator for this work. It is used in drops on a spot plate, and about $\frac{1}{2}$ ml. of the titrated liquid is added, continuing the addition of alkali until the mixture on the spot plate, which is yellow at first, is green (i.e., blue discoloured by ferric hydroxide). If greater accuracy is required, the test should be repeated, adding 90 per cent of the alkali (found as above) at once, and filtering before going on to the end point.

1 ml. N/10 sodium hydroxide used for 100 ml. mine water

= 0·28 lb. calcium oxide per 1,000 gallons.

= 0·35 lb. of lime containing 80 per cent CaO per 1,000 gallons.

It is worth noting that neutralized ferric sulphate is capable of corroding iron ($Fe_2(SO_4)_3 + Fe = 3Fe(SO_4)$). If this were not so, it would be sufficient to neutralize the free acid down to pH 5 only, when it would be too weak to attack metals. It is the presence of ferric sulphate which renders it necessary to neutralize down to the true neutral point, which is pH 7. Although neutralized aluminium sulphate is not corrosive, it is scarcely possible to titrate so as to distinguish between aluminium and ferric sulphates. It is not possible even approximately to determine the amount of lime required for neutralization by the old method of determining total sulphate and deducting the sulphates of the bases present.

Ferrous sulphate is not corrosive in itself, and even when oxidized does not give rise to a measurable amount of free acid. The equation:—

$$2FeSO_4 + 3H_2O + O = 2Fe(OH)_2HSO_4 \text{ (basic ferric sulphate)}$$

represents the oxidation. Now the product which would ionise into $Fe(OH)_2^+$ and HSO_4^- happens to be almost insoluble in water; consequently scarcely any ionisation (or formation of HSO_4^- ion) can occur.

Though controversial, the subject is most important. Watson and Cooper (J.C.M.M.S., 1921, 32) remark: "In view of the very great expense actually incurred by neglect of correct neutralization, it is an immediate and pressing necessity that rapid and accurate methods of testing be known and used, and that clear records be kept and periodically examined by those responsible for the upkeep of metal work underground". The process given above is at least theoretically correct.

Direct Determination of Lime-Requirement.

A sample of the water is first tested qualitatively with methyl red indicator. If the colour given is pure yellow without trace of orange or red, the water requires no lime. Otherwise the following quantitative test is carried out:

500 ml. of the water, in a measuring cylinder, is treated with 1 ml. of saturated lime water. After vigorous shaking, a small sample of the mixture is removed and tested with one drop of methyl red solution. If the colour is red or orange the water is still acid, and a further addition of 1 ml. of the lime water to the main bulk of the water is made, and the test continued in this way, 1 ml. at a time, until a small sample gives a pure yellow with methyl red. If a large precipitate is produced by the lime water, it should be allowed to settle slightly, so that a fairly clear sample can be obtained for the indicator test.

1 ml. pure saturated lime water contains 0·0012 gram calcium oxide, but the specimen used should be checked by titration with decinormal acid in presence of phenolphthalein. 1 ml. lime water used as above corresponds to 2·4 pounds calcium oxide per million pounds of mine water, or to 24 lb. calcium oxide per million gallons.

The following rough and ready method for engineers and pumpmen underground is useful. A small dropping bottle is filled with a stronger lime solution, such that, say, five drops of lime water from the bottle on 100 ml. sample corresponds to 1 lb. of lime per 1,000 gallons. Addition of sugar is necessary to get enough lime into solution.

100 ml. of the water to be examined is measured into a white enamelled mug, ten drops of bromothymol-blue added, and lime water drop by drop from standard bottle till alkalinity is shown. From the number of drops required the official responsible can tell what change in the lime feed is necessary.

Lime (containing calcium oxide in varying amounts) being cheap, is almost universally used for neutralizing mine waters; the great objection to its use being the formation of calcium sulphate in neutralization. The solubility of calcium sulphate may be taken as 20 lb. per 1,000 gallons, and it is not advisable to add lime so that more than 18 lb. calcium sulphate per 1,000 gallons will result from the reaction. Isolated occurrences of saturation do not matter, but the quality of the water at the various sumps or main pumping stations should be studied so as to avoid a too free deposition of calcium sulphate, thereby closing up pipes and pumping columns. If it is found impossible to neutralize the water for this reason, it should be remembered that on neutralizing a mine water containing free acid, ferric and ferrous sulphates, free acid is the first to be neutralized, then ferric sulphate, ferrous sulphate being the last to react. Bearing this in mind, it may be possible to add sufficient lime to just neutralize free acid and ferric sulphate. In this way calcium sulphate may usually be kept at a figure well below saturation.

Hydrogen Sulphide in Mine Water.

Reagents:—

(1) Standard sodium thiosulphate (N/40) = 6·205 gram $Na_2S_2O_3.5H_2O$ per litre.

(2) Starch indicator.

(3) Standard iodine solution (N/40) = 3·173 gram per litre. Dissolve the iodine in 100 ml. of a 20 per cent solution of potassium iodide and make up to one litre with distilled water.

Method.

1. Syphon 500 ml. of the sample into a graduated cylinder.
2. Pipette 10 ml. of N/40 iodine solution into each of two Erlenmeyer flasks.
3. Add about 1 gram of potassium iodide crystals to each.
4. Add 200 ml. of distilled water to one flask.
5. Syphon 200 ml. of the sample from the cylinder into the other flask.
6. Titrate both the distilled water flask and the sample with N/40 sodium thiosulphate using starch as an indicator near the end of the titration. Record the ml. of thiosulphate used in each case.

Equations of reaction:—

$$H_2S + I_2 = 2HI + S$$
$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

Calculation.

Let S = ml. of sodium thiosulphate used for sample.
and D = ml. of sodium thiosulphate used for distilled water.

$$\frac{(S - D) \times 426}{\text{ml. of sample}} = \text{p.p.m. hydrogen sulphide.}$$

Boiler Waters.

As large quantities of water are evaporated in steam boilers it will be evident that the soluble salts in the feed water will gradually be concentrated in the boiler and will eventually be deposited out of solution as a sludge, an incrustation or a scale. The principal scale-forming substances generally found in water are the bicarbonates, sulphates and chlorides of calcium and magnesium. The bicarbonates, on heating, give off carbon dioxide and are precipitated as carbonates of calcium and magnesium, becoming increasingly insoluble in boiling water, and, precipitated in the form of heavy crystals, form, with the carbonates of calcium and magnesium, silica, and oxides of iron and aluminium, a cement-like scale of great hardness. As this scale interferes with efficient heat transference, it is desirable that as much of these salts as possible be removed in water softening plants.

Feed Water.

In addition to the periodical analysis of the water supply routine tests should be carried out on the feed water, to determine the temporary and permanent hardness from which data the efficiency of the softening plant can be controlled. Where treatment takes place in the boilers, this data is necessary to determine the nature of such treatment.

In view of the close relationship between dissolved oxygen in boiler feed water and corrosion of boilers, it may be necessary to examine the feed water from time to time for the presence of this gas.

Estimation of Dissolved Oxygen (Modification of Winkler's Method).

The method is based on the absorption of oxygen by a flocculent precipitate of manganous hydroxide, formed by the reaction between

manganous chloride and alkaline potassium iodide. The oxygen converts the manganous hydroxide to manganic hydroxide. Acidification by hydrochloric acid releases free iodine in direct proportion to the amount of oxygen absorbed. The liberated iodine is then titrated, at a temperature below 26°C., with standard sodium thiosulphate using starch as indicator. Reagents required:—

(1) Potassium permanganate—3·95 grams per litre.
(2) Potassium oxalate—20·00 grams per litre.
(3) Manganous chloride—33·0 grams per litre.
(4) Alkaline potassium iodide—70 grams KOH and 10 grams KI per 100 ml.
(5) Sodium thiosulphate (N/40)—6·205 grams per litre.

Procedure.—A conical flask of about 300 ml. capacity is fitted with a three-hole stopper. To one hole is fitted the water inlet which is connected to the water supply by means of pressure tubing. This tubing can be closed by means of a screw clip. In the case of a hot water feed, a cooling device, consisting of a water-cooled copper coil through which the feed water passes, must be fitted between the feed pipe and the flask. To another hole is fitted the water outlet from which the water is led to waste through rubber tubing. This tubing can be closed by means of a spring clip. To the third hole is fitted a shortened micro-burette of about 10 ml. capacity.

The two clips and the burette stop-cock are opened and the inlet tube is connected to the water supply. A few litres of water are allowed to run through the apparatus in order to displace all the air. Care must be taken to see that no air bubbles remain in the flask.

The two clips and the stop-cock are now closed, the apparatus is disconnected and the water is shaken out of the burette.

One ml. of 50 per cent sulphuric acid is pipetted into the burette, the burette stop-cock is opened and the acid is drawn into the flask by careful manipulation of the outlet clip. Care must be taken to avoid drawing any air into the sample. In a similar manner, sufficient permanganate solution to give the sample a slight pink colour, after the sample has been mixed and left standing for ten minutes, is added. In this manner all nitrates, iron and organic matter, which would interfere at a later stage, are removed. The excess permanganate is now destroyed by the addition of 1 ml. of the oxalate solution.

If nitrates, iron and organic matter are known to be absent, these first three steps may be omitted.

One ml. of the manganous chloride is now added, followed immediately by the addition of 4 ml. of the alkaline iodide solution. The flask is now wrapped in a dark cloth in order to exclude light and the contents mixed by inversion and rotation. After ten minutes the solution is run into a beaker containing 5 ml. of concentrated hydrochloric acid. The whole is now titrated with the standard sodium thiosulphate solution using starch as indicator.

$$\frac{\text{ml. N/40 Thio.} \times 200}{\text{volume of flask in ml.}} = \text{milligrams per litre of dissolved oxygen.}$$

NOTE.—It is customary to report dissolved oxygen as milligrams per litre and not as p.p.m. The figure in either case is the same.

In the titration with sodium thiosulphate the temperature must not exceed 26°C. as the sensitivity of the starch indicator decreases at a higher temperature.

BLOWDOWN WATER.

In all cases where boiler waters are chemically treated, routine testing of the blowdown should be carried out in order to avoid under or over treatment. Following is a useful routine scheme of analysis for blowdown water:—

H = Total hardness to Clarke's soap solution.
P = Alkalinity to phenolphthalein.
M = Total alkalinity (alkalinity to methyl orange).
O = Caustic alkalinity. Obtained by titrating 50 ml. of the sample to which 2 ml. of a 10 per cent solution of barium chloride has been added, using phenolphthalein as indicator.
S = Total soda alkalinity. Indicated as being present when M exceeds H. Calculated by subtracting H from M.
N = Free sodium carbonate. Indicated as being present when S exceeds O and is obtained by subtracting O from S.
[N] = Free lime $Ca(OH)_2$. Present when O exceeds S. Calculated by subtracting S from O.
[S] = Permanent hardness when H exceeds M. Calculated by subtracting M from H.

M may be calculated as being 2P – O.

NOTE.—In the above scheme of analysis all alkalinity determinations are carried out on 50 ml. of the sample using N/10 sulphuric acid. Results are all expressed in terms of calcium carbonate.

1 ml. N/10 sulphuric acid = 100 p.p.m. calcium carbonate.

In addition to the foregoing determinations, it is necessary to test periodically for total dissolved solids, chlorides, sulphates and also for phosphates if this substance is used in treatment. Chlorides and sulphates are both expressed as sodium salts. Phosphates in the blowdown will not normally exceed about 10 p.p.m., and can therefore be most conveniently estimated colorimetrically by the following method.

Standard Solutions Required:—

(*a*) Sulphuric Acid Solution:—To 200 ml. of distilled water add 65 ml. of concentrated sulphuric acid and dilute to 500 ml.

(*b*) Molybdate Solution:—Dissolve (without heat) 17·5 grams of pure ammonium molybdate in about 200 ml. of distilled water. To another 200 ml. of distilled water add 10·5 ml. of concentrated sulphuric acid. Mix the two solutions and make up to 500 ml. This solution must be stored in the dark.

(*c*) Hydroquinone Solution:—Dissolve 5 grams of pure hydroquinone in 500 ml. of distilled water, and add 0·3 ml. of concentrated sulphuric acid. Care must be taken that all the hydroquinone is in solution before adding the acid. This solution gradually darkens in colour but will give satisfactory results for about three weeks if stored in the dark.

(*d*) Carbonate—Sulphite Solution:—In 500 ml. of distilled water dissolve 100 grams of pure anhydrous sodium carbonate and 24 grams of pure anhydrous sodium sulphite.

(*e*) Standard Phosphate Solution:—A solution containing 100 p.p.m. of phosphate is obtained by dissolving 0·139 gram of dibasic ammonium phosphate [$(NH_3)_2HPO_4$] in a litre of distilled water.

Procedure.—To 5 ml. of the filtered boiler water in a 50 ml. Nessler tube, add the reagents, measured by separate pipettes, in the following order. After each addition swirl the sample to mix thoroughly.

1 ml. sulphuric acid solution.
1 ml. molybdate solution.
1 ml. hydroquinone solution.

Now allow the solution to stand for 5 minutes, and allow the olive green colour, which will appear when phosphates are present, to develop to its maximum intensity. During this period of 5 minutes, measure 2 ml. of the carbonate—sulphite solution into a separate 50 ml. Nessler tube. At the end of the 5 minutes pour the treated solution rapidly into the tube containing the carbonate-sulphite solution pouring backwards and forwards a few times to ensure thorough mixing. The blue colour of the phosphate compound develops rapidly and, as it is not permanent, its intensity should be measured as soon as possible. This is done by comparing the colour with that developed by a suitable series made up by dilutions of the standard phosphate which have been treated in the same manner as the sample. This determination can be more rapidly and efficiently carried out by using a colorimeter of the visual, or preferably of the photo-electric type.

Determination of Emulsified Oil in Water.

To about 400 ml. of the water add 0·25 gram chemically pure alum. Boil and add ammonia to precipitate hydrated alumina; the cloudy appearance of the water due to the oil at once disappears, the oil being taken up by the precipitate. Filter and dry in an oven at 105°C. Extract the oil from the precipitate with ether in a Soxhlet apparatus, and weigh, or, if a Soxhlet is not available, place the funnel containing paper and precipitate over a small, weighed flask, and wash precipitate with a fine jet of ether from the wash bottle till free from oil. Connect flask to a condenser, distil off the ether, and weigh flask and oil residue. In some cases the oil can be directly extracted from the water (acidified) by shaking with ether in a separating funnel.

Condenser Waters.

Condenser waters should be tested regularly, more especially in modern plants in which the condensed water goes straight to the hot well or boiler feed.

It is advisable to make a hardness test and a qualitative test for sulphates, as these will show if any tubes are leaking and any unduly large quantity of the cooling water is contaminating the condensed steam. As a rule cooling pond waters are high in sulphates, so a qualitative test can be done by acidifying 100 ml. with hydrochloric acid and adding a few drops of barium chloride solution. With a little experience it is possible to assess from the amount of barium sulphate precipitated the state of the condensers and to determine whether tubes are leaking.

A dionic conductivity test gives better information as to condenser leaks but the necessary apparatus is seldom available in a Witwatersrand assay office. Where a regular check is kept on condenser water this apparatus will prove a great time saver in addition to giving better information.

Cooling-Dam Waters.

A modern power plant requires very large quantities of water for cooling condensers, etc. On the Rand this is generally stored in large dams, with elaborate cooling devices for the hot return water. Evaporation in these dams is very rapid, especially in the dry windy season.

The main source of supply for many of these dams is the water pumped from the mine, already containing a large amount of calcium sulphate, and in the dry season, if a careful check is not maintained, it can easily happen that the water may become saturated with calcium sulphate, and the condensing plant rendered useless. A good cooling water should contain:—

(*a*) No lime present as such (free calcium hydroxide).
(*b*) Very little calcium carbonate.
(*c*) No free acid or ferric sulphate.
(*d*) No ferrous salts (sulphates).
(*e*) Calcium sulphate as much below saturation point as can be economically maintained with good working results.
(*f*) Dissolved solids in as low a proportion as can be maintained, allowing for calcium sulphate.
(*g*) No sign of algae.
(*h*) No chlorides.

Excess of lime (as $Ca(OH)_2$) is seldom met with, but should be tested for with phenolphthalein. If an alkaline reaction is shown the lime must be determined.

Calcium carbonate is very seldom found, but should be tested for with methyl orange and N/10 acid. Calcium is generally present as bicarbonate.

Ferrous sulphate, which is found occasionally, can be tested for by acidifying with sulphuric acid and adding a freshly washed crystal of potassium ferri-cyanide, any blue colour developing indicating the presence of ferrous sulphate. If neutralized it can be removed by filtration.

If a calcium sulphate content of not more than 16 lb. per 1,000 gallons is maintained in conjunction with a dissolved-solids figure of not more than 3,600 parts per 1,000,000, practically no trouble from deposition of calcium sulphate is found.

In conjunction with the cooling-dam water, the "make-up" to it should be examined regularly, and any tendency towards the occurrence of the undesirable substances mentioned in the previous paragraph counteracted as soon as possible.

Waste and Polluted Waters.

These effluents are analysed to determine whether they contain constituents which may pollute streams.

The type of analysis to be carried out can be decided only by studying the history of the water in question, its source and possible addition

of pollution due to chemicals, organic waste, etc. Careful assessment of the time that stagnant waters have accumulated in a particular locality is important. A study of the terrain over which a waste water is flowing may give evidence of pollution or concentration of harmful elements.

Drinking Water.

No matter what the chemical characteristics of a water intended for human consumption may be, it is absolutely necessary for the water to be subjected to bacteriological examination. This, of course, falls outside the province of the assayer and need not be considered here. As regards the chemical examination of the water, in addition to the tests already described, the following determinations may be required:—

(1) Small quantities of poisonous metals such as copper, lead, etc.
(2) Free and saline ammonia.
(3) Nitrogen as nitrate and nitrite.
(4) Organic nitrogen.
(5) Free chlorine.
(6) Oxygen absorbed from permanganate.
(7) Biochemical oxygen demand.
(8) Iodide.
(9) Degree of colour.
(10) Description of odour.
(11) pH value.

For a description of methods for the determination of the above constituents and characteristics, the reader is advised to consult a work dealing specifically with the analysis and control of drinking water.

WATER TREATMENT.

The treatment of water for boiler purposes, etc., is usually the responsibility of the Engineer on the mines of the Witwatersrand to-day, but a fundamental knowledge of the subject will be useful to assayers

Water treatment consists of:—

1. Coagulation by coagulants.
2. Water softening.

Coagulation and Coagulants.

Coagulation is a preliminary treatment of the water prior to the water softening process. Coagulants are used:—

(1) To remove natural suspended and colloidal material,
(2) To remove materials which do not settle readily in chemical treatment processes,
(3) To assist in filtration, by forming mats on sand filters.
(4) To assist in the vacuum filtration of sewage sludge.

A coagulant reacts with the natural alkalinity in solution in the liquid treated, or with other added chemicals, to form an insoluble, flocculent precipitate. The precipitate clarifies the liquid by coagulating, absorbing and entraining suspended and colloidal material. It may also remove colours and gases in solution. A portion of the precipitate formed in water filtration plants is carried through the sedimentation basins to be

deposited on the filter beds where it further assists in the clarification of the water and removal of colour, odour and taste-producing compounds.

The chemicals most commonly used as coagulants in water treatment are aluminium sulphate (alum), iron sulphate, copper sulphate and sodium aluminate. Their use results in the formation of the hydroxides or aluminates which are the effective coagulating agents. In some waters containing magnesium, or iron salts, use is made of the magnesium hydroxide formed upon the addition of lime. Alum is the most widely used coagulant. The amount of alum or other chemicals cannot be exactly determined from the reaction equations as there are many variables affecting the reactions. Actual plant experience is necessary with each particular water.

Water Softening.

The general and most economical softening treatment for water consists of treatment with lime to remove all bicarbonates and excess of carbon dioxide together with all magnesium salts. This is followed by treatment with sodium carbonate in sufficient quantity to precipitate all remaining calcium salts. (i.e. When permanent hardness is present as well.)

The following are the reactions:—

(1) $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$

(2) $Mg(HCO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O$

(3) $MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$

From equation (3) it will be seen that the non-carbonate hardness, due to the presence of magnesium salts, is converted into non-carbonate calcium hardness.

(4) $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$

The precipitation of magnesium hydroxide, calcium carbonate and suspended matter (silica, etc.) is accelerated by the addition of sodium aluminate ($Na_2Al_2O_4$), which acts as a coagulant.

It will be noticed from the equations that calcium carbonate and magnesium hydroxide are precipitated, either alone or together in every reaction. This is of course due to the fact that their solubility in water is very low.

When softening water by the soda-lime process, the amount of each chemical required can be calculated when the following information is available:—

1. Free carbon dioxide (CO_2).
2. Bicarbonate alkalinity (temporary hardness).
3. Magnesium.
4. Non-carbonate hardness (permanent hardness).

Lime Requirement.—It will be evident from the equation that the total lime required is equivalent to the sum of the bicarbonate alkalinity, carbon dioxide and magnesium content.

In taking carbon dioxide as an example for calculation, the following equation is used:—

$$\underset{44\cdot01}{CO_2} + \underset{74\cdot096}{Ca(OH)_2} = CaCO_3 + H_2O$$

As the analysis of lime supplies is reported in terms of percentage calcium oxide, the reacting quantities are:—

$$\underset{44\cdot01}{CO_2} + \underset{56\cdot08}{CaO} = CaCO_3$$

One part carbon dioxide therefore requires 1·274 parts calcium oxide, and water containing one part per million carbon dioxide (or 10 lb. carbon dioxide per 1,000,000 gallons) will require 0·01274 lb. calcium oxide per 1,000 gallons. If the lime contains 80 per cent calcium oxide,

$$\frac{100}{80} \times 0\cdot01274 = 0\cdot015925 \text{ lb. lime}$$

will be required per 1,000 gallons for every part per million carbon dioxide present.

The lime required per 1,000 gallons of water for bicarbonate alkalinity is 0·0056 lb. calcium oxide (100 per cent) per part per million of such alkalinity.

p.p.m. magnesium × 0·02306 = lb. calcium oxide required per 1,000 gallons.

Soda Carbonate Requirement.—p.p.m. non-carbonate hardness (or permanent hardness) × 0·0106 = lb. sodium carbonate required per 1,000 gallons of water.

Allowance should be made for the percentage purity of the soda ash.

Caustic soda is used in some cases for softening water. The reactions are as follows:—

$$CaH_2(CO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$
$$MgH_2(CO_3)_2 + 4NaOH = Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$$
$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

Water Softening (Other Processes).

Although it is desirable that as much of the hardness as possible be removed outside the boiler in a soda-lime plant, there is practically no boiler in existence where the feed water is entirely free from hardness.

Sometimes, due to local conditions, difficulty is experienced with the deposition of calcium carbonate in a hard crystalline form after the water has left the softening plant. This phenomenon is known as "after-precipitation", and is usually due to the interfering effect of magnesium salts. Plant overload, the presence of organic matter, etc., also contribute to this cause. For this reason the use of the following processes in conjunction with the soda-lime process will lead to greater efficiency in the conditioning of boiler water with a view to preventing the formation of scale, etc. The reagents used are available commercially under well-known trade names.

Phosphate Process.—The process involves the use of either sodium hexa metaphosphate, disodium phosphate or trisodium phosphate. These phosphates are introduced into the feed water of the boiler so that calcium phosphates are formed at high temperatures as a sludge inside the boiler. The sludge is eliminated by a periodic "blowdown" of the boiler.

Equations:—

$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2SO_4$$
$$3MgSO_4 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 3Na_2SO_4$$
$$3CaH_2(CO_3)_2 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 6NaHCO_3$$
$$3MgH_2(CO_3)_2 + 2Na_3PO_4 = Mg_3(PO_4)_2 + 6NaHCO_3$$

Phosphate Organic Treatment.—In this process use is made of the combined reagents, sodium phosphate and certain tannins. The action of the phosphate is as mentioned above. An additional safeguard against incrustation is provided by the tannins present which are absorbed by, and coat, any solid particles in suspension in the water, preventing their adherence to the metal and to one another.

Sterilization of Cooling Dam Waters.

The use of sodium hypochlorite (NaOCl) is often resorted to under *carefully controlled* conditions. The solution obtained commercially carries about 15 per cent chlorine and may be added so that the water to be treated will receive 1·04 parts chlorine per 1,000,000. This will destroy organic matter (algae) which is a carrier of iron hydroxide, silica, etc., which become scale in the cooling mechanism.

Swimming Bath Water.

This water is generally circulated by means of a centrifugal pump through an enclosed sand filter of adequate size. A drip feed of aluminium sulphate solution is fed into the intake side of the pump to form a flocculent precipitate of aluminium hydroxide on the surface of the sand. A separate feed of a solution of "Alfloc A Briquettes" speeds up precipitation and helps to prevent haziness in the water due to the formation of a delayed "floc" which otherwise may develop after the water has passed through the filter bed. These briquettes, which consist mainly of sodium aluminate, make the use of soda ash unnecessary. This ensures the removal of fine suspended particles in the bath water, as well as the absorption of the greater part of the bacteria. As the water emerges from the filter tank it is aerated by means of a venturi restriction into which air is drawn from the atmosphere. A regular feed of chlorine may be introduced by using a solution of sodium hypochlorite. The addition of ammonium chloride or sulphate is advantageous as it combines with the chlorine to form "chloramine" which is far more persistent, causes less irritation to bathers and is not so readily decomposed by ultra violet light. The sodium hypochlorite and the ammonium salt must be added separately. Chlorine may also be added as chlorine gas, in which case ammonia gas should be used. The residual chlorine concentration should be kept between 0·2 and 0·5 p.p.m. The water can be tested regularly with complete outfits available for this purpose. Germicidal lamps for water disinfection are also obtainable and installation details can be obtained from the manufacturers.

Copper sulphate is added at intervals, the concentration being kept below 1·0 p.p.m. This acts as a suppressant for algae growth. It should not, however, be added more than once or, at the most, twice a week as algae have a habit of acclimatizing themselves to copper sulphate.

The amount of aluminium sulphate used per day depends on the circulating capacity of the pump, the area of the filter and size of the bath.

Five pounds per day is used in one installation where the water circulates at the rate of 10,000 gallons per hour and the bath holds 100,000 gallons.

Stainless steel tanks are advisable for holding the aluminium sulphate solution as it is corrosive. Vulcanite or glass stopcocks, rubber stoppers, glass sight feed tubing and rubber tubing are indispensable.

The aluminium sulphate rate of feed must be adjusted so that the water entering the bath is still slightly alkaline. Excessive feed will acidify the water to such an extent that complete precipitation of aluminium hydroxide will be prevented, allowing it to pass through the sand filter to the bath, where it is thrown out of solution by the greater alkalinity of the main bulk of water. The water entering the bath from the filter should show a greenish blue colour when tested with bromothymol blue indicator.

An additional feed of soda carbonate solution may be needed where make-up water is acid.

The ideal operating condition is to keep the water between the neutral point of pH 7·0 and about 7·4. At a higher pH the smell of chlorine is more noticeable. The increase in acidity due to constant daily aluminium sulphate feed is counteracted by the alkalinity available in most make-up water, which it is advisable to add at a constant rate to replace evaporation losses and scum-channel overflow. Sufficient draining outlets for the overflow should be provided to prevent accumulation in the scum-channel and possible re-entry of overflow water into the bath.

Germicidal lamps to keep away mosquitoes, moths, etc., are also useful around a swimming bath. They cost only a few pence more than ordinary globes and are also of value in the home.

CHAPTER XV.

THE SAMPLING AND ANALYSIS OF COAL AND COKE AND THE TESTING OF LUBRICATING AND FUEL OILS.

The following chapter has a double value. Apart from the information on coal, coke and oils the section on the sampling of coal is capable of a much broader application.

The principles involved and the limits of accuracy apply to any material having a similar form.

With a few exceptions the methods used for sampling coal in bulk can be used, e.g., for sampling gold ore which is being delivered to the crushing plant. The methods for reducing the gross sample also apply to any material of a similar shape.

These methods of sampling are extracts from the "S.A. Standard Specifications for the Sampling of Coal and Coke" by kind permission of the S.A. Bureau of Standards.

SAMPLING OF BROKEN COAL DURING TRANSIT.

From Conveyor Belts.—The necessary number of increments may conveniently be collected by taking shovelfuls of coal from the belt or from its discharge end at fixed intervals of time. Care should be taken to include both the centre and the sides of the stream of coal in the increments either by taking the increment right across the stream of coal or by taking the increments in rotation from one side, from the centre, from the other side, from the centre and so on. If the thickness of the coal stream on the conveyor varies from time to time, then the increments taken should represent this variation. A convenient method of operation in such circumstances is to take all the coal from a marked off segment of the conveyor each time this segment passes the sampling point. If some of the coal that is being sampled is larger in size than the selected increment size, then such large lumps, when included in an increment, should be broken across the bedding plane of the coal and only a sufficient quantity of the lump retained as the increment. All the increments should be placed as they are taken in a suitable bag or box labelled with full particulars of the sample.

From Colliery Tubs.—A sample of run-of-mine coal can be taken from colliery tubs at any convenient point by taking shovelfuls from each tub or from each fifth or tenth tub as it passes, and observing some regular order, e.g., from the front of the first, the middle of the second, the back of the third and so on for successive tubs.

From Railway Trucks.—Railway trucks may be satisfactorily sampled during either loading or unloading operations:

(*a*) When a truck is being loaded from a chute the increments may be taken at equal time intervals from the chute as described under Conveyor Belts. If the truck is being loaded by hand or from baskets then the requisite increments can be conveniently

obtained by setting aside every hundredth or two-hundredth shovelful or basketful. The intervals between increments should be so regulated that the requisite number of increments are obtained by the time the truck is fully loaded.

(*b*) When a truck is being unloaded by hand a sample may be obtained in a manner similar to that used during hand loading. Alternatively, the top layer of coal is removed to one-sixth of the depth of the truck and from the surface thus exposed increments are taken at regular intervals along three lines, one down the centre and the other two one-sixth of the total width from each side respectively. The coal is then removed to half the total depth of the truck and the sampling of the new surface repeated in the same way, and finally the coal is removed down to five-sixths of the total depth of the truck and the fresh surface again sampled as before. The number of increments taken from each line and level is dictated by the accuracy requirements of the sample. In the case of trucks discharged through a hopper bottom or by tippling, sampling is very difficult and should be avoided if possible. The discharge takes place so rapidly and so much segregation occurs in the discharged stream of coal that the taking of randomly-distributed increments is practically impossible. It is recommended that samples should not be taken under these conditions, but that the coal be sampled before the truck is emptied by one of the methods described in following sections, or after discharge.

(*c*) If the manner of loading a truck is known, it is sometimes possible to obtain a satisfactory sample of the coal without unloading the truck. Thus, if the truck has been loaded from a chute by commencing at one end and gradually moving the truck under the chute as it is filled, the coal will lie in the truck in inclined strata and the upper surface of the truck will represent the contents with reasonable accuracy. When such a method of loading has been used increments may be collected from the surface of the coal at equal intervals along three lines parallel to the length of the truck and spaced one-sixth of the width of the truck from each side and along the centre respectively. This method of sampling is not recommended if any appreciable segregation into sizes has occurred during the loading of the truck and is not applicable to trucks which have been "top dressed" or in which the surface of the coal has been picked over or stacked in any way after loading. The method can generally be applied to small coal, but is not reliable for large coal (above cobble size).

Sampling Large Coal in Trucks and Stacks.

Large coal in loaded trucks and in stacks cannot be conveniently sampled by hand unless it is certain that the surface layer of coal correctly represents the whole. When segregation of the coal particles has occurred during the loading of a truck or the building of a stack, a sample, however carefully taken by hand from the surface, will not necessarily represent the whole bulk of the coal. Large and cobble coal stored under these conditions can be conveniently and expeditiously sampled by means of a mechanical suction drill sampler which avoids the necessity for taking

large increments by hand, reduces the weight of the gross sample, allows of the accurate sampling of the whole bulk of the coal without disturbing it and reduces the possibility of personal error.

Apparatus.—The process of sampling coal with a mechanical suction drill sampler consists of drilling a suitable number of holes through the thickness of the material to be sampled and extracting and collecting the coal so drilled out, the material thus removed constituting the sample. The mechanical sampler consists of three connected parts. The first part consists of a power driven motor operating an auger drill rod tipped with a cutting edge, the drill rod being encased in a cylindrical sheath of slightly smaller diameter than that of the cutting edge and greater than that of the drill rod so that the drill rod can move freely within the sheath. The sheath is fixed at one end to the drill motor housing and near this point an aperture in the sheath is provided which aperture gives access to the space between the drill rod and the sheath.

The second part consists of the container in which the sample is collected. This has two apertures, one of which is connected in a suitable manner to the aperture on the drill sheath so that a current of air may be caused to flow from the cutting edge through the sheath into the container and out through the second aperture. A filter is inserted within the container in such a manner as to collect in the container any solid material carried by the air stream.

The third part consists of a suitable device for producing the current of air required to carry the drilled material from the cutting edge through the path described into the container where this material is retained by the filtering medium and forms the sample.

The Drilling Procedure.—Cobble or round coal contained in trucks or stacks is sampled by drilling a suitable number of holes by means of the coal drill vertically into the coal. The holes should be equally spaced over the surface of the coal to be sampled.

The drill only is operated on the top of the truck, the suction cleaner remaining at ground level.

The drill is held vertically with the bit resting on the coal, the trailing cable and rubber hose being supported by hooks at the edge of the truck.

Before commencing to drill the fan motor should be started. The drill motor is then set in motion and the drill rod allowed to penetrate the coal bed. No unnecessary pressure should be exerted on the drill unless the weight of the drill is insufficient to force the rod through the coal.

On completion of the hole the drill rod is withdrawn, while the drill continues to rotate in order to clear the sheath completely of coal. This procedure also facilitates the withdrawal of the drill rod.

It is essential for the success of the sampling operation that the cutting edge of the bit should be sharp.

Collection of the Sample.—After the necessary number of holes has been drilled, the coal sample should be removed from the sample container through the bung hole. The last traces of sample should be removed by agitating the filter cloth to free adherent dust and by tapping the sample container.

NOTES.—(1) The suction drill sampling machine may be used for coal of cobble size and larger. Even when the coal is superficially wet the machine can be used, as the air current dries the coal drillings sufficiently to prevent choking of the machine with wet dust.

(2) The nature of the sampling process makes it inadvisable to accept the sample as representing the "as sampled" moisture content of the coal.

The Accuracy of the Gross Sample.

Weight of Increment.—It has been established that the accuracy of a gross sample of coal taken by increments is a function only of the heterogeneity of the coal, the size of the increments and the number of increments taken.

The heterogeneity of the coal varies with its particle size and with its origin and is reasonably constant for the graded product of a particular colliery.

The size of the increment affects the accuracy of the gross sample within limits. When the increment size is small, an increase in size greatly increases the accuracy of the sample, but beyond a limiting size of increment, the accuracy of the sample is very little affected. There is no object, therefore, in unduly increasing the increment size, since this only increases the size of the bulk sample with consequent greater liability to error in the sample reduction process.

In Table 1 the most suitable sizes of increments for sampling South African coals, having regard to all the factors influencing increment size, are set out.

Table 1.

WEIGHTS OF STANDARD INCREMENTS.

Size of Coal.	Usual Designation.	Weight of Increment.
+4″ square mesh ..	Round coal (or run-of-mine)	18 lb.
−4″ +1¾″ square mesh ..	Cobble coal	10 lb.
−1¾″+¾″ square mesh ..	Nut coal	4 lb.
−¾″ +¼″ square mesh ..	Pea coal	1 lb.
−¼″ square mesh ..	Duff coal	¼ lb.

When mixed sizes of coal are sampled the weight of the increment should correspond to that of the largest size of coal in the mixture.

The number of increments to be taken from a coal of any particular size depends on the accuracy desired in the gross sample, the accuracy being proportional to the number of increments.

It is immaterial whether the coal to be sampled consists of one truck load or one hundred truck loads, if in each case the same number of increments of equal weight be taken, the two samples will have the same accuracy and will represent the whole bulk of the coal equally truly. This generalization holds in all cases provided that the degree of heterogeneity of the coal does not vary through the bulk to be sampled. This proviso may be considered to be satisfied when the coal originates from one colliery, in which case the number of increments and consequently the total weight of the bulk sample required to give a definite degree of accuracy does not vary with the total weight of the coal to be sampled.

In practice this generalization sometimes requires modification. In sampling a large consignment of coal derived from one colliery the minimum number of increments required for the desired accuracy may be

taken at equally distributed points spread over the consignment, but when the consignment consists of coal from different sources, and especially when the different coals are present in unequal distribution, then the even distribution of the minimum number of increments over the whole consignment may fail to include one of the types of coal present in its proper proportion. Under the latter conditions it is necessary to increase the number of increments so that at least one is taken from each truck in the consignment or to sample separately the coal from each source.

The foregoing considerations apply to gross samples consisting of increments collected by hand.

It has been shown by Bushell (loc. cit.) that the portions of coal collected from individual holes by the Drill Sampling Machine are comparable to increments taken by hand.

By the application, therefore, of the "Theory of Errors" and the conception of the "Average Error" it has been shown that:

(1) The number of increments to be taken or holes to be drilled is independent of the total weight of the consignment, provided that the increments or holes are uniformly distributed.

(2) The number of increments to be taken or holes drilled must be varied according to the average error of the coal.

The average error of a particular coal can be determined by taking or drilling a predetermined number of increments or holes in a single truck, or, conversely, if the average error is known the number of increments to be taken or holes to be drilled can be calculated to give the required degree of accuracy.

The number of increments to be taken from, or holes to be drilled in a single truck load or consignment in order to collect a gross sample conforming to a degree of accuracy such that in ninety-nine cases out of a hundred the ash content of the sample will be within plus-minus one unit of the true ash content is determined as follows:—

Ten samples, each consisting of ten equal increments of standard size or holes, should be taken from one consignment (truck load) of the coal and the ash percentage in each sample determined. The numerical deviation (neglecting the algebraic sign) of each ash percentage from the average of all ten ash percentages is then calculated.

From the application of the Law of Errors to the sampling of coal it has been shown that

$$R = \frac{0{\cdot}85a}{\sqrt{n}}$$ where a average error per increment
n number of increments
R probable error of the sample.

If $R = 0{\cdot}26$ then in 99 cases out of 100 the sample will be within 1 per cent of the true ash.

$$\text{thus } n = \left[\frac{0{\cdot}85a}{0{\cdot}26}\right]^2$$

$$\text{again } A = \frac{a}{\sqrt{n_1}} \text{ or } a = A\sqrt{n_1}$$

where A is the average error of samples each made up of n_1 increments or holes of average error a

$$\text{therefore } n = \left[\frac{0{\cdot}85\ A\sqrt{n_1}}{0{\cdot}26}\right]^2 = \left[\frac{0{\cdot}85A}{0{\cdot}26}\right]^2 n_1$$

$$= \left[\frac{0{\cdot}85}{0{\cdot}26}\right]^2 \times \left[\frac{\text{(sum of the numerical deviations from the average ash percentage}}{\text{(the number of samples taken)}}\right]^2 \times \left[\begin{matrix}\text{Number of incre-}\\ \text{ments or holes in}\\ \text{each sample taken}\end{matrix}\right]$$

or, if ten samples each of ten holes are taken, the number of holes required for a sample to have the above degree of accuracy for practical purposes is equal to:

$$\left[\begin{matrix}\text{The sum of the numerical deviations}\\ \text{for each sample from the average ash}\\ \text{percentage.}\end{matrix}\right]^2$$

The number of increments or holes as determined in the above manner should be used for all samples of this particular type of coal.

By practical test, the number of increments of standard weight required to give an accuracy such that, in 99 cases out of 100, the ash percentage of the sample is within one unit of the true ash content, have been determined for different types of South African coals (see Bushell, loc. cit.). As a general rule, the data set out in Table 2 may be accepted.

TABLE 2.

MINIMUM NUMBER OF INCREMENTS REQUIRED FOR GROSS SAMPLE SAMPLING BY INCREMENTS TAKEN BY HAND.

Type of Coal.	Ash Content.	Weight of Increment.	No. of Increments.	Weight of Gross Sample.
		lb.		lb.
Round Coal (or run-of-mine)	<13%	18	20	360
Round Coal (or run-of-mine)	>13%	18	40	720
Cobble Coal	<13%	10	20	200
Cobble Coal	>13% <16%	10	50	500
Cobble Coal	>16%	10	100	1,000
Nut Coal	<13%	4	15	60
Nut Coal	>13% <16%	4	30	120
Nut Coal	>16%	4	60	240

When mixed sizes of coal are sampled, the number of increments taken should correspond to that specified for the largest size of coal in the mixture.

The number of increments required in sampling Pea and Duff coal is similar to that required for Nut coal.

Practical tests with the drill sampling method have shown that, in general, a gross sample of the required accuracy is obtained from Round coal from the Natal Coalfields by collecting 40 drill increments. For Transvaal coals the number of drill increments necessary for Round coal (+4″ square mesh) is 30 and for Cobble coal (−4″ + $1\frac{3}{4}$″ square mesh) is 45. For mixtures of Round and Cobble coal an intermediate number of holes is required.

The accuracy of a gross sample can be varied by varying the number of increments or holes specified above, thus:

(1) If *double* the number of increments be taken or holes drilled, the accuracy of the sample will be such that, in 99 cases out of 100, the ash percentage in the sample will be within 0·7 units of the true ash percentage and the calorific value will be within 0·1 lb. per lb. units of the true value.

(2) If *half* the number of increments be taken or holes drilled, the accuracy of the sample will be such that, in 99 cases out of 100, the ash percentage in the sample will be within 1·4 units of the true ash percentage and the calorific value will be within 0·2 lb. per lb. units of the true value.

(3) If *one-quarter* of the number of increments be taken or holes drilled, the accuracy of the sample will be such that, in 99 cases out of 100, the ash percentage in the sample will be within two units of the true ash percentage and the calorific value will be within 0·3 lb. per lb. units of the true value.

The Reduction of the Gross Sample.

The process of reducing the gross sample to a size suitable for laboratory testing consists of alternatively crushing, mixing and dividing the sample. The process of dividing gives rise to errors which may be considerable but which can be reduced to a minimum under suitable conditions. The errors involved in sub-dividing a sample increase with the extent of the sub-division but are less the smaller the size of the coal particles. Thus, whereas a sample of coal of one inch size cannot be reduced to less than 160 lb. in weight without introducing a considerable error, a coal of quarter of an inch size can be reduced to 8 lb. in weight without introducing a greater error.

The minimum weights to which samples may be sub-divided are set out in Table 3.

Table 3.

MINIMUM WEIGHTS FOR SUB-DIVISION OF SAMPLES

Size of largest Particles.	Minimum Weight after Sub-division.
2 ins.	640 lb.
1 ins.	160 lb.
$\frac{1}{2}$ ins.	40 lb.
$\frac{1}{4}$ ins.	8 lb.
$\frac{1}{8}$ ins.	3 lb.
B.S. Sieve No. 8	1 lb.
B.S. Sieve No. 16	160 gm.
B.S. Sieve No. 25	30 gm.

British Standard Test Sieve, see British Standard Specification No. 410-1931.

Method for Low-Grade Ores.—(Applicable also to rich ores.)

Required: Platinum dish. Cinchonine (or quinine) solution—25 grams in 200 ml. of 1 : 1 hydrochloric acid.

Decomposition.—Decomposition may be achieved by fusing with anhydrous sodium sulphate or by the method already described.

Separation and Determination.—Add an excess of ammonium hydroxide to the beaker. (This will dissolve any tungstic acid. It will also precipitate any iron or aluminium that may be present. This, with any siliceous matter must be filtered off and well washed with hot ammonia water. The filtrate will contain the tungsten.)

Boil the filtrate to low bulk, cool and add 20 ml. of strong hydrochloric acid, 5 ml. of strong nitric acid and 3 ml. of cinchonine solution to precipitate all the tungsten. Filter the cold mixture, returning the first filtrate if at all cloudy. If a film appears on the sides of the beaker, wash it with hot dilute ammonia. Add hydrochloric acid and wash into the filter paper with dilute cinchonine solution. Then wash the filter paper well with the dilute cinchonine. The filter paper now contains all the tungsten precipitate with, perhaps, a little silica. Place the filter with the precipitate in a weighed platinum dish and ignite. Cool and add a little hydrofluoric acid and heat to dryness. Ignite again and weigh. Weight less weight of dish is WO_3.

Vanadium.

Occurrence.—The principal ore of vanadium is vanadinite $(3Pb_3VO_4)_2$. $PbCl_2$. Vanadinite is found associated with lead deposits in numerous places in the Transvaal. The most extensive deposit is at Zeerust in the Marico district.

Detection.—Borax bead test—oxidizing flame, colourless to yellow when hot, greenish yellow when cold; reducing flame, brownish when hot, emerald green when cold. Microcosmic bead test—oxidizing flame dark yellow when hot, light yellow when cold; reducing flame, brown when hot, emerald green when cold.

Method of Assay.

Required: Standardized N/10 potassium permanganate solution.

Discussion.—The ore is digested in sulphuric acid and taken to fumes. After dilution, the precipitated lead sulphate and silica is filtered off. Potassium permanganate powder is added to remove any organic matter from the filter paper and to ensure that the iron is all in the ferric state. On repeated boiling with hydrochloric acid the V_2O_5 is reduced to V_2O_4.

$$V_2O_5 + 2HCl \rightleftharpoons V_2O_4 + H_2O + Cl_2.$$

The reaction is reversible, so the boiling down and addition of more acid is necessary to remove the chlorine. A final fuming, with the sulphuric acid present, removes the hydrochloric acid.

The vanadium is now titrated with N/10 potassium permanganate to a permanent pink colour.

$$2KMnO_4 + 3H_2SO_4 + 5V_2O_4 = K_2SO_4 + 2MnSO_4 + 5V_2O_5 + 3H_2O.$$

From the equation 1 ml. N/10 potassium permanganate $\equiv 0{\cdot}005095$ gram vanadium $\equiv 0{\cdot}00909$ gram V_2O_5.

Decomposition.—Weigh out one to five grams of the finely ground sample. Treat in a beaker with 30 ml. 1 : 1 sulphuric acid and boil to fumes. The lead precipitate may make the assay "bump". It is best to grip the beaker in a holder and agitate continuously over an open flame. Should a portion of the sample not decompose then fuse a fresh assay with sodium peroxide in an iron crucible. Leach out with water and fume with sulphuric acid as above.

Separation and Determination.—Maintain at the fuming point for ten minutes. Cool, dilute to about 75 ml. and filter. Wash with water and return the filtrate to the beaker. This filtration is only to remove the gangue and prevent "bumping".

Return the beaker to the hot plate. Add sufficient powdered potassium permanganate to produce a pink colour that persists on boiling. Add 50 ml. strong hydrochloric acid. Boil nearly to fumes. Cool slightly and add 25 ml. more hydrochloric acid. Boil nearly to fumes again and note the colour, which should be blue. A greenish colour indicates that further boiling with hydrochloric acid is necessary. However, if a large amount of iron is present, the pure blue colour will not be attained. Finally, take to fumes for one minute. Cool and dilute to 200 ml. Titrate hot with potassium permanganate in the usual manner.

1 ml. N/10 potassium permanganate = 0·005095 gram vanadium.

Zinc.

Occurrence.—The most important ore is zincblende or sphalerite (ZnS). Zinc is also found in small quantities as smithsonite ($ZnCO_3$) and calamine ($2ZnO.SiO_2.H_2O$). In South Africa, zinc is found associated with galena in the Marico district.

Detection.—On charcoal—incrustation yellow when hot, white when cold. With cobalt nitrate—incrustation, dirty grass green.

Method of Assay.

Required: Potassium ferrocyanide solution. 22 grams per litre. See standardization below.

Discussion.—The ore is digested with hydrochloric and nitric acids and taken to fumes with sulphuric acid. After dilution, a strip of aluminium foil is added and the solution boiled. The aluminium precipitates most of the copper as metal. This obviates the precipitation of a large amount of copper sulphide later, and thus prevents a measure of co-precipitation of zinc which would otherwise take place.

The copper is filtered off. Any remaining copper, cadmium or bismuth is precipitated with hydrogen sulphide and filtered off.

After the removal of hydrogen sulphide and the oxidation with bromine, the iron is precipitated with ammonium chloride and ammonium hydroxide and filtered off. The iron is re-dissolved and re-precipitated to ensure that no zinc is left in the precipitate.

The solution is titrated with potassium ferrocyanide, using uranium acetate as an external indicator.

The titration reaction is:

$$3ZnCl_2 + 2K_4Fe(CN)_6 = Zn_3K_2[Fe(CN)_6]_2 + 6KCl.$$

Decomposition.—Weigh out 0·5 gram of the finely powdered sample. Treat in a beaker with 10 ml. strong hydrochloric acid and 3 ml. strong nitric acid. Heat until ore is decomposed. If undecomposed material

Grind this sample until the whole passes a No. 25 B.S. Sieve (30 mesh cement sieve) and reduce by mixing and quartering or other mechanical means until not less than 1½ oz. remain.

Grind this sample until the whole passes a No. 60 B.S. Sieve (60 mesh cement sieve), mix well and transfer to an air-tight tin or stoppered bottle labelled with details of the sample.

This sample is now sufficiently fine for analytical purposes.

Special Moisture Sample.

When it is desired to determine the moisture content of the coal as sampled the gross sample should be collected in an air-tight box provided with a well-fitting lid, each increment being transferred to the box as it is taken.

The gross sample should then be crushed to ¼" size rapidly and quartered as speedily as possible until 16 lb. remain.

The sample is then rapidly quartered and one 8 lb. sample transferred immediately to an air-tight tin. The second 8 lb. sample can then be further reduced to form the laboratory test sample.

The air-tight tin containing the ore sample should be sealed and labelled "Special Moisture Sample" together with particulars of the sample. The tin and contents should then be weighed, the weight recorded on the label, and despatched to the laboratory without delay.

Moisture "Superficial".

The psecial moisture sample contained in the air-tight tin is poured out into a non-absorbent, non-corrodible tray. Weigh the tray plus the coal. Spread the coal out to dry in a dust free atmosphere until the change in weight does not exceed 0·1 per cent per hour. Final weight of coal plus tray subtracted from weight of coal plus tray before drying = weight of moisture. Express the loss of moisture as percentage of the original weight of coal.

Moisture of Air-Dried Coal.

Weigh 2 grams of coal or coke from the air-dried laboratory sample in a shallow weighing vessel of about 2" diameter, provided with a well-fitting cover. Heat the uncovered coal to constant weight in a steam jacketed oven (1 hr. to 2 hr.). Allow the covered dish to cool in a desiccator and weigh again. Express the percentage loss of weight as moisture.

Total Moisture or Moisture "As Received".

If X = percentage superficial moisture or percentage loss of weight in air-drying.

Y = percentage moisture after air-drying.

Then the total moisture or moisture "as received"

$$= X + Y\left(1 - \frac{X}{100}\right)$$

ANALYSIS OF COAL AND COKE AND THE TESTING OF LUBRICATING AND FUEL OILS.

Proximate Analysis.

Analysis and testing are usually carried out on the air-dried 60 mesh (B.S.) laboratory sample kept in a well-stoppered bottle.

1. Moisture.

Determine moisture as previously described for the determination of the moisture of air-dried coal.

2. Volatile Matter.

(*a*) *Apparatus.*—A cylindrical crucible of translucent silica having a lid of the same material shall be employed. The dimensions should be as follows:—

Crucible.	
Total height	38 mm.
External diameter	25 mm.
Internal diameter	22 mm.
Lid.	
Internal over-all diameter	27 mm.
Diameter of well	21 mm.
Depth of well (ext.)	4 mm.

The combined weight of a crucible and lid shall not be less than 12 gm. nor more than 14 gm. The stand on which the crucible is placed in the muffle consists of the ring refractory material which forms a universal fireclay gas-mantle support. A gas or electrically heated muffle furnace in which a zone of constant and uniform temperature can be maintained is used. The temperature shall be measured with a thermocouple whose bare junction is midway between the base of the crucible in its stand and the floor of the muffle.

(*b*) *Method.*—Weigh an empty silica crucible and lid and place 1 gram of air-dried coal in the crucible. The crucible is tapped on a hard surface so that the coal forms a layer of even thickness on the bottom of the crucible. Adjust the temperature to a steady value of 925° C. Insert the covered crucible containing the coal to be tested and heat for a period of exactly seven minutes from the time of insertion. Cool the crucible rapidly to prevent oxidation, at first upon a cold iron slab, finally in a desiccator, and weigh. Express the loss of weight as a percentage of the weight of coal taken and deduct from this the percentage moisture present in the coal, which must be separately determined on the same day.

Note.—More than one determination may be carried out in the muffle at the same time provided the heat capacity of the muffle is such that with an initial temperature of 925° C. a minimum temperature of 910° C. is regained within three minutes from the time of insertion of the charged crucibles.

(*c*) *Modified method for coke, anthracite or low volatile non-coking coals.*—Place two discs of asbestos each 25 mm. diameter and 1 mm. thick on the inner ring projections of the legs of the gas mantle ring and support the

Dry and ignite, oxidizing the filter ash in the usual manner with a drop of nitric acid and sulphuric acid, and then weigh. If a Gooch crucible is used, dry only at 105° C. The weight of sulphur = the weight of the barium sulphate × 0·1373. A blank determination is carried out under the same conditions and the weight of barium sulphate found in the blank is deducted from that obtained in the determination proper.

NOTE.—For coals containing more than two per cent of sulphur, take only 0·5 gm. of coal for the determination.

The foregoing methods for the determination of the proximate analysis of coal are substantially the same as described in B.S.S. No. 1016—1942 or S.A.S.S. No. 1—1943.

ULTIMATE ANALYSIS.

The ultimate analysis of coal comprises the determination of the carbon, hydrogen, nitrogen, oxygen (by difference) content. The ultimate analysis of coal as well as the determination of minor constituents, such as phosphorus, arsenic and chlorine are seldom required, if ever, in the evaluation of stores on the gold mines.

A full description of the standard methods for the determination of the ultimate analysis and the determination of minor constituents of coal and coke is given in B.S.S. No. 1016—1942 or S.A.S.S. No. 1—1943.

PHYSICAL TESTS.

(1.) CALORIFIC VALUE.

For the determination of the calorific value of coals for the purpose of purchase and sale, the standard method (B.S.S. 1016—1942) is considered to be too elaborate. The following abridged method which eliminates corrections for nitric and sulphuric acids and simplifies radiation correction is recommended by the South African Bureau of Standards (S.A. Std. 5—1940) and is given by kind permission of the S.A.B.S. for comparative routine tests:—

APPARATUS.—(1) *Combustion Bomb.*—Use a high pressure bomb of the Berthelot or Scholes types. The inside of the bomb is constructed of or lined with an acid resisting material. The capacity of the bomb is such that, when filled with oxygen at the working pressure, it contains at least two and a half times the amount of oxygen required for the combustion of the charge.

(2) *Calorimeter.*—Use a brightly polished metal calorimeter with a working capacity of between two to three litres. The water equivalent of the calorimeter together with the bomb and the working charge of water is between two and a quarter and three and a half kilograms.

(3) *Stirring the Calorimeter Water.*—Stir the water in the calorimeter by means of a mechanical stirrer, operating at such a speed that, when the temperature of the water is rising rapidly, the temperature, plotted against the time, lies on a smooth curve. Operate the stirrer at a constant speed. The rate of stirring is such that, when the calorimeter and its jacket are both at room temperature, the operation of the stirrer does not raise the temperature of the calorimeter water by more than 0·001° C. per minute.

(4) *Calorimeter Jacket.*—The calorimeter is surrounded by an outer jacket containing at least five times as much water as the total water equivalent of the bomb and calorimeter charged with water. The water jacket is provided with an insulating cover to protect the calorimeter from air draughts. The calorimeter is supported centrally within the jacket by means of insulating supports. A glass plate support is not recommended, a three point cork or hard rubber support is to be preferred.

(5) *Thermometers.*—The thermometers used should be certified by an approved testing authority. They should be graduated to 0·01° C. and used with their certified corrections. The water equivalent of the calorimeter is determined for each thermometer used and, if a thermometer of the Beckmann type be used, the water equivalent of the calorimeter is determined at various temperatures likely to be experienced, say, when the zero of the thermometer corresponds to 15°, 20°, 25° C., and the appropriate value is used when the calorimetric determinations are made.

(6) *Bomb Crucible.*—The crucible for holding the coal is made of platinum or silica and is supported within the bomb and does not rest in contact with its walls.

(7) *Firing Wire.*—Ignite the coal in the bomb by means of either platinum, nickel, iron, copper or other suitable wire. If a wire is used which burns during the firing or combustion of the coal, the weight of wire used should be a minimum; 5 cm. of No. 40 gauge iron wire is recommended. The current used to heat the firing wire should be sufficiently strong to cause the coal to ignite immediately.

(8) *Oxygen.*—The oxygen used for combustion must be free from hydrogen or other combustible material.

(9) *Briquetting Press.*—A briquetting press in which solid briquettes of about one gram in weight can be made may be required. The press must be freed from grease before use and thoroughly cleaned and greased immediately after use.

(10) *Firing Mechanism.*—A source of electric current of from four to ten volts pressure is required. This may be supplied from a transformer or a battery. The current available should be sufficient to cause a piece of firing wire of the length used in the tests to glow brightly and fuse within one second when suspended freely in air. Flexible leads, broken by a firing key, should be provided to connect the source of supply to the terminals of the bomb.

Determination of the Water Equivalent of the Apparatus.—Determine the water equivalent of the calorimeter by the combustion of a known weight of pure benzoic acid or a standard hydrocarbon oil in the bomb. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation and method of conducting the test are the same as for the determination of the Calorific Value of the coal.

The benzoic acid or hydrocarbon oil to be used should be obtained from a reliable supplier together with a certificate stating the heat of combustion per gram of the specimen.

The benzoic acid should be carefully dried before use by being kept for at least two days in a desiccator over concentrated sulphuric acid, and must be kept in a desiccator except when being weighed or pressed into briquettes.

ture variations as possible. A table or bench on an inside wall of a room with a south aspect is recommended.

Keep a ten to twenty gallon tank of water in the room so as to ensure an adequate supply of water approximating in temperature to that of the room.

Method of Conducting the Test.—(1) Fill the calorimeter jacket with water, the temperature of which must not differ from the temperature of the surrounding air by more than 2° C. A temperature of 1° C. above the air temperature is recommended.

(2) Clean and dry the bomb and the calorimeter.

(3) Weigh out 1·0 gram of the coal sample in a scoop to the nearest half-milligram. Transfer this coal to the bomb crucible using a brush to ensure complete transference. Place the crucible in position in the bomb. Measure off a definite length of firing wire, preferably about 5 cm., and attach the two ends securely to the bomb terminals in such a manner that a loop of wire is embedded in the coal in the crucible. The quantity of firing wire used must be the same for all tests.

(4) Add 10 to 15 ml. of water to the bomb (according to type used) and assemble the bomb, which should be tightened until it is gas-tight. Unnecessary force should be avoided.

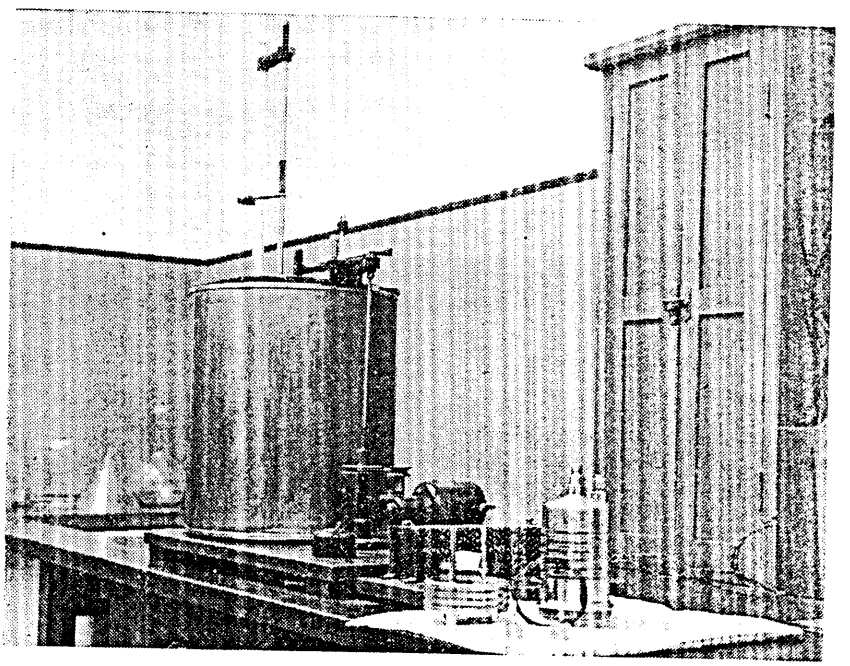


Fig. 76. Apparatus used for the determination of Calorific Value showing calorimeter fitted with stirring apparatus and thermometer. The Scholes Bomb is in the foreground.

(*With acknowledgment to East Gedald Mines Ltd.*)

(5) Charge the bomb slowly with oxygen (in such a way as to avoid blowing the coal out of the crucible) until the pressure in the bomb is 30 atmospheres. Close the valves.

(6) Fill the calorimeter with a weighed or measured quantity of water, which should be sufficient to cover the bomb when in position leaving only the firing terminals above the water level. The water is weighed or measured to the nearest gram or millilitre and the same quantity of water is used for each test. The temperature of the water should be lower than that of the water in the calorimeter jacket*, preferably to a degree equal to two-thirds of the rise in temperature on combustion. The desired temperature can generally be obtained by mixing tap water and water from the tank in the room.

(7) Place the calorimeter in the water jacket, and the bomb in the calorimeter, ascertain that the bomb is gas-tight, connect the terminals to the firing mechanism through the open key, adjust the stirrer so that it does not touch the bomb or the calorimeter and place the covers and thermometer in position taking care that the thermometer does not touch the side of the bomb. The thermometer should always be placed in the same position relative to the bomb and the wall of the calorimeter.

(8) Start the stirrer and observe the thermometer. Initially, the temperature recorded will be erratic. When the change of temperature has become substantially steady, the actual test may be begun.

(9) *Preliminary Period.*—Read and record the temperature accurately, estimating the temperature to the nearest 0·001 °C, and continue readings for four minutes at one-minute intervals, tapping the thermometer lightly at the level of the top of the mercury column during ten seconds prior to each reading to prevent the mercury meniscus from sticking.

The thermometer may be conveniently read through a small magnifying lens held with its axis at right angles to the thermometer stem. By reading always along the axis of the lens where the graduations on the thermometer appear straight, errors due to parallax are avoided.

The rate of rise in temperature per minute during this period should be positive. If the rate of change of temperature be erratic, readings should be continued at one minute intervals until the rate of change is steady over a period of four minutes.

(10) *Chief Period.*—At the end of the fourth minute, complete the electric circuit by momentarily closing the firing key to ignite the coal in the bomb. The key should not be closed for more than two seconds in order to avoid heating the bomb. Watch the rise in temperature of the calorimeter and note the minute during which the temperature reaches a maximum, and at the end of that minute read the temperature accurately. Record the time and temperature (see example).

If the coal does not ignite when the firing key is closed, make two further temperature readings in the preliminary period, and again close the firing key. If the coal does not then ignite the source of the failure should be sought and the test repeated.

(11) *After Period.*—Continue the temperature readings at one minute intervals after the end of the chief period, until the fall in temperature per

---

* Agitation of the water in the outer calorimeter jacket by blowing air into it, or by stirring before commencing a determination, will secure a uniform temperature of the water jacket.

minute, which at first is slow, has assumed a substantially steady rate as shown by five consecutive readings. If the temperature does not fall, the test is discarded and the whole procedure repeated.

(12) Remove the bomb from the calorimeter and release the pressure by slowly opening the valve. Open the bomb and inspect the inside. If any trace of coal or of a sooty deposit is observable the combustion has not been complete and the test must be repeated.

(13) Wash out the bomb, empty the calorimeter and allow both to drain in preparation for the next test.

Calculation of Result.—The Calorific Value or Evaporative Power of the coal, expressed in pounds of water evaporated at boiling point by one pound of fuel, is the water equivalent of the calorimeter at the appropriate temperature, multiplied by the corrected rise in temperature and divided by the latent heat of steam at 100°C. (i.e., 539 calories per gram).

The Calorific Value in British Thermal Units per pound is the water equivalent of the calorimeter multiplied by the corrected rise in temperature and multiplied by 1·8.

The corrected rise in temperature is determined by means of the following formula:—

$$T = t + mf - (f + i)$$

where:—

- T is the corrected rise in temperature;
- t is the observed rise in temperature during the chief period;
- m is the duration of the chief period in minutes, that is the difference between the time of the first reading after the maximum temperature is attained and the time of firing;
- f is the average fall of temperature per minute in the after period;
- i is the average rise of temperature per minute in the preliminary period.

The "preliminary period" is the four-minute interval covered by five temperature readings immediately prior to the moment of firing.

The "after period" is the four minute interval between the time of the first temperature reading after which the rate of fall of temperature is substantially constant and the fourth reading thereafter.

The Calorific Value of the fuel then is:—

$$\frac{WT}{539} \text{ in lb./lb. units.}$$

or $WT \times 1{\cdot}8$ in B.Th.U. per lb.

Where W is the water equivalent of the calorimeter,
T is the corrected rise in temperature.

The following example indicates the method of calculation:—

Water equivalent of Calorimeter = 3,402 gm.

Time.	*Temp.*	*Change in temp.*	
0 min.	2·734	0·005	Preliminary Period.
1	2·739	0·004	
2	2·743	0·004	
3	2·747	0·003	

	Time.	*Temp.*	*Change in temp.*	
Coal fired.				
	4	2·750		Chief Period.
	5	3·34		
	6	4·38		
	7	4·64		
	8	4·693		
Maximum				
	8·40	4·708		
	9	4·707	−0·001	
	10	4·706	0·002	After Period.
	11	4·704	0·002	
	12	4·702	0·001	
	13	4·701	0·002	
	14	4·699		

Average rate of rise in preliminary period =
$(0·005 + 0·004 + 0·004 + 0·003) \div 4 = +0·004 = i$

Average rate of fall in after period =
$(0·002 + 0·002 + 0·001 + 0·002) \div 4 = +0·0017 = f$

Time of chief period =
9 min. − 4 min. = 5 min. = m

Rise in temperature of chief period =
$4·707 - 2·750 = 1·957$°C. = t

Corrected rise in temperature =
$1·957 + (5 \times 0·0017) - (0·0017 + 0·004) = 1·957 + 0·008 - 0·006$
$= 1·959$

Calorific Value of coal = $3{,}402 \times 1·959 \times 1·8$
= 11,996 B.Th.U per lb.

The Calorific Value should be rounded off to the nearest 10 B.Th.U. units, i.e., 12,000 B.Th.U. per lb.

$$\text{or Calorific Value} = \frac{3402 \times 1·959}{539} = 12·36 \text{ lb./lb.}$$

NOTES.—Certain coals show a tendency to jump from the bomb crucible on firing with the result that they are incompletely burnt. Such coals may often be successfully burnt by reducing the oxygen pressure in the bomb from 30 to 25 atmospheres or by grinding the coal finer. Alternatively, they may be burnt in the form of briquettes made as described under the determination of the water equivalent.

Coals of very low volatile content and coke are frequently incompletely burnt in the combustion. Such coals can be completely burnt by the addition of a small amount of medicinal paraffin of known heat of combustion. The following procedure should be adopted:—Weigh the bomb crucible containing the one gram of coal, add one small drop of medicinal paraffin and re-weigh. The difference in weights is the weight of paraffin added. Proceed with the determination of the Calorific Value as previously described and subtract from the Calorific Value found, the heat of combustion of the weight

of paraffin used, e.g., if 0·0215 grams of paraffin were added and the heat of combustion of the paraffin is 10,990 calories per gram, subtract $10{,}990 \times 0{\cdot}0215 = 236$ calories or $236 \times 1{\cdot}8 = 425$ B.Th.U. or $236 \div 539 = 0{\cdot}44$ lb./lb.

(2) Swelling Index or Woodall Duckham Swelling Number (W.D.S.N.).

The determination from a crucible coke button of the swelling power of a coal is a usual test in evaluating its coking propensity.

Apparatus.

(i) Translucent silica crucible, squat shape, and silica lid with ring handle of the following dimensions is used:—
External height 26 mm. $\pm$ 0·5 mm.
External diameter at top 41 mm. $\pm$ 0·75 mm.
Internal diameter at base not less than 11 mm.
The capacity approximately 17 ml.

(ii) A triangle consisting of 6-6·5 mm. external diameter translucent silica tubing mounted on chrome-nickel wire, the length of the side being 63-64 mm., the diameter of the inscribed circle being approximately 32 mm.

(iii) Teclu burner, $\frac{1}{2}$ inch diameter.

(iv) Draught shield made of asbestos cement piping approximately 6 inches long with 4 inches internal and $4\frac{3}{8}$ inches external diameters.

The piping has three slots at one end, 1 inch in depth, in which the wire portions of the silica triangle rest. The gas pressure and the gas and air supplies for the Teclu burner are adjusted so that the flame is approximately 12 inches long. It is generally found that with the base of the crucible just above the tip of the blue cone of the gas flame a temperature of about 820°C. is maintained on the inner surface of the crucible.

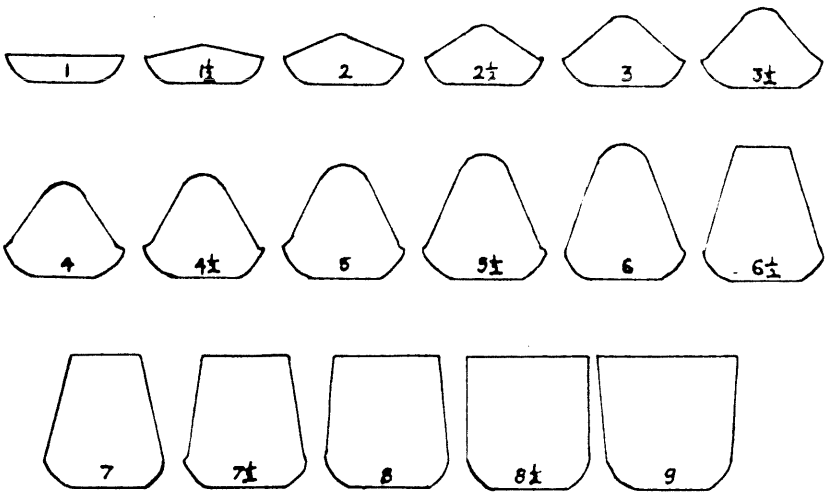


Fig. 77. Standard Profiles and Corresponding Swelling Numbers.

METHOD OF TEST.—Weigh 1·0 gm. of air-dried coal freshly ground to pass 72 mesh B.S. test sieve into the crucible and lightly tap crucible 12 times on bench to level surface of the coal. Cover crucible with lid and place it upright in the silica triangle supported in the draught shield. Light the gas and heat until the flame of the burning volatile matter dies out and, in any case, for not less than 2½ minutes. After cooling, remove button and compare it with the standard numbered outlines in figure.

1 denotes a residue of definite coke structure but no swelling.

1_f denotes a residue easily friable and possessed of no coke structure.

1_p denotes a residue in powder form. A value of 3 or more indicates definite coking possibilities.

(3) SPECIFIC GRAVITY.

Introduce 3 to 4 gm. of air-dried 60 mesh coal or coke into a 50 ml. tared S.G. bottle, cover it with a layer of distilled water and connect to a water pump and heat gently to boiling point in a water bath for ½ hour. Fill the bottle with distilled water, bring to the correct temperature, dry and weigh. Should any scum collect in the neck of the S.G. bottle, it should be stirred with a thin glass rod which can be conveniently cleaned by rinsing down the particles attached to it by water from a wash-bottle.

The difference in this weight and weight of the S.G. bottle filled with distilled water at the same temperature is the weight of water displaced by the coal.

$$\text{Specific gravity} = \frac{\text{Weight coal taken}}{\text{Weight of displaced water}}.$$

(4) FUSION TEMPERATURE OF COAL OR COKE ASH.

Heat the coal (or coke), reduced to pass through ⅛ inch B.S. test sieve, in a thin layer at a temperature of 775°C., ± 25 C., in a well-ventilated muffle, and thoroughly mix the resulting ash to an impalpable powder in an agate mortar. On no account must an iron mortar or pestle be used.

The quantity of coal (or coke) required will vary with its ash content. As a rule 1·5 gm. of ash is sufficient for each ash pyramid.

Make the ash into a stiff paste using a 10 per cent solution of dextrin in water and press into a suitable mould to form a triangular pyramid 1 inch high and ¼ inch along each side of the base, one side of the pyramid being perpendicular to the base. After removal of the pyramid from the mould (which has previously been coated with a thin layer of petroleum jelly) mount it on a "refractory" base, dry and place in gas or electric furnace capable of being heated to high temperatures and provided with an observation hole.

First maintain the temperature at 800°C. under oxidizing conditions for a sufficient length of time to burn off the dextrin and jelly. Then alter the atmosphere of the furnace to mildly-reducing conditions and raise the temperature to about 1,000°C. Maintain the rate of heating above this point at about 4-5°C. per minute until the pyramid begins to deform. Then slow the rate of heating down to about 2-3°C. per minute until the pyramid fuses to a blob.

Measure the temperature of the pyramid by means of an optical pyrometer, preferably of the disappearing filament type.

NOTE.—When a gas-fired furnace is used, the most convenient method of obtaining a mildly-reducing atmosphere is to introduce partially-burnt gas or a mixture of fresh and burnt gas into the interior of the muffle.

When an electric furnace is used introduce regulated streams of hydrogen and carbon dioxide supplied from cylinders.

TESTING LUBRICATING OILS.

Although there is no simple laboratory method for testing the important properties of oiliness or performance of lubricating oils under service conditions, methods have been laid down in "Standard Methods of Testing Petroleum and its Products" by the chemical standardization of the Institute of Petroleum for determining such properties as viscosity and flash-point, etc.

Of greater importance than the testing of new lubricating oils is the control of impurities in regenerated or reclaimed lubricating oils. Impurities which are known to be harmful when present in excessive quantities in lubricating oils can be detected by such determinations as water and solid matter, viscosity index, mineral acidity, saponification value, corrosion, carbon residue and crankcase dilution, etc.

(1) VISCOSITY.

In order to determine the viscosity index and the S.A.E. number of lubricating oils, having S.A.E. numbers between 10 and 40, the viscosity of the oil must be determined at least at three temperatures, i.e., 100°F. and 210°F. for viscosity index and 130°F. for S.A.E. number. Lubricating oils having S.A.E. numbers from 50 to 70 need have their viscosities determined at 100°F. and 210°F. only.

The Redwood (I.P.T. standard methods) or Saybolt viscosimeters may be used, but preferably the viscosity should be determined in absolute units, e.g., in the Ubbelohde Apparatus. (Zur Viskosimetri (1936) L. Ubbelohde Jnl. Inst. Petroleum Tech. 22, 32,41 (1936)).

The viscosity is expressed in Saybolt or Redwood seconds, the S.A.E. number can be obtained from the following table:—

Crankcase Oils S.A.E. No.	At 130°F.				At 210°F.			
	Saybolt Seconds.		Redwood Seconds.		Saybolt Seconds.		Redwood Seconds.	
	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.	Minimum.	Maximum.
10	90	< 120	78	< 104	—	—	—	—
20	120	< 185	104	< 161	—	—	—	—
30	185	< 255	161	< 225	—	—	—	—
40	255	—	225	—	—	< 80	—	< 69·5
50	—	—	—	—	80	< 105	69·5	< 90
60	—	—	—	—	105	< 125	90	< 107·5
70	—	—	—	—	125	< 150	107·5	< 129·5

A fairly reliable determination of the S.A.E. number can be obtained by determining the time required for an air-bubble of standard size to travel through a given column of oil in a standardized tube and comparing this with the time of travel when the tube contains oils of known S.A.E. number under otherwise identical conditions. Reference oils should preferably lie on the border between different S.A.E. numbers.

The viscosity index (Dean and Davis) is determined by the method outlined by Dean and Davis. Viscosity Variations of Oils with Temperature. Chemical and Metallurgical Engineering, Vol. 36, No. 10, page 618 (1929).

(2) Mineral Acidity.

Shake 100 grams of the oil vigorously in a tap funnel for one minute with an equal weight of warm distilled water, which should be neutral. Allow the water to separate and then run into a clean flask, cool and titrate with N/10 potassium hydroxide, using methyl orange as indicator. The result should show no free mineral acid.

(3) Saponification Value.

Mix a quantity of oil weighing about 5-7 grams, but not more than 10 grams, with 25 ml. of N/2 alcoholic KOH (free from carbonates). Boil the mixture vigorously for three hours under reflux. Thereupon cool rapidly and run 50 ml. of alcohol and 20 ml. of N/2 hydrochloric acid into the mixture from pipettes. Complete the titration using N/10 hydrochloric acid and Alkali Blau as indicator. Run a blank similarly and simultaneously. From the difference in quantity of acid required for blank and assay tests calculate the saponification value.

S.V. expressed as (mg. KOH/gram of sample) $= \frac{y \times 28{\cdot}05}{x}$

(y = ml. $\frac{N}{2}$ KOH used.)

(x = weight of sample.)

The saponification value as determined will represent the sum of free acid and saponifiable matter. Subtract the acidity value from the saponification value to obtain the saponifiable value.

Determine the acidity value thus:

(4) Total Acidity.

Weigh not less than 10 grams of the oil into a flask and add 50 ml. of 95 per cent of alcohol (neutral at 40° to 50°C.). Heat the mixture to boiling point on a water bath, allow to boil for five minutes, and shake well to ensure solution of the acids in the alcohol.

Add one millilitre of 0·5 per cent solution of phenolphthalein, and cool the mixture to 40° or 50°C. and titrate as quickly as possible with N/10 potassium hydroxide (free from carbonate).

Express the results as the number of milligrams of potassium hydroxide necessary to neutralize the acidity of one gram of the sample.

Holtzafel and Snyman give the following method for estimating acidity in highly coloured oils:—

Weigh out 20 grams of the oil and place in a 500 ml. Erlen-Meyer flask containing 100 ml. neutral carbon tetrachloride. Add 300 ml. pure distilled water, close the flask with a rubber bung and shake vigorously.

Titrate directly with N/10 sodium hydroxide using phenolphthalein as indicator. Shake and allow to settle after each addition of sodium hydroxide.

The oil settles in a few seconds.

By using this method the end point is easily seen.

(5) CORROSION.

Immerse in the oil a piece of copper foil 1 inch square polished by means of a piece of cotton wool and No. 150 carborundum powder and bent into the form of a cylinder. Heat the oil and its contents on a water bath at 100°C. (212°F.) for 12 hours. No appreciable discolouration of the copper should result.

(6) CONRADSON CARBON RESIDUE.

The apparatus consists of the following:—

(*a*) *Porcelain Crucible.*—Porcelain crucible, wide form, glazed throughout, or a silica crucible; 29 to 31 ml. capacity, 46 to 49 mm. (1·81 to 1·93 in.) in rim diameter.

(*b*) *Iron Crucible.*—Skidmore iron crucible, flanged and ringed, 65 to 82 ml. capacity, 53 to 57 mm. (2·07 to 2·20 in.) inside and 60 to 67 mm. (2·36 to 2·64 in.) outside diameter of flange, 37 to 39 mm. (1·46 to 1·54 in.) in height supplied with a cover without delivery tubes and having the vertical opening closed. The horizontal opening of about 6·5 mm. (0·26 in.) must be kept clean. The outside diameter of the flat bottom should be 30 to 32 mm. (1·18 to 1·26 in.).

(*c*) *Iron Crucible.*—Spun sheet-iron crucible, with cover; 78 to 82 mm. (3·07 to 3·23 in.) in outside diameter at the top, 58 to 60 mm. (approximately 2·3 in.) in height, and approximately 0·8 mm. (0·03 in.) in thickness. Place at the bottom of this crucible, and level before each test, a layer of about 25 ml. of dry sand, or enough to bring the Skidmore crucible, with cover on, nearly to the top of the sheet-iron crucible.

(*d*) *Wire Support.*—Triangle of bare nichrome wire, of approximately No. 15 I.W.G. gauge having an opening small enough to support the bottom of the sheet-iron crucible at the same level as the bottom of the asbestos block or hollow sheet-metal box, paragraph (*f*).

(*e*) *Hood.*—Circular sheet-iron hood, from 120 to 130 mm. ($4\frac{3}{4}$ to $5\frac{1}{4}$ in.) in diameter, the height of the lower perpendicular side to be from 50 to 53 mm. (2 to $2\frac{1}{8}$ in.); provided at the top with a chimney 50 to 60 mm. (2 to $2\frac{1}{2}$ in.) in height and from 50 to 56 mm. (2 to $2\frac{1}{4}$ in.) in inside diameter, which is attached to the lower part with the perpendicular sides by a cone-shaped member, bringing the total height of the complete hood from 125 to 130 mm. ($5\frac{1}{8}$ in.). The hood may be made from a single piece of metal provided the foregoing dimensions are adhered to. As a guide for the height of the flame above the chimney, attach a bridge made of approximately 3 mm. ($\frac{1}{8}$ in.) iron or nichrome wire, at a height of 50 mm. (2 in.) above the top of the chimney.

(*f*) *Insulator.*—Asbestos block, refractory ring, or hollow sheet-metal box, 150 to 175 mm. (6 to 7 in.) in diameter if round or on a side if square, 32 to 38 mm. ($1\frac{1}{4}$ to $1\frac{1}{2}$ in.) in thickness, provided with a metal-lined, inverted cone-shaped opening through the centre; 83 mm. ($3\frac{1}{4}$ in.) in diameter at the bottom, and 89 mm. ($3\frac{1}{2}$ in.) in diameter at the top.

In the case of the refractory ring no metal lining is necessary, provided the ring is of hard, heat-resistant material.

(*g*) *Burner.*—Burner, Meker type, 24 mm. (1 in.) in diameter by 155 mm. (6 in.) in height, suitable for either manufactured or natural gas.

PROCEDURE.—(*a*) Weigh to the nearest 5 mg. a 10 gram sample of the oil to be tested, free from moisture and other suspended matter, into a tared porcelain or silica crucible containing two glass beads about 0·1 in. in diameter. Place this crucible in the centre of the Skidmore crucible. Level the sand in the large sheet-iron crucible and set the Skidmore crucible on it in the exact centre of the iron crucible. Apply covers to both the Skidmore and the iron crucibles, the one to the latter fitting loosely to allow free exit to the vapours as formed.

(*b*) On a suitable stand or ring, place the bare nichrome wire triangle and on it the insulator. Next centre the sheet-iron crucible in the insulator with its bottom resting on top of the triangle, and cover the whole with the sheet-iron hood in order to distribute the heat uniformly during the process.

(*c*)Apply heat with a high, strong flame from the Meker-type gas burner, so that the pre-ignition period will be $10 \pm 1{\cdot}5$ min. (a shorter time may start the distillation so rapidly as to cause foaming or too high a flame). When smoke appears above the chimney, immediately move or tilt the burner so that the gas flame plays on the sides of the crucible for the purpose of igniting the vapours. Then remove the heat temporarily, and before replacing, adjust by screwing down the pinch-cock on the gas tubing so that the ignited vapours burn uniformly with the flame above the chimney but not above the wire bridge. Heat may be increased, if necessary, when the flame does not show above the chimney. The period of burning the vapours should be 13 ± 1 min. If it is found impossible to meet the requirements for both flame and burning time, the requirement for burning time is the more important.

(*d*) When the vapours cease to burn and no further blue smoke can be observed, readjust the burner and hold the heat as at the beginning so as to make the bottom and lower part of the sheet-iron crucible a cherry red and maintain for exactly 7 min. The total period of heating should be 30 ± 2 min. which constitutes an additional limitation on the tolerances for the pre-ignition and burning periods. There should be no difficulty in carrying out the test exactly as directed with the gas burner of the type named, using city gas (about 550 B.Th.U.) with the top of the burner about 2 inches below the bottom of the crucible. The time periods should be observed with whatever burner and gas is used.

(*e*) Remove the burner and allow the apparatus to cool until no smoke appears (about 15 minutes), and then remove the cover of the Skidmore crucible. Remove the porcelain or silica crucible with heated tongs, place in the desiccator, cool and weigh. Calculate the percentage of carbon residue on the original sample.

(7) CRANK-CASE DILUTION:

APPARATUS.—(*a*) *General.*—The apparatus consists of a glass flask heated by a gas-burner flame or electricity, and provided with a reflux water condenser discharging into a trap for collecting the distillate. The trap serves to collect and measure the diluent, returning condensed water to the still.

(*b*) *Trap.*—The trap is made of well-annealed glass, graduated from 0 to 12·5 ml. in 0·1 ml. divisions. The error of any indicated capacity must not be greater than 0·05 ml.

(*c*) *Flask.*—The glass flask is of the short-neck, round-bottom type, with a nominal capacity of one litre.

(*d*) *Condenser.*—The condenser is of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 9·5 to 12·7 mm. (⅜ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap is ground off at an angle of 60°.

(*e*) *Burner.*—The gas burner should preferably be of the Meker type, 1 in. in diameter, and the orifice used should be such that a narrow flame coming to a point about 4 in. above the top of the burner can be obtained.

PROCEDURE.—(1) Mix the sample thoroughly and measure 25 ml. into a 25 ml. graduated cylinder and transfer to the flask. By washing out the cylinder with hot water only a negligible amount of oil will be left in the graduated cylinder. Add approximately 500 ml. of water to the flask and assemble the flask, after filling the trap with water. Place the tip of the condenser directly over the indentation in the trap.

(2) Apply heat with the full flame as indicated in paragraph (*a*). The rate should be such that refluxing starts within from 7-10 minutes after the heat is applied, the water being at room temperature initially.

N.B.—Success of the method depends upon heating at such a rate that boiling is continuous and vigorous enough to prevent the oil from forming, even momentarily, a continuous film on top of the water.

NOTE 1.—As a check on the rate of distillation, make a determination on a fresh oil containing 15 per cent of added diluent. The oil used should have a flash point of 400°F. or over and the diluent used should have an initial boiling point of 300 to 320°F. and an end point of 400 to 420°F. At least 13·5 per cent of the diluent should be obtained by this method on boiling for 60 minutes.

NOTE 2.—Bumping with a tendency to froth over is often experienced with dirty oils and may be prevented in several ways, namely, by the addition of bits of broken glass, by the addition of steel wool, or by the addition of about 5 ml. of concentrated hydrochloric acid.

(3) Make readings of the amount of diluent at the following times, taken from the time that refluxing starts; 5, 15, and 30 min., and each 15 min. following, until the test is complete.

Determine the completion of the test on the basis of either or both of the following criteria:—

No. 1.—Test is complete when the volume of diluent increases by not more than 0·1 ml. in any 15 min. period during the course of the test.

No. 2.—Test is complete when the volume of diluent obtained in a given time indicates completion, as follows:—

Time from start of refluxing.	*Test is completed if apparent volume of diluent collected is equal to or less than*
5 min.	0·1 ml.*
30 min.	2·0 ml.
60 min.	4·0 ml.
90 min.	7·0 ml.

*Report as "No dilution".

(4) Generally, criterion No. 1 defines the completion of the test, but when the test continues to a point at which any of the conditions described under criterion No. 2 are encountered, the latter defines the completion of the test.

(5) When the test is complete by either of the criteria in paragraph (3) the heat is turned off. After standing at least 15 minutes, to allow the distillate to settle clear and to cool to approximately room temperature, the volume of diluent is read. The percentage dilution is obtained by multiplying this final volume by four.

Testing of Fuel Oils.

For buying and storing purposes it is generally sufficient to test the calorific value and the flash-point of the oil.

Calorific Values.

The calorific value of diesel and heavy fuel oils is determined the same way as that of coal. When the calorific value of light volatile oils such as petrol is being determined certain precautions are necessary. The quantity of petrol taken should not exceed 0·3 gm. and it should be sealed into a glass capsule strong enough not to collapse under the oxygen pressure in the bomb. The sealed capsule containing the petrol is placed in the crucible together with about 0·1 to 0·2 gm. of medicinal paraffin of known calorific value, the firing of which breaks the glass capsule. As in the case of the calorific value determination of coke a correction is made for the heat generated by the medicinal paraffin.

Flash-Point Determination.

For oils having a flash-point below 120°F. the Abel apparatus is used. In the case of oils having a flash-point between 90°F. and 120°F. the method is slightly modified—the air chamber which surrounds the oil cup is filled with cold water at a depth of 1·5 in., and the heating vessel or water bath filled as usual, but also with cold water. The temperature of the oil is raised at the rate of 2°F. to 2·25°F. per minute and test flame first applied when the temperature has reached 80°F. For oils having a flash-point above 120°F. the Pensky-Martens apparatus is used. A full description of the Abel and Pensky-Martens apparatus and the two methods of procedure are given in "Standard Methods of testing Petroleum and its Products".

Acknowledgement is made to the Institute of Petroleum from whose publications quotations have been taken. To keep up-to-date readers are advised to study these publications which are revised periodically.

Chapter XVI.

THE ANALYSIS OF MINE STORES.

Borax.

This material is usually supplied to the mines as fused borax, $Na_2B_4O_7$. It can also be obtained in two hydrated forms, the one containing 5 molecules, and the other 10 molecules of water of crystallization.

Alkali borates react to methyl orange as if they were solutions of hydroxides; the free boric acid producing no colour change in methyl orange. The total soda may be determined by titrating with standard acid using this indicator.

$$\begin{aligned} 1 \text{ ml. N/10 hydrochloric acid} &\equiv 0{\cdot}0031 \text{ gram } Na_2O \\ &\equiv 0{\cdot}0101 \text{ gram } Na_2B_4O_7. \end{aligned}$$

If adulteration with an alkali is suspected, the boric acid content must be determined.

Procedure.—Weigh out 2 grams of the finely agated material and dissolve in freshly boiled distilled water, heating if necessary (the dehydrated salt is not easily dissolved). Cool and make up to 250 ml. Determine the total alkali in 50 ml. of this solution by titrating with N/10 hydrochloric acid using methyl orange as indicator.

Exactly neutralize another 50 ml. of the solution by adding the same quantity of hydrochloric acid indicated by the previous titration. This will produce boric acid corresponding to the amount of borate present in the solution. Boil for a few minutes in a flask fitted with a reflux condenser to expel carbon dioxide which will be present if the borax contains carbonates. The condenser will return the slightly volatile boric acid. Remove from the source of heat, rinse the condenser into the flask and cool Add 25 grams of glycerol (Glycerine) and titrate with N/10 sodium hydroxide using phenolphthalein as indicator. When the pink colour of the indicator appears add a further 10 grams of glycerol. Should this addition discharge the pink colour continue the titration and repeat this procedure until the pink colour is no longer discharged by the addition of more glycerol.

$$2B_2O_3.6H_2O + 4NaOH = 4NaBO_2 + 8H_2O$$

$$\begin{aligned} 1 \text{ ml. N/10 NaOH} &\equiv 0{\cdot}0035 \text{ gram } B_2O_3 \\ &\equiv 0{\cdot}00505 \text{ gram } Na_2B_4O_7. \end{aligned}$$

Water is determined by loss on strong ignition. Chlorides, if present, are determined in the usual manner by titration with standard silver nitrate using potassium chromate as indicator.

The Sampling and Analysis of Calcium Carbide.

Carbide is usually delivered in 200 lb. drums with a screw type lid.

The minimum number of drums to be sampled depends on the size of the consignment according to the following table:

Weight of Consignment.	*Minimum No. of Drums.*
60 lb. — 1 ton	1 drum
1 ton — 2 tons	2 drums
2 tons— 10 tons	3 ,,
10 tons— 50 tons	4 ,,
50 tons—100 tons	5 ,,
Over 100 tons	6 ,,

Sampling.

Precautions.—Owing to the affinity which carbide has for moisture all sampling and handling must be done as rapidly as possible and the sample must not be handled with bare hands. The sampling time should not exceed 5 minutes per drum.

Method of Sampling.—The drum is opened and the contents are spread out on a level floor covered with waterproof material. Four equal scoops are taken from different places and put into a sample container which is carefully sealed to exclude air or moisture. The sample should weigh not less than 7 lb. The remaining carbide is replaced in its original drum, the floor swept, and the next drum opened and sampled in a similar manner. Thus if you have a consignment of 2-10 tons of carbide, you should have at least 3 separate samples.

Each sample in turn must now be crushed to approximately 7 mm. (approx. $\frac{1}{4}$ in.), but not bigger than 20 mm. (approx. $\frac{3}{4}$ in.), and re-sealed in its container.

Analysis. Method 1.

The gravimetric method—i.e., weighing the amount of liberated dry acetylene gas.

Apparatus.—The apparatus consists of a 1,000 ml. conical flask to which is fitted a 3 holed rubber bung. Through the first hole is a straight stop cock. In the second hole is a separating funnel, the end of which is drawn to a point. The glass stopper of the funnel is replaced by a rubber bung through which passes a piece of glass tubing, also drawn to a point. To the third hole in the rubber bung in the conical flask is fitted a delivery tube connected to a drying tube of calcium chloride. This piece of apparatus while in use is kept in a water bath of flowing water at approximately 15°C.

Method.—The separating funnel is filled with saturated salt solution and fitted to the conical flask. Any adhering moisture is wiped off and nitrogen gas is passed through the apparatus by way of the straight stopcock for two minutes. The stopcock is then closed and the nitrogen bottle is disconnected. The apparatus is weighed in grams to within 20 mgm.

The sample container is opened, the contents sieved through a 1 mm. mesh sieve (approximately 20 mesh Tyler) and all the minus product is discarded. This is regarded as dust and if retained in the sample will give

a low result. (Incidentally the makers allow for 5 per cent dust in each drum.) The plus product is then placed on a sheet of paper and given a quick mixing.

By means of a spatula or scoop, taking dip samples, approximately 200-250 grams of carbide is placed in the conical flask. The rubber ring, with funnel, etc., is replaced and the apparatus is again swept with nitrogen and weighed as before. The difference in weight gives the weight of carbide.

The whole apparatus is placed in water and the stopcock of the funnel is opened so that the saturated salt solution drips from the tapered end of the funnel at the rate of one drop per second.

After the dripping has been allowed to continue for 6 hours, the stopcock is turned off and the apparatus is allowed to stand for another two hours, when all reaction between the carbide and the salt solution will be complete.

The apparatus is removed from the water bath, dried, and nitrogen is passed through as before until all smell of acetylene has disappeared at the outlet. The nitrogen bottle is disconnected and the apparatus is again weighed. The loss in weight will give the weight of acetylene gas liberated.

The formula for calculation is:—

$$\frac{\text{Wt. of gas in grams}}{\text{Wt. of carbide in grams}} \times 14{\cdot}43 = \text{cubic ft. acetylene/lb. carbide at 60 F. and 30" mercury.}$$

The average carbide supplied to the mines should yield not less than 4·560 cu. ft./lb.

Testing for Impurities.

After allowing the gas liberated by the method just described to pass through the apparatus until all the nitrogen has been displaced, a portion is collected over saturated salt water. 100 ml. of this gas is drawn into an Orsat apparatus and passed into a tube containing fuming sulphuric acid until a constant reading is obtained. After each passage through the fuming sulphuric acid, the gas is passed into a potassium hydroxide solution to remove any acid vapours.

The residual gas, insoluble in the fuming sulphuric, gives the percentage impurities.

The harmful impurities found in acetylene are sulphur compounds reported as H_2S with an allowable maximum of 0·15 per cent. and phosphorus compounds reported as PH_3 with an allowable maximum of 0·06 per cent.

Testing for Hydrogen Sulphide.

Reagents required are:

Sodium Hypochlorite
Concentrated Nitric Acid (sp. gr. 1·400)
Hydrochloric Acid (5 per cent solution)
Barium Chloride (10 per cent solution)
Hot distilled water.

The sodium hypochlorite is prepared by passing chlorine into caustic soda solution, diluting, and then saturating with sodium bicarbonate *in excess*. Available chlorine must not be less than 0·5 per cent.

To the calcium chloride tube of the carbide apparatus previously described, two 10 bulb absorption tubes are attached in series. These contain 100 and 50 ml. of sodium hypochlorite respectively. A blank sulphur and phosphorus determination must be made on an equivalent amount of the hypochlorite solution.

A minimum of 70 grams of screened calcium carbide is added to the apparatus, and the procedure for the generation of the gas previously described is repeated. After complete decomposition of the carbide the sodium hypochlorite is transferred to a beaker and boiled until free of acetylene. This solution is now oxidized by adding small successive quantities of nitric acid, taken to dryness, baked and redissolved in warm distilled water. It is then acidified with hydrochloric acid and filtered. The filtrate is brought to the boil and 10 ml. of a 10 per cent solution of barium chloride is added and the whole allowed to stand for some hours to allow for complete precipitation of barium sulphate. The barium sulphate is filtered off, washed till free of chlorides, dried, ignited and weighed.

Calculation:

$$\frac{\text{Wt. of barium sulphate in grams}}{\text{Wt. of gas in grams}} \times 11{\cdot}25 = \text{per cent by volume of hydrogen sulphide.}$$

Testing for Phosphorus.

The Ammonium Phospho-Molybdate method is used on the filtrate from the sulphur determination.

Reagents required.—Ammonium Molybdate solution. This is prepared by dissolving 50 grams ammonium molybdate in 100 ml. water, 100 ml. ammonium hydroxide is added and poured in successive quantities into 750 ml. nitric acid. The mixture is kept cool while adding, and then allowed to stand for 3 hours, after which it is filtered.

Ammonium Hydroxide	(sp. gr. 0·88)
Nitric Acid	(sp. gr. 1·400)
Nitric Acid	(1 per cent solution)
Potassium Nitrate	(1 per cent solution)
Sodium Hydroxide	(N/5 solution)
Sulphuric Acid	(N/5 solution)

Method.—The filtrate from the sulphur determination is neutralized with ammonium hydroxide, then made slightly acid with nitric acid, warmed to 70°C., 30 ml. ammonium molybdate solution added, and the whole is placed on a warm plate for one hour to precipitate the phospho-molybdate. The precipitate is transferred to a Gooch crucible and washed with one per cent nitric acid and then washed free of acid with one per cent potassium nitrate. The precipitate is transferred to a beaker and dissolved in 50 ml. N/5 sodium hydroxide.

The excess sodium hydroxide is titrated with N/5 sulphuric acid using phenolphthalein as an internal indicator.

The formula for calculation is:

$$\frac{(b - c)\,N \times 0{\cdot}1139}{W \times 5} = \text{per cent } PH_3 \text{ by volume.}$$

W is weight of gas
b is total NaOH used
N is normality factor of standard acid (H_2SO_4)
c is number of ml. standard H_2SO_4, i.e., excess NaOH.

Buying and Selling of Calcium Carbide.

Buyers may claim a rebate in price and sellers a higher figure if the gas yield is lower or higher respectively than the following figures:—

Carbide graded between:

15—120 mm.	. . . . .	4·56 cu. ft./lb.
7— 15 ,,	. . . . .	4·32 ,,
4— 7 ,,	. . . . .	4·08 ,,
2— 4 ,,	. . . . .	3·84 ,,
1— 2 ,,	. . . . .	3·60 ,,

The buyers may also refuse to accept delivery of carbide with a gas yield below the following:

15—120 mm.	. . . . .	4·32 cu. ft./lb.
7— 15 ,,	. . . . .	4·08 ,,
4— 7 ,,	. . . . .	3·84 ,,
2— 4 ,,	. . . . .	3·60 ,,
1— 2 ,,	. . . . .	3·42 ,,

ANALYSIS. METHOD 2.

The volumetric method—i.e., measuring the volume of the liberated gas.

This is not a standard method but is useful for doing quick estimations on large consignments.

The apparatus required for this method consists of a cylinder measuring 3 ft. × 8 in. diameter, to which is attached a calibrated glass tube indicating the number of ml. inside the cylinder. The generating flask is as previously described but with only a separating funnel and delivery tube attached. The tube is connected to the top of the cylinder. On the side, near the bottom of the cylinder, is an outlet tube attached to a reservoir open to the air. The reservoir is also fitted with a glass tube down the one side but this is not graduated. The reservoir required for the above size cylinder is equal to a four gallon paraffin tin.

Method.—The reservoir is filled with water saturated with either salt or acetylene, and the reservoir is then raised until the water fills the cylinder to the zero mark on the calibrated glass tube.

60 grams of previously sieved and mixed carbide, crushed as previously described, is accurately weighed out and placed in the generating flask. The stopper with funnel, etc., is replaced and the stopcock of the separating funnel, previously filled with water saturated with either salt or acetylene, is opened.

Care must be taken to allow only a small quantity of saturated water to react with the carbide at a time. The reservoir is lowered to allow the liberated acetylene to pass into the cylinder, the gas displacing the water.

When the reaction in the generating flask is complete, which takes about 20 minutes, the reservoir is raised or lowered until the water in each container is at the same level so that pressure inside the cylinder is the same as atmospheric pressure. The amount of water displaced is read off. This is equivalent to the volume of the gas liberated. The results are calculated as follows:—

Multiply number of ml. gas by 0·0004272. This gives cu. ft. acetylene at 60°F. and 30″ mercury per lb. carbide.

Four estimations on each sample are sufficient for an accurate average.

Determination of Available Chlorine in Bleaching Powder (Chloride of Lime).

The sample is well but quickly mixed and 5 grams are weighed out. This is placed in a mortar and a little water is added. The mixture is rubbed to a smooth cream. More water is then rubbed in with the pestle, when the mixture is allowed to settle a short while and then poured off into a litre flask. The sediment is again rubbed with water and poured off. This is repeated until the whole of the sample is conveyed into the flask without loss and the mortar washed quite clean. The flask is then filled to the mark with distilled water, well shaken and 20 ml. of the milky liquid is taken out with a pipette, emptied into a beaker, and an excess of a solution of potassium iodide added.

$$Cl_2 + 2KI = 2KCl + I_2$$

The mixture is diluted somewhat, acidified with acetic acid, and the liberated iodine titrated with N/10 thiosulphate and starch.

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

1 ml. N/10 thiosulphate solution $\equiv 0{\cdot}003546$ gram chlorine.

Ferrosilicon.

Ferrosilicon is used extensively in heavy media separation processes for the control of gravities. The following determinations may be called for:—

A. Grading.
B. Specific Gravity.
C. Non Magnetic Material.
D. Silicon.
E. Iron.
F. Carbon.

Grading.

100 grams of the sample is weighed out and graded through the following set of Tyler Standard Screens: 48, 100, 200, 325.

Specific Gravity.

Normally the specific gravity may be determined directly against water, using a 50 ml. specific gravity bottle and 10 grams of the sample. The sample, however, may contain particles having a high surface-tension making it impossible to wet it completely with water. When this condition occurs, numerous particles of ferrosilicon will be seen floating on the surface of the water. In these circumstances the specific gravity is determined using paraffin in place of water, the resultant specific gravity relative to paraffin being multiplied by the specific gravity of paraffin to give a correct result. Specific gravity of ferrosilicon relative to paraffin multiplied by specific gravity of paraffin equals True Specific Gravity.

Non-Magnetic Material.

For this determination, 10 grams of the sample is weighed out and spread on a piece of black glazed paper. A magnet enclosed in a paper bag, or some other non-magnetic material, is passed over the surface of the ferro-

silicon. The magnetic material adhering to the undersurface of the paper bag is transferred to another sheet of glazed paper where it is deposited by pulling the paper bag away from the magnet. Should the above procedure not be observed, difficulty will be experienced in releasing the magnetic particles from the magnet.

The non-magnetic material remaining is collected, and the operation described above is repeated until no further separation is obtained, then the accumulated non-magnetic portions are weighed and reported as a percentage.

Silicon.

Duplicate portions of ·5 gram of the sample are mixed intimately with 3 grams of sodium peroxide in a 50 ml. nickel crucible and fused over a flame, commencing at a low heat and finishing very hot. Should the reaction be too violent due to the presence of finely divided uncombined silicon, use 5 grams of sodium carbonate, or 5 grams of fusion mixture (4 parts Na_2CO_3, 1 part KNO_3) in place of the sodium peroxide and proceed as above.

N.B. Ferrosilicon does not digest satisfactorily with mineral acids. After fusion, allow the melt to cool and leach into a 250 ml. beaker containing 25 ml. concentrated sulphuric acid in 100 ml. water. Boil and evaporate to strong fumes for half an hour. This will dehydrate or "fix" the silica previously converted to a soluble form (silicic acid) by the fusion. The solution is cooled, diluted to 200 ml. with water, boiled and filtered through a wet, Whatman No. 40 filter paper. The residue is washed several times with hot water and is then transferred to a platinum crucible, dried, ignited, cooled in a desiccator and the crucible plus contents is weighed. 4 drops of concentrated sulphuric acid and 20 ml. pure hydrofluoric acid are now added. The hydrofluoric acid is boiled off and the remainder is taken to fumes. The crucible is placed in a hot muffle for several minutes, withdrawn, cooled and again weighed. The loss in weight is due to silica and is reported as silicon.

$$\% \ SiO_2 \times \frac{28{\cdot}06}{60{\cdot}06} = Si\%$$

N.B. The silica present is volatilized as silicon tetrafluoride.

(Note.—The HF must be pure or else allowance for impurities must be made. See "Working Hints", Chapter XVII.)

Iron.

The filtrate from the silica determination is made up to 500 ml. and an aliquot portion, say 100 ml. is used for the iron determination. Any one of the standard volumetric or gravimetric methods may be used.

Carbon.

Carbon in ferrosilicon is determined in a manner similar to the assay of carbon in steel. 2 grams of the sample is mixed with 5 grams of carbon-free red lead in an alundum combustion boat. This is placed in a combustion furnace and the carbon dioxide evolved is collected in the usual manner in a 20 per cent solution of potassium hydroxide.

Kaffir Beer—Percentage Alcohol.

The principle of the method is to distil the liquid until all the alcohol has passed over with the distillate.

The volume of the distillate must be exactly equal to the volume of beer taken because the underlying principle is to obtain a solution of alcohol in water which contains the same amount of alcohol per unit volume as does the beer.

The beer should be analysed as soon as received; if this is not convenient a little sulphuric acid or mercuric chloride should be added to arrest fermentation.

Method.—100 ml. of the beer is taken, placed in a 500 ml. distillation flask, and a little caustic soda or milk of lime is added (this removes free carbon dioxide, acetic or other volatile acids). The volume is then made up to 250 ml. with distilled water and the flask attached to a Liebig condenser. Heat is applied gently until the boiling point is reached. Gentle boiling is continued until about 80 ml. of distillate is obtained.

(Note.—If the beer is boiled too violently at first there is danger of losing alcohol due to incomplete condensation. Alcohol boils at 78°C. and it will all pass over with the first few ml. of distillate.)

The distillate is made up to exactly 100 ml. and then cooled to 15·5°C. An empty specific gravity flask is brought to the same temperature, filled to the mark, wiped dry, and weighed. The weighing is repeated with the flask full of distilled water also at 15·5°C. The weight of the dry flask is subtracted and the specific gravity of the distillate is calculated. The percentage of alcohol is obtained by reference to the alcohol tables (See Appendix).

Most alcohol tables are calculated for a temperature of 15·5°C., but if the tables used have been calculated for a different temperature the specific gravity of the distillate must be determined at that particular temperature.

Lead Acetate.

5 grams of the lead acetate sample is weighed out, dissolved in distilled water, and made up to 500 ml.

This is filtered and aliquot portions of 50 ml. are taken to which 2 ml. of acetic acid are added. The solution is diluted slightly, heated to boiling and titrated with ammonium molybdate, using a solution of tannin, on a spot plate, as indicator.

The ammonium molybdate is made up by dissolving 9 grams of the reagent in one litre of water. The solution is standardized against pure lead.

$$(NH_4)_2MoO_4 + Pb(C_2H_3O_2)_2 = PbMoO_4 + 2NH_4C_2H_3O_2$$

1 ml. ammonium molybdate ≡ 0·0095 gram lead.

$Pb \times 1{\cdot}831 = Pb(C_2H_3O_2)_2.3H_2O$ (Lead acetate)

The Sampling of Lime and the Estimation of Available CaO.

Method of Sampling.

As lime is not delivered in airtight containers, the operations of sampling should be carried out as soon as possible after arrival at the

mine, but in no case later than 24 hours thereafter. Sampling operations should be carried out under cover, preferably in a shed which can be set aside solely for this purpose. The breaking and quartering operations are carried out on a clean surface that will not break or mix up with the lime or have any action upon it. A good cement or steel surface would be found to meet these requirements. A wooden floor should not be used. The place where the sampling is performed must be removed from all sources of contamination by carbon dioxide and water. The operations of sampling must be carried out as quickly as possible to prevent undue exposure to atmospheric influences. In all cases where the degree of fineness is specified, this should be taken only as a guide, and actual sieving should be avoided.

Unslaked Lump Lime.—When sampling unslaked lump lime, put up in bags containing approximately 200 lb., one of the following methods may be adopted:—

(*a*) Where crushing machines are not available or when it is not desired to crush the lime before use:

Two bags are taken from each truck. These are then turned out and crushed until fine enough to pass through a $1\frac{1}{2}''$ linear mesh sieve. The product is then mixed and quartered down three times in the usual manner until a sample of approximately one-eighth of the original amount has been obtained. This is crushed until it is fine enough to pass through a sieve of $\frac{1}{2}''$ linear mesh and the product again mixed and quartered down until a sample of 10 to 20 lb. has been obtained. This product is then crushed until fine enough to pass through a I.M.M. Standard 30 mesh linear screen (aperture 0·0166 inch) (N.B.—Tyler 35 linear mesh has an aperture of 0·0164 inch) and reduced by successive quartering until a sample of about 3—4 lb. in weight is obtained. This is spread out evenly on a clean surface. By dipping at regular intervals over the whole surface three amounts sufficient to fill three bottles or air-tight tins or containers of not less than 4 oz. capacity are obtained.

(*b*) Where suitable crushing machinery (e.g., a ball mill) is available:

The bags selected as in (*a*) above should be emptied into the crusher, and, as the contents discharge, portions should be taken with a shovel or scoop at regular intervals. The portions thus abstracted must not be less than 5 per cent in weight, with a minimum of 30 lb., of the sample crushed, a minimum of 20 portions being taken. These are then thoroughly mixed on a suitable floor and quartered down until a sample of about 3—4 lb. is obtained, which is then treated as in method (*a*).

(*c*) When sampling lump unslaked lime in trucks, the following method of sampling should be adopted:

After the truck has been partially discharged, samples of lime are taken from the length of the exposed faces, so that a total sample of 200 lb. weight is obtained. This sample is crushed to approximately $\frac{3}{4}''$ size and then mixed and quartered down until a sample of $1\frac{1}{2}$ to 2 lb. is obtained. This product is then crushed until fine enough to pass through a 30 mesh linear screen. After spreading out evenly on a clean surface this sample is dipped at regular intervals over the whole surface to give an amount sufficient to fill three 4-oz. bottles. A disc grinder of the Braun or Hush type is suitable for the final grinding.

Every endeavour should be made to minimize the exposure of the sample to the atmosphere.

Ground or Crushed Lime and Slaked Lime.—A sample of at least 1 lb. is taken by means of a grain sampler from every twentieth bag in the consignment and placed immediately in an air-tight container. The quantity thus obtained is thoroughly mixed and, if necessary, quartered down to 3—4 lb. as in method (*a*).

NOTE.—The final samples of about 4 oz. weight should be enclosed in bottles with tightly fitting dry stoppers or in such other receptacles as will entirely prevent admission of air. Before transmission for analysis, the receptacle must be sealed and securely packed in such a manner that the sample may not be injured in any way during transit.

TESTING (CaO).

The sample, which is fine enough to pass through a 30-mesh sieve, is contained in an air-tight vessel. It is crushed as rapidly as possible until it is sufficiently fine to pass through an I.M.M. Standard 60 linear mesh screen (aperture 0·0083) or Tyler 65 linear mesh screen (aperture 0·0082), but actual sieving should be avoided. It is then returned to the receptacle to prevent unnecessary exposure to the air.

Analysis.—The whole sample is spread out in a layer about $\frac{1}{2}''$ thick on glazed paper and rather more than 2 grams dipped out in small quantities from a number of points. This 2 gram portion is reduced in an agate mortar to a fine powder free from grit. 2 grams of this are carefully weighed out and agitated with 1 litre of a 2 per cent cane sugar solution free from carbon dioxide or 1 gram with $\frac{1}{2}$ litre of 2 per cent sugar solution.

If a shaking machine is available, two hours continuous agitation should be given. If not, three hours intermittent agitation—i.e., shaken not less frequently than once in five minutes, every care being taken to prevent coagulation of the lime.

After agitation the solution is filtered, the first 100 ml. being rejected, and 50 ml. of the filtrate is titrated with N/10 or N/5 sulphuric acid using rosolic acid as indicator; or the solution is allowed to stand until clear and 50 ml. of the clear solution is pipetted off and titrated as above. Undue exposure to the atmosphere must be avoided during titration.

Calculation:

$$\underset{56\cdot08}{CaO} + \underset{98\cdot082}{H_2SO_4} = CaSO_4 + H_2O$$

1 litre N/10 sulphuric $\equiv$ 2·804 grams CaO

1 ml. N/10 sulphuric $\equiv$ 0·002804 grams CaO

If 50 ml. were taken for titration and this required x ml. N/10 sulphuric,

then 50 ml. contain $x \times 0\cdot002804$ grams CaO

1,000 ml. contain $x \times 0\cdot002804 \times 20$ grams CaO

i.e. 2 grams lime contain $x \times 0\cdot002804 \times 20$ grams CaO

$$\text{Percentage available CaO} = x \times \frac{0\cdot002804 \times 20}{2} \times 100$$

$$= x \times 2\cdot804\%$$

Number of ml. N/10 acid taken multiplied by 2·804 gives the percentage CaO when using the above quantities.

Estimation of Available Oxygen in Commercial Manganese Dioxide.

The method depends on the reaction of manganese dioxide and oxalic acid in presence of sulphuric acid.

$$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2$$

The oxalic acid converts the manganese dioxide to the MnO condition.

$$MnO_2 + H_2C_2O_4 = MnO + H_2O + 2CO_2$$

and the sulphuric acid converts the manganese oxide to the sulphate.

$$MnO + H_2SO_4 = MnSO_4 + H_2O$$

Thus only one atom of oxygen is available for the oxidation of the oxalic acid.

The crystallized oxalic acid has the formula: $H_2C_2O_4.2H_2O$ with molecular weight 126·068, so that 86·93 parts of manganese dioxide, containing 16 parts available oxygen, would react theoretically with 126·068 parts of crystallized oxalic acid. In practice a known excess of oxalic acid is used, and the residue after reaction is titrated with standard permanganate solution.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Method.—5 grams of sample and 7·5 grams of oxalic acid are weighed out and transferred to a conical flask of about 750 ml. capacity. About 250 ml. of water and about 20 ml. sulphuric acid (pure) are added and the flask is allowed to stand on a water-bath until the reaction is complete and only gangue is left. The solution is filtered into a graduated litre flask, washed well and when cool is made up to the mark. 100 ml. of this solution is heated to 80°C., and the excess of oxalic acid is titrated with N/10 potassium permanganate.

Assume that x ml. of permanganate are required.

1 ml. of N/10 potassium permanganate = 0·0063 gram oxalic acid.

Multiply by 10 for a litre of filtrate.

(10x × 0·0063) grams = total oxalic acid left in the litre flask, to be deducted from the original 7·5 grams.

$(7{\cdot}5 - 0{\cdot}063x) \times \frac{86{\cdot}93}{126{\cdot}068}$ = grams manganese dioxide in 5 grams of sample, from which the percentage is calculated.

The "available oxygen" is the percentage of manganese dioxide multiplied by $\frac{16}{86{\cdot}93} = 0{\cdot}1841$.

Determination of Potassium Cyanide in Cyanide Supplies.

The sample must be taken immediately the case is opened and kept in a sealed bottle. 5 grams of the quickly powdered sample is dissolved in distilled water, previously boiled and cooled, and made up to 500 ml. 25 ml. is titrated in a flask with N/20 silver nitrate, using potassium iodide as indicator. 1 ml. N/20 silver nitrate indicates 2·6 per cent KCN.

Care must be taken throughout that the sample on which the determination is to be made is exposed to the air for as short a time as possible as moisture and carbon dioxide react very quickly with sodium and potassium cyanide.

Sampling and Valuation of "Aero" Brand Cyanide.

Sampling.

Ten drums of each lot of 4,000 lb. must be sampled. The combined weight of the sample should be one pound.

The sample is taken by inserting a sampling rod the full depth of each drum.

Estimation of Total Cyanide.

Reagents.

Standard N/10 Silver Nitrate.—17 grams of pure silver nitrate is dissolved in 200 ml. of distilled water, filtered and made up to one litre.

Soda-Lead Mixture.—200 grams of anhydrous sodium carbonate is dissolved in 700 ml. water and filtered. Then 20 grams of lead acetate ($Pb(CH_3CO_2)_23H_2O$) is dissolved in 200 ml. water. The latter is filtered and the filtrate is added to the sodium carbonate solution. The mixture should be well shaken before being used.

Alkaline Iodide Indicator.—30 grams potassium iodide is dissolved in a litre of 10 per cent sodium hydroxide solution.

Standardization.

The silver nitrate is standardized against an accurately weighed sample of pure sodium chloride previously dried for one hour at 105°C.

Determination.

200 ml. water is placed in a 500 ml. volumetric flask and the neck of the flask is carefully dried.

A 5 gram sample of the flake cyanide is rapidly and accurately weighed and transferred to the flask by means of glazed paper. The sides of the flask are washed down and the contents are mixed with a swirling motion. The flask is agitated at intervals for 15 minutes and then 30 ml. of the soda-lead solution is added, the latter being well mixed before measuring. The solution is agitated every five minutes for half an hour. The volume is then made up, the solution is thoroughly mixed and it is filtered through a dry filter into a dry flask. The first 25 ml. is rejected, the beaker being rinsed with the rejected portion. The filtration is continued until at least 150 ml. has been collected.

100 ml. of the filtered solution is measured out, placed in an 800 ml. beaker, diluted to 400 ml. and 5 ml. of the indicator solution is added.

This solution is titrated with the standard silver nitrate solution until a faint blue opalescence shows permanently against a black background.

$$AgNO_3 + 2NaCN = AgNa(CN)_2 + NaNO_3$$

1 ml. N/10 silver nitrate $\equiv 0{\cdot}0098$ grams sodium cyanide.

or $\equiv 0{\cdot}013$ grams potassium cyanide.

The action of the soda-lead solution is to precipitate any soluble sulphides, which may interfere with the titration end point, as lead sulphide. The sodium carbonate reacts with the calcium cyanide to form an equivalent quantity of sodium cyanide, the calcium being precipitated as the insoluble calcium carbonate.

Sampling and Valuation of Liquid Cyanide.

Sampling.

Liquid cyanide is usually transported in road tank wagons and pumped into storage tanks on the mine. A sampling cock should be provided on the transfer line and a continuous sample run into a Winchester quart bottle throughout the time the cyanide is being transferred.

When transfer is complete, the Winchester bottle is thoroughly shaken and poured into three sample bottles. One sample is for the Buyer, one for the Seller and one is kept as a check.

Valuation of Total Cyanide.

Method.

Reagents.—(1) Approximately ten per cent solution of potassium iodide.
(2) Standard N/10 silver nitrate.

Standardization.—The N/10 silver nitrate is standardized against pure, dry sodium chloride, using potassium chromate as indicator.

1 ml. N/10 $AgNO_3$. ≡ 0·005846 gram NaCl.

Procedure.—Fill a Lunge-Rey pipette, which has been previously twice rinsed with the freshly shaken sample, and weigh. Run about 2½ grams of sample into approximately 300 ml. distilled water in a 400 ml. flask. The tip of the pipette should be kept close to the surface of the water. Add five drops of the potassium iodide indicator and titrate immediately against the standard silver nitrate solution. Before titration wet the bottom of the beaker and during the titration stand it on a black glazed tile. Add the silver nitrate, stirring gently until a permanent opalescence is observed. This is the end point. Read the burette and re-weigh the Lunge-Rey pipette. Carry out a second determination in exactly the same way and take the average of the two determinations.

1 ml. N/10 silver nitrate ≡ 0·00921 gram calcium cyanide.

The results of the two determinations should agree within 0·04 per cent and the Buyer's and the Seller's results are expected to agree within 0·2 per cent.

Determination of Available Sulphuric Acid in Sodium Bisulphate.

5 grams of the crushed sample is dissolved in distilled water and the solution is made up to one litre.

50 ml. of this solution is titrated with N/10 sodium carbonate using methyl orange as indicator.

1 ml. N/10 sodium carbonate ≡ 0·0049 gram available sulphuric acid.

Grams $H_2SO_4 \times 400 = \%\ H_2SO_4$

Sodium Carbonate.

Commercial sodium carbonate is usually tested for sodium carbonate, sodium bicarbonate, sodium hydroxide, sodium chloride and combined water or loss on ignition.

5 grams of the material is dissolved in distilled water, previously boiled and cooled, and diluted to 1 litre. 50 ml. of this solution is used for the following tests:—

(1) The 50 ml. portion is titrated with N 10 sulphuric acid using phenolphthalein indicator.

In this titration the sulphuric acid neutralizes all the sodium hydroxide and converts the sodium carbonate to sodium bicarbonate.

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$
$$2Na_2CO_3 + H_2SO_4 = Na_2SO_4 + 2NaHCO_3$$

Let the amount of sulphuric acid used be x ml.

(2) Methyl orange indicator is now added and the titration is completed.

In this titration the sulphuric acid reacts with the sodium bicarbonate forming sodium sulphate.

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$$

Let the amount of sulphuric acid used be y.

Then $x + y$ is the total acid used.

If $2x$ be greater than $x + y$, sodium hydroxide is present, and $x - y$ gives the acid equivalent of the sodium hydroxide, while $2y$ = sodium carbonate.

If $2x$ be less than $x + y$, bicarbonate is present, and $y - x =$ bicarbonate, while $2x$ = sodium carbonate.

(Bicarbonates and hydroxides cannot be present simultaneously in the same solution as they react to form sodium carbonate.

$$NaOH + NaHCO_3 = Na_2CO_3 + H_2O)$$

After titration to the methyl orange end-point one drop of the sodium carbonate solution is added to remove the trace of excess acid and the chlorides are determined by titration with N 10 silver nitrate, using potassium chromate indicator.

Calculations.—The reaction between sodium carbonate and sulphuric acid is represented as follows:—

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$
$$106{\cdot}004 \quad 98{\cdot}082$$

1 litre N/10 sulphuric acid ≡ 5·3002 grams Na_2CO_3
1 ml. ,, ,, ,, ≡ 0·0053 ,, ,,

The reaction between sodium hydroxide and sulphuric acid is represented as follows:—

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$
$$2 \times 40{\cdot}005 \quad 98{\cdot}082$$

1 litre N/10 sulphuric acid ≡ 4·0005 grams NaOH
1 ml. ,, ,, ,, ≡ 0·004 ,, ,,

The reaction between sodium bicarbonate and sulphuric acid is represented as follows:—

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$$
$$2 \times 84{\cdot}015 \quad 98{\cdot}082$$

1 litre N/10 sulphuric acid ≡ 8·4015 grams $NaHCO_3$
1 ml. ,, ,, ,, ≡ 0·0084 ,, ,,

The reaction between sodium chloride and silver nitrate is represented as follows:—

$$\underset{169\cdot888}{AgNO_3} + \underset{58\cdot454}{NaCl} = AgCl + NaNO_3$$

1 litre N/10 silver nitrate ≡ 5·8454 grams NaCl
1 ml. ,, ,, ,, ≡ 0·0058 ,, ,,

As 50 ml. of the original solution is tested, all calculations are made on the basis of the 0·25 gram of the sample present.

The Analysis of Zinc Shavings for Impurities.

Tin.

20 grams of sample is dissolved in dilute nitric acid, boiled, allowed to settle, filtered, washed, and the precipitate is dried, ignited and weighed as stannic oxide.

If tin is absent, or if there is no appreciable amount of tin in the sample, as is usually the case, the solution need not be filtered.

Lead.

The filtrate is neutralized with ammonia and then re-acidified with acetic acid; the lead is precipitated by adding potassium dichromate and boiling for a few minutes.

The lead chromate precipitate is collected on a tared filter paper, washed well with very dilute acetic acid, dried at 100°C. and weighed.

Lead chromate × 0·64 = Lead.

Iron.

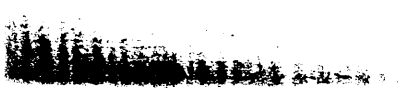
5 grams of sample is weighed out and placed in a 150 ml. flask. 20 ml. of water and 10 ml. of hydrochloric acid are added and the mixture is heated. When the action slows down 30 ml. of 30 per cent sulphuric acid is added. When the zinc is all dissolved the solution is diluted slightly and filtered quickly. (The residue on the filter consists chiefly of lead.) The filtrate is well diluted and the iron is titrated with N/10 potassium permanganate.

1 ml. N/10 potassium permanganate ≡ 0·0056 grams Iron.

Cadmium.

20 grams of the sample is accurately weighed out and treated with just sufficient hydrochloric acid to dissolve all the zinc with the exception of about half a gram. This is to ensure that the bulk of the zinc is removed and will not, therefore, complicate the separation of the cadmium at a later stage. The residue, which consists of the balance of the zinc, together with the lead and cadmium, is filtered off and washed twice; the residue is dissolved in a little nitric acid. 1 ml. of sulphuric acid is added and the solution is evaporated to fumes. The assay is cooled and diluted to 20 ml. with water, heated to dissolve the cadmium sulphate and the lead sulphate is filtered off.

The filtrate is made alkaline with excess ammonia, boiled and any bismuth is filtered off; the filtrate is made slightly acid with sulphuric acid and the cadmium is precipitated from the hot solution with hydrogen sulphide.



The residue is filtered off, and after washing a few times with hydrogen sulphide water, is washed back into the beaker where a little potassium cyanide is added and it is shaken until any copper sulphide is dissolved.

The cadmium sulphide is filtered through a small paper, washed well with hydrogen sulphide water and then dissolved in hot 50 per cent hydrochloric acid; the solution is caught in a weighed porcelain crucible, a few drops of sulphuric acid are added and it is evaporated to dryness using as low a temperature as possible to drive off the final traces of sulphuric acid.

The residue is weighed.

Cadmium sulphate $\times$ 0·539 = Cadmium.

Arsenic.

20 grams is weighed out, dissolved in dilute nitric acid, evaporated nearly to dryness, sulphuric acid is added and the mixture is evaporated to the first appearance of white fumes. (Caution: prolonged fuming must be avoided as arsenic is volatile.) After dilution the lead sulphate is filtered off and some sodium sulphite is added to reduce the iron and arsenic. The excess sulphur dioxide is boiled off and hydrogen sulphide is passed through the hot solution to precipitate the arsenic which is then filtered off, digested with ammonium carbonate to redissolve it, re-acidified with hydrochloric acid and re-precipitated with hydrogen sulphide.

The residue is again filtered off and re-dissolved in hydrochloric acid and bromine. The solution is made ammoniacal and the arsenic is now precipitated with magnesia mixture, allowed to stand overnight, filtered, washed well with very dilute ammonia water, dried, ignited and weighed as magnesium pyro-arsenate ($Mg_2As_2O_7$).

$Mg_2As_2O_7 \times 0{\cdot}483$ = Arsenic.

Alternatively, Dr. Franckel's distillation method may be used. (See under Arsenic in Chapter XVII.)

Zinc Fume: Determination of Metallic Zinc and Zinc Oxide.

Metallic Zinc.

A 500 ml. graduated flask is thoroughly dried. To this flask 7 grams of *pure* powdered ferric sulphate and 0·50 grams of the zinc dust (or fume) is added. The flask is shaken until they are thoroughly mixed. It is important that the zinc does not lie in clots on the bottom of the flask, hence the reason for the flask being perfectly dry. (Caution: C.P. ferric sulphate is often contaminated with free sulphuric acid which, if present, gives low results.)

25 ml. cold distilled water is now added, the flask is closed by means of a ground glass stopper and agitated for about 15 minutes, by which time the zinc dust should be dissolved. 300 ml. of 50 per cent sulphuric acid is added and the solution made up to the mark with distilled water. 100 ml. of this solution is titrated with N/10 potassium permanganate or with N/10 potassium dichromate, in the latter case potassium ferricyanide is used as an outside indicator. This titration should be done in an atmosphere of carbon dioxide.

The principle of the method is the reduction of the ferric sulphate to ferrous sulphate by the solution of zinc.

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4$$

0·10 grams zinc reducing 0·1708 grams of iron from the ferric to the ferrous condition.

N/10 potassium permanganate contains 3·1605 grams potassium permanganate per litre.

1 ml. N/10 potassium permanganate = 0·0056 grams iron
= 0·00327 grams zinc.

N/10 potassium dichromate contains 4·9035 grams potassium dichromate per litre.

1 ml. N/10 potassium dichromate = 0·0056 grams iron.
= 0·00327 grams zinc.

Each solution is standardized with pure ferrous ammonium sulphate which contains 14·24 per cent iron.

If iron is present in the zinc fume it will be necessary to dissolve 1 gram of the fume in sulphuric acid and find the number of ml. N/10 permanganate required. A proportionate amount must be deducted from the previous titration.

Total Zinc.

0·5 grams of zinc fume is treated with a small amount of dilute hydrochloric acid and sufficient bromine water to completely oxidize the sample. When the zinc is completely dissolved the solution is filtered and the filter washed. A few grams of ammonium chloride is added to the filtrate which is then boiled, allowed to cool, made slightly ammoniacal and again boiled, filtered and washed. If there is much iron present it will be necessary to redissolve the iron precipitate, re-precipitate with ammonia and filter. The two filtrates are mixed. The filtrate is slightly acidified with hydrochloric acid (about 5 ml. excess) heated to 70°—80° C. and titrated with potassium ferrocyanide, uranyl nitrate or acetate on a spot plate being used as outside indicator.

The solution is then filtered, made acid, again using 5 ml. excess, and the titration completed.

The standard potassium ferrocyanide contains 43·06 grams per litre.

1 ml. = 0·0115 gram zinc.

It is necessary to standardize the ferrocyanide by dissolving pure zinc in hydrochloric acid and bromine and treating this assay in exactly the same way as the assay for the zinc fume.

By determining the amount of metallic zinc and then the total amount of zinc, the zinc present as zinc oxide can be found by difference.

$$Zn \times 1{\cdot}245 = ZnO.$$

Method of Determining Penetration of Zinc Sulphate in Treated Wood.

1. Preparation of Required Solutions:—
   - (*a*) Solution of potassium ferricyanide 1 per cent
   - (*b*) Solution of potassium iodide 1 ,, ,,
   - (*c*) Solution of *soluble* starch 5 ,, ,,

In order to obtain satisfactory results the starch solution must be boiled until the starch is in solution. This solution will not keep long and therefore must be reasonably fresh when used.

2. Methods of Application:—

(A) If atomiser available:—

10 ml. of each of the three stock solutions are mixed and the mixture is poured into the atomiser. The disc of wood is evenly sprayed all over. The treated part of the wood will turn deep blue instantly, while the untreated part does not change in colour.

(B) If no atomiser is available:—

A few drops of solution (*a*) are placed on the disc of wood, starting from the edge, covering the complete sector or wedge. As soon as solution (*a*) has penetrated the wood, a mixture of equal quantities of solutions (*b*) and (*c*) are applied in the same manner. The treated part of the wood will turn a deep blue.

The disc of wood to be tested should be reasonably dry, and freshly cut.

Chapter XVII.

ASSAY OF BASE METALS.

Although the assaying of base metal ores is fully covered in most text books on assaying and quantitative analysis, it is felt that a chapter dealing with the commoner base metals found in South Africa should be included in this book.

This chapter gives the form in which the base metals occur and the locality in which they may be found. The methods of assay, which have been selected for their proved accuracy, do not need expensive and intricate apparatus.

Included in this chapter also, are a number of useful working hints, methods of detection by dry-way reactions and an abbreviated group separation table.

Working Hints.

In this chapter the phrase "pass hydrogen sulphide for 30 minutes" will sometimes be found. This is merely to stress the fact that the solution under examination must be saturated with the gas. An experienced assayer will know that the saturation point has been reached when the precipitate starts coagulating and the solution becomes clear, or, in some cases, colourless.

Any operation involving the evolution of acid fumes must be performed under a ventilated hood or in a fume cupboard.

For weighing hygroscopic substances accurately the use of a weighing bottle is essential.

To "filter by decantation" means that the precipitate is allowed to settle in the beaker and the supernatant liquor is poured into the filter. The precipitate is then washed by adding water to the beaker and shaking. The precipitate is allowed to settle and the wash water again poured into the filter. When the water has drained off, the precipitate is finally washed into the filter.

Silica, under certain conditions, is partially soluble. By evaporating to dryness and baking, or by fuming with sulphuric acid, however, the silica is dehydrated and rendered insoluble in the acids used to complete the assay. This process will be alluded to in later instructions merely as "dehydrating the silica".

Hydrofluoric acid is used to volatilize pure silica and thus separate it from other insolubles. Before the figure for "silica by difference" is accepted, however, a blank must be run to ascertain what insolubles are contained in the hydrofluoric acid itself.

When preparing a dilute solution of any acid, the acid should always be added to the water. This is particularly true of sulphuric acid.

When an assay has been "taken to fumes" with sulphuric acid it is imperative that the assay be thoroughly cooled before being diluted. The water should be added very cautiously, a little at a time, with constant stirring to avoid spirting.

Ammonium salts may be removed from an assay by first taking to dryness and then heating over a naked flame until white fumes are no longer evolved. During this heating the beaker must be moved freely in the flame so that all parts of the vessel are heated in turn and with as even a distribution of heat as possible.

Very fine grinding can be achieved by grinding a pulverized ore in an agate mortar to which some alcohol has been added. The finely ground particles float on the surface of the alcohol and may be decanted. This grinding and decanting is continued until the whole sample has been finely pulverized. This procedure must not be used for any element which is subject to oxidation (e.g., sulphur in pyrite).

Removal of nitric acid is achieved by repeated additions of hydrochloric acid followed by heating. Nitric acid is shown to have been completely removed when, after a further addition of hydrochloric acid and the application of heat, no more nitrous fumes are evolved.

Notes on the Preparation of a Solution for Qualitative Analysis.

Use small quantities of the powdered solid and examine for solubility in the following order:—

1. In water.
2. In dilute hydrochloric acid.
3. In strong hydrochloric acid.
4. In dilute nitric acid.
5. In strong nitric acid.
6. In aqua regia.
7. Fuse with sodium carbonate and dissolve the melt in water.

Test the solubility, first in the cold and then on heating. If there is a residue of silica after the hydrochloric acid digestion, remove by baking, filtering and volatilizing with hydrofluoric acid before examining the precipitate for metals of Group 1.

If any part of the solid is soluble in any of the solvents, *filter off that portion and treat separately.* The residue is then treated with the remaining reagents.

Group Separation.

Group Reagents.

Group One.	Add hydrochloric acid.
Group Two.	Add hydrochloric acid and pass hydrogen sulphide gas.
Group Three.	Add just sufficient nitric acid to oxidise completely (5 to 10 drops) and boil. Then add ammonium chloride and ammonium hydroxide in excess.
Group Four.	Add ammonium chloride, ammonium hydroxide and pass hydrogen sulphide gas (or add yellow ammonium sulphide).
Group Five.	Add ammonium chloride, ammonium hydroxide in excess and ammonium carbonate.
Group Six.	Add ammonium chloride, ammonium hydroxide and sodium phosphate.
Group Seven.	Various.

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Metals precipitated in the various groups and the usual colour of the precipitates.

Group One.	Silver, lead and mercury (all white).	
Group Two.	Arsenic (yellow).	Antimony (orange).
	Tin (-ous dark brown). (-ic dirty yellow).	Mercury (black).
	Lead (black).	Copper (brownish black).
	Bismuth (brownish black).	Cadmium (yellow).
Group Three.	Aluminium (white).	Iron (reddish brown).
	Chromium (bluish green).	Silica (white).
Group Four.	Nickel (black).	Cobalt (black).
	Manganese (buff or pink).	Zinc (white or greenish).
Group Five.	Barium, Strontium, Calcium (all white).	
Group Six.	Magnesium (white).	
Group Seven.	Ammonium—Odour of NH_3 when boiled with sodium hydroxide.	
	Potassium—Flame test gives violet colour.	
	Sodium—Flame test gives intense yellow colour.	

N.B.—This table is merely designed to indicate in which groups the various metals are found. For the proper identification of any metal it is essential that at least two confirmatory tests be done. These tests will be found in any standard text book on qualitative analysis.

The Preparation and Standardization of Solutions Required in Base Metal Assaying.

Iodine. N/10 12·692 grams per litre.

Iodine is sparingly soluble in water, but readily dissolves in a strong solution of potassium iodide. Therefore, dissolve 24 grams of potassium iodide in a minimum of water. Add 12·692 grams pure re-sublimed iodine. When dissolved make up to 1,000 ml.

Standardization.—Weigh out 0·3957 gram pure arsenious oxide. Dissolve by warming with a dilute solution of sodium hydroxide. Make up to 200 ml. in a measuring flask. Take 50 ml. portions (containing 0·098925 gram arsenious oxide) and using phenolphthalein as indicator, add hydrochloric acid from a burette until just acid. Cool to room temperature. Add 3 grams of sodium bicarbonate (see assay for arsenic and antimony) and a little starch solution. Titrate to a permanent blue colour with the iodine solution.

By atomic weights:—

$$\begin{aligned} As_2 &= 149{\cdot}82 \\ O_3 &= 48{\cdot}00 \\ \hline & 197{\cdot}82 \end{aligned}$$

197·82 grams arsenious oxide contains 149·82 grams arsenic. Therefore, 0·098925 gram arsenious oxide contains

$$\frac{149{\cdot}82 \times 0{\cdot}098925}{197{\cdot}82} \text{ gram}$$

$$= 0{\cdot}07492 \text{ gram arsenic.}$$

$$\text{Therefore 1 ml. iodine} \equiv \frac{0{\cdot}07492}{x} \text{ grams arsenic.}$$

$$\text{Therefore 1 litre iodine} \equiv \frac{74{\cdot}92}{x} \text{ grams arsenic.}$$

Now the equivalent weight of arsenic = 37·46 grams.

$$\text{Normality of iodine} = \frac{\text{grams arsenic} \equiv 1 \text{ litre iodine}}{\text{gram equivalent of arsenic}}$$

$$= \frac{74{\cdot}92}{x \times 37{\cdot}46}$$

1 ml. N/10 iodine ≡ 0·003746 gram arsenic.
≡ 0·006088 gram antimony.
≡ 0·005935 gram tin.

POTASSIUM PERMANGANATE. N/10 3·16052 grams per litre.

The required weight of permanganate may be derived from the hypothetical equation:—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + \text{"5 O"}$$

Since "O" is bi-valent the equivalent weight of permanganate is $2KMnO_4 \div 10 = 31{\cdot}6052$ grams. Therefore an N/10 solution contains 3·16052 grams per litre.

Dissolve 3·16052 grams pure potassium permanganate in water and dilute to one litre.

Standardization.—Weigh out 0·5043 gram pure oxalic acid crystals ($H_2C_2O_4.2H_2O$), and place in a 200 ml. measuring flask. Dissolve in 100 ml. 1 : 1 sulphuric acid and make up to 200 ml. Take 50 ml. portions (0·12607 gram $H_2C_2O_4.2H_2O$), dilute to 200 ml., heat to 80°C. and titrate with the permanganate to a permanent pink colour. Let the burette reading be x ml.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

By atomic weights $5H_2C_2O_4.2H_2O = 630{\cdot}34$.

Therefore the equivalent weight of oxalic acid = 63·034 grams.

$$\text{From titration, 1 ml. permanganate} \equiv \frac{0{\cdot}12607}{x} \text{ grams oxalic acid.}$$

$$\text{Therefore 1 litre permanganate} \equiv \frac{126{\cdot}07}{x} \text{ grams oxalic acid.}$$

$$\text{Normality of permanganate} = \frac{\text{grams oxalic acid} \equiv 1 \text{ litre permanganate}}{\text{gram equivalent of oxalic acid}}$$

$$= \frac{126{\cdot}07}{x \times 63{\cdot}034}$$

1 ml. N/10 potassium permanganate ≡ 0·01045 gram bismuth.
≡ 0·005584 gram iron.
≡ 0·005095 gram vanadium.
≡ 0·001648 gram manganese by the method given.

SODIUM THIOSULPHATE. N/10 24·8206 grams per litre.

It will be seen from the equation

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

that the equivalent weight is the molecular weight.

By atomic weights $Na_2S_2O_3.5H_2O = 248·206$. Therefore an N/10 solution contains 24·8206 grams per litre.

A solution of sodium thiosulphate is prone to decomposition caused chiefly by bacterial action. If the water is boiled to drive off carbon dioxide and 0·1 gram sodium carbonate is mixed with the sodium thiosulphate solution, it will remain stable for a longer period.

Dissolve 24·82 grams of pure crystallized sodium thiosulphate and 0·1 gram anhydrous sodium carbonate in boiled distilled water and make up to 1 litre. Store the solution in a dark cupboard.

Standardization.—Although sodium thiosulphate can be obtained in a very high state of purity, the water of crystallization is variable. Hence the solution must be standardized.

Place about 100 ml. cold water and 5 ml. glacial acetic acid in a beaker. Run in about 35 ml. of standardized N/10 potassium permanganate solution. Add 6 ml. 50 per cent potassium iodide solution and titrate with the thiosulphate solution. When the end point is approached add a little starch solution and finish the titration carefully.

Let the permanganate burette reading be x ml. and the thiosulphate burette reading be y ml.

$$\text{Then normality of thiosulphate} = \frac{x \times \text{normality of permanganate}}{y}$$

1 ml. N/10 sodium thiosulphate ≡ 0·001734 gram chromium
≡ 0·006357 ,, copper
≡ 0·012692 ,, iodine.

ALUMINIUM.

Occurrence.—Bauxite—$Al_2O_3.2H_2O$ and cryolite—Na_3AlF_6, the chief ores of aluminium, are not found in concentrated deposits in South Africa. However, aluminium silicates of various complex forms are present in most rocks.

Detection.—Charcoal block, cobalt nitrate test—residue blue and unfused.

Method of Assay.

Solutions required.—

Ammonium phosphate	..	..	100 grams per litre.
Sodium thiosulphate	..	..	200 ,, ,, ,,
Ammonium acetate	..	..	200 ,, ,, ,,

Discussion.—Decomposition of the ore is obtained by fusion with sodium hydroxide, with subsequent dissolution in hydrochloric acid. The silica is dehydrated and removed by filtration. The aluminium is precipitated as aluminium phosphate by the addition of ammonium phosphate and sodium thiosulphate in the presence of acetic acid. Hydrochloric acid prevents the precipitation of ferric phosphate. Sodium thiosulphate neutralizes the mineral acids, liberating sulphurous acid and

reduces the iron to the ferrous state. Ferrous phosphate is soluble under these conditions. Acetic acid is needed to maintain weak acidity during boiling to prevent the precipitation of phosphates other than aluminium.

Aluminium phosphate is partially soluble in cold acetic acid, but on boiling, it is completely insoluble. It is important, therefore, to keep the assay at boiling point while filtering. There is a continuous precipitation of sulphur which will make the filtrate turbid.

For the above reasons the exact quantities given in the method of assay must be used.

Decomposition.—Fuse 4 grams sodium hydroxide in an iron crucible until spattering ceases. Add 0·5 gram of the finely powdered sample. Cover the crucible with a lid and fuse at 400—500°C. (dull red heat). Place the cold crucible and cover, in a beaker containing 100 ml. water. Warm to dissolve the melt. Remove and rinse off the crucible and lid. Acidify with hydrochloric acid, evaporate to dryness and bake at about 120°C.

Take up in 50 ml. water and 10 ml. strong hydrochloric acid. Heat until soluble salts are dissolved. Filter and wash with hot water. Receive the filtrate in a 600 ml. beaker.

Separation and Determination.—Dilute the filtrate to 400 ml. with cold water and cool to room temperature. Add 30 ml. ammonium phosphate solution. With constant stirring add dilute ammonium hydroxide until a faint turbidity forms. Add 1·5 ml. hydrochloric acid or sufficient to clear the solution. Add 40 ml. sodium thiosulphate solution. Boil for two minutes and add 15 ml. ammonium acetate solution and 6 ml. glacial acetic acid.

Boil for 15 minutes and filter through an ashless paper. Keep the solution boiling all the time. Wash ten times with boiling water. Dry the paper and ignite in a weighed porcelain crucible at a red heat (500°C.). Calculate the weight as aluminium phosphate

$$AlPO_4 \times 0{\cdot}4180 = Al_2O_3$$
$$AlPO_4 \times 0{\cdot}2212 = Al$$

ANTIMONY.

Occurrence.—Murchison Range, Pietersburg district, North Eastern Transvaal. Also small deposits near Steynsdorp, Barberton area. Occurs chiefly as grey crystalline stibnite (Sb_2S_3), together with its oxidation products, stibiconite ($Sb_2O_3(OH)_2$) and senarmonite (Sb_2O_3).

Detection.—In closed tube—white, yellow or black sublimate. In closed tube with charcoal and soda—white sublimate or black mirror insoluble in sodium hypochlorite. Charcoal block test, oxidizing flame—white incrustation near assay. With cobalt nitrate—dirty green.

Method of Assay.

Solution required.—A standardized N/10 solution of iodine.

Discussion.—The sulphide ore is soluble in strong hydrochloric acid.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Oxidized ores may not be completely decomposed by acid treatment and are best fused with sodium hydroxide.

All hydrogen sulphide must be boiled off after decomposition or sulphur will precipitate when the solution is diluted. However, boiling to dryness must be avoided as antimony trichloride is volatile at temperatures approaching 220°C. Since antimony trichloride forms antimony oxychloride, which is insoluble, on dilution, tartaric acid is added to prevent this.

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

$$SbCl_3 + KHC_4H_4O_6 + 3NaHCO_3 = K(SbO)C_4H_4O_6 + 3NaCl + 2H_2O + 3CO_2$$

Any pentavalent antimony present is reduced by sodium sulphite. If iron is present in the ore, which is usually the case, the antimony must be precipitated as sulphide and filtered from the iron in solution. Any arsenic present is filtered off when the antimony sulphide is redissolved. This separation of antimony and arsenic is effective and complete in strongly acid solutions.

When the hydrogen sulphide has been boiled off, the antimony is ready for titration with iodine, after the addition of sodium bicarbonate.

(1) $$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI$$

Since the above reaction is a reversible one the action can proceed from right to left as fast as from left to right. The excess sodium bicarbonate ensures that the hydriodic acid is neutralized as it is formed and thus allows the reaction to proceed to finality, from left to right.

The reactions, taking into account the presence of tartaric acid and sodium bicarbonate are:—

Firstly:—

Equation (1) $$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

Secondly:—

$$K(SbO)C_4H_4O_6 + I_2 + 4NaHCO_3 = KHC_4H_4O_6 + Na_2HSbO_4 + 2NaI + H_2O + 4CO_2$$

Whence 1 ml. N/10 iodine ≡ 0·006088 gram antimony.

If alkalis other than sodium bicarbonate are present, hypoiodates are formed which give an incorrect result.

Decomposition.—For ores fairly high in antimony take 0·5 gram, for low grade ores take 1 gram of the finely powdered sample. Decompose with strong hydrochloric acid in a beaker on a hot plate. If decomposition of ore is difficult fuse with sodium hydroxide in an iron crucible and dissolve the melt in strong hydrochloric acid.

Separation and Determination.—Boil off hydrogen sulphide. Add 2—3 grams tartaric acid and dilute to 100 ml. Add 2—3 grams sodium sulphite and boil until all sulphur dioxide is expelled.

Pass hydrogen sulphide into the solution for 30 minutes. Filter by decantation and wash with hydrogen sulphide water. Wash the precipitate back into the beaker with a little water, finishing off with 1 : 1 hydrochloric acid.

Boil gently until the antimony sulphide is dissolved, adding strong hydrochloric acid if necessary. The antimony sulphide is not soluble in dilute acid.

If much arsenic is present it is advisable to redissolve the arsenic precipitate and repeat the precipitating and filtering in order to pick up any antimony that might be occluded in the sulphide of arsenic.

Add 2—3 grams tartaric acid and dilute to 100 ml. Filter off any arsenic residue at this stage. Add a drop of phenolphthalein indicator and neutralize with a strong solution of sodium hydroxide. Make slightly acid again with dilute hydrochloric acid. The hydroxide and hydrochloric acid are best added from burettes in order to avoid a large excess.

Cool and add 3—4 grams of sodium bicarbonate dissolved in 150 ml. water.

Titrate with N/10 iodine, using starch solution as indicator.

1 ml. N/10 iodine ≡ 0·006088 gram antimony.

ARSENIC.

Occurrence.—Found in central Transvaal associated with bismuth and tin ores. Also found in auriferous reefs in the Lydenburg and Barberton districts. It is usually associated with antimony deposits. The most common form is arsenopyrite or mispickel ($FeAs_2.FeS_2$).

Detection.—Closed tube test—black mirror, sometimes reddish yellow sublimate, garlic odour. Open tube test—white sublimate. Charcoal block, oxidizing flame—white incrustation far from assay, garlic odour.

Method of Assay.

Required.—N/100 standardized iodine solution and N/10 standardized iodine solution.

The apparatus employed consists of a 100 ml. Erlenmeyer flask connected to a condenser tube of approximately $\frac{3}{8}$ inch diameter. The joint should be of ground glass as rubber stoppers contain traces of arsenic. The condenser tube should rise vertically for approximately 4 inches to give a fractionating effect. The tube is then curved to a downward slope for 6 inches and dips into a receiving Erlenmeyer flask of 100 ml. capacity.

Discussion.—The method depends on the formation of arsenic trichloride by the action of hydrazine hydrochloride, potassium bromide and hydrochloric acid on the ore. The arsenic trichloride is distilled off (B.P. 122°C.), dissolved in water and titrated with iodine.

$$AsCl_3 + 3H_2O \quad = H_3AsO_3 + 3HCl$$
$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI.$$

The reaction with the iodine is reversible. For this reason, sodium bicarbonate is used to react with the hydriodic acid as it is formed, and so cause the reaction to go completely to the right. Normal carbonates or caustic alkalis must not be used, as they react with iodine. (Compare assay for antimony and standardization of iodine.)

Decomposition.—Weigh out 0·5 gram of the finely ground sample and place in the distilling flask. Digest on a hot plate with 10 ml. 1 : 1 nitric acid and 5 ml. 1 : 1 sulphuric acid. Add a few chips of unglazed porcelain to ensure even and rapid boiling. Heat until fumes of sulphur dioxide are driven off. The arsenic will then be in the trivalent condition.

Separation and Determination.—Cool the flask. Add 5 ml. water, 1 gram hydrazine hydrochloride, 1 gram potassium bromide and 10 ml. strong hydrochloric acid. Wash down the neck of the flask with 8 ml. water and assemble the apparatus. Place 12 grams of sodium bicarbonate in 50 ml. water in the receiver. Mark the distilling flask at half the volume of the liquid and distil down to this mark.

Remove the heat and rinse off the condenser tube into the receiver. Now add 5 ml. strong hydrochloric acid and 10 ml. water to the distilling flask and again distil to half the volume, using 8 grams sodium bicarbonate and 50 ml. water in a second receiver.

Cool the receiving flasks and titrate with standard iodine using starch as indicator.

If the arsenic value is low, then use the N/100 solution, but if the arsenic content is high the N/10 solution may be used.

The sum of the titrations is taken.

1 ml. N/10 iodine ≡ 0·0003746 gram arsenic.

Barium.

Occurrence.—Barytes, barite or heavy spar ($BaSO_4$), is found in many places in South Africa. The presence of silica in the ore and the limited extent of the deposits make exploitation uneconomical. A deposit south of Postmasburg is being worked. Barium is often encountered in ores of arsenic, antimony, copper, lead, manganese, silver and zinc.

Detection.—Flame test—yellow green. Charcoal block and soda test—fuses and sinks in.

Method of Assay.

Discussion.—Partial decomposition of the ore is obtained with hydrochloric and nitric acids. Baking dehydrates the silica.

The presence of sulphuric acid is required to ensure that the barium remains insoluble as sulphate when the gangue is dissolved in hydrochloric acid. Ammonium chloride is added to form a soluble double salt with any lead present.

On filtering, silver, now in the form of chloride, is removed from the residue by washing with ammonium hydroxide.

Fusion of the sulphate residue with a mixture of potassium and sodium carbonates, effects complete decomposition, and converts the barium to the carbonate. The mixed carbonates fuse more readily than either of the single salts. The barium carbonate is filtered off and dissolved in hydrochloric acid.

The barium is finally precipitated from the chloride solution as pure barium sulphate by the addition of sulphuric acid.

Decomposition.—Weigh out 0·5 gram of ore. Boil it for 2 minutes with 10 ml. 1 : 1 hydrochloric acid in a Phillips beaker. Add 5 ml. strong nitric acid. Evaporate to dryness and bake.

Separation and Determination.—Cool and add 20 ml. 1 : 1 hydrochloric acid, 5 drops strong sulphuric acid and 5 grams ammonium chloride.

Boil, filter and wash with hot water. Wash the residue with warm 1 : 1 ammonium hydroxide until the filtrate gives no precipitate with hydrochloric acid.

Place the filter paper and residue in a platinum dish. Dry on a hot plate and then burn off the paper. Stir in 5 grams of a mixture of potassium and sodium carbonates and fuse. Dissolve the melt in hot ammonia water. Filter and wash with ammonia water. (Barium carbonate is less soluble in ammonia water than in pure water.)

Test a drop of the filtrate on a black spot plate with a drop of a slightly acidified solution of barium chloride. When no precipitate of barium sulphate is formed, the washing is complete.

Wash the residue into a beaker and dissolve with 10 ml. 1 : 1 hydrochloric acid. Take care to avoid loss by spattering. Filter through the same filter paper to dissolve any carbonate remaining there. Receive the filtrate in a 600 ml. beaker. Wash the residue with hot, 1 per cent hydrochloric acid solution.

Dilute the filtrate to 300 ml. Heat nearly to boiling, and add dropwise, 20 ml. 10 per cent sulphuric acid. Allow to stand until cool. Filter through a double, ashless paper and wash with hot water. Dry and ignite the paper and residue in a weighed porcelain crucible. The ignited barium sulphate should be perfectly white.

Weight of $BaSO_4 \times 0{\cdot}5885 = Ba$.

Bismuth.

Occurrence.—Bismuth minerals are not commonly found in large quantities in South Africa. Bismuth is found chiefly as bismuth glance or bismuthinite (Bi_2S_3) in deposits of arsenopyrite, chalcopyrite and in gold and pyrite of the Pilgrim's Rest area. Native bismuth is also found at Kuisib, South West Africa.

Detection.—On charcoal—dark orange incrustation when hot, paler when cold. With potassium iodide and sulphur—scarlet incrustation, yellow near assay. With soda—brittle silver-white bead.

Method of Assay.

Required.—N/10 standardized solution of potassium permanganate.

Discussion.—On treating the ore with nitric acid, bismuth nitrate is formed. This is converted to bismuth subnitrate by dilution.

$$Bi(NO_3)_3 + H_2O = BiO(NO_3) + 2HNO_3$$

By adding oxalic acid, bismuth oxalate is precipitated.

$$2BiO(NO_3) + 2H_2C_2O_4 = Bi_2O(C_2O_4)_2 + 2HNO_3 + H_2O$$

Oxalic acid is liberated from this precipitate by sulphuric acid.

$$Bi_2O(C_2O_4)_2 + 2H_2SO_4 = 2H_2C_2O_4 + Bi_2O(SO_4)_2 \qquad (1)$$

The oxalic acid is then titrated with potassium permanganate.

$$5H_2C_2O_4 + 3H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O \qquad (2)$$

From equation (1) $\quad Bi \equiv H_2C_2O_4$

From equation (2) $\quad 5H_2C_2O_4 \equiv 2KMnO_4$

Whence: $\quad 2KMnO_4 \equiv 5Bi$

Therefore 1 ml. N/10 permanganate $\equiv 0{\cdot}01045$ gram bismuth.

Decomposition.—Weigh out 1 gram of the finely powdered sample. Digest in a beaker with 10 ml. nitric acid. Evaporate to dryness. Add 5 ml. nitric acid and 25 ml. water. Boil and dilute to 100 ml.

Separation and Determination.—Add 5 grams oxalic acid and boil for 5 minutes. Decant the supernatant liquor through a filter paper. Boil the precipitate with 50 ml. water and decant again. Repeat the washing until the filtrate is free of acid.

Treat the filter paper with 20 per cent sulphuric acid, receiving the filtrate in the beaker containing the precipitate. Add sufficient sulphuric acid to dissolve the precipitate and then a slight excess.

Heat to 80°C. and titrate with N/10 potassium permanganate to the pink end-point.

1 ml. N/10 potassium permanganate $\equiv 0{\cdot}01045$ gram bismuth.

CHROMIUM.

Occurrence.—Extensive deposits of variously modified forms of chromite ($FeO.Cr_2O_3$) exist in the Lydenburg and Rustenburg areas in the Transvaal. Small deposits are also found at Isitilo, Natal.

Detection.—Borax bead test—oxidizing flame, yellow-green; reducing flame, emerald. Microcosmic bead test—oxidizing flame, red when hot and green when cold; reducing flame, green. Soda bead test—opaque blue-green.

Method of Assay.

Required.—Standardized N/10 sodium thiosulphate. Manganese sulphate solution, 10 grams per 100 ml. Potassium iodide solution, 40 grams per 100 ml.

Discussion.—Complete decomposition of the ore is obtained by fusion with sodium peroxide. Sodium chromate is formed. Manganese sulphate aids the rapid decomposition of the excess sodium peroxide.

The chromate is dissolved in water and the residue filtered off. Hydrochloric acid, added to the filtrate, converts the chromate to dichromate.

$$2Na_2CrO_4 + 2HCl = Na_2Cr_2O_7 + 2NaCl + H_2O.$$

On the addition of potassium iodide, iodine is liberated.

$$Na_2Cr_2O_7 + 6KI + 14HCl = 2CrCl_3 + 2NaCl + 7H_2O + 3I_2 + 6KCl \quad (1)$$

The iodine is titrated with sodium thiosulphate.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \quad (2)$$

From equations (1) and (2):—

$$Cr_2 \equiv 3I_2 \equiv 6Na_2S_2O_3.$$

Whence 1 ml. N/10 sodium thiosulphate $\equiv$ 0·001734 gram chromium.
$\equiv$ 0·002534 gram Cr_2O_3.

Decomposition.—Weigh out 0·5 gram of the finely powdered sample that has been dried on a water bath. Fuse in a spun iron crucible with 5 grams sodium peroxide. Do not heat above a dull red heat as excessive corrosion of the crucible will take place. When fusion is complete, allow the crucible to cool. Place it upright in a beaker containing water, the level of which is a little below the level of the crucible. Cover the beaker and upset the crucible by means of a glass rod inserted under the cover glass. The melt will dissolve rapidly.

Separation and Determination.—Wash the glass rod and cover glass. Remove the crucible and wash it well. Add 1 ml. manganese sulphate solution. If manganese sulphate is not used, boil for 1 hour to destroy the excess peroxide.

Cool and transfer to a 500 ml. graduated flask and make up to the mark. Filter through a dry filter paper. Discard the first 50 ml. Take 200 ml. portions of the filtrate (equivalent to 0·2 gram of sample) and add a slight excess of hydrochloric acid. The colour of the solution changes from yellow to orange. Instead of filtering, the iron hydrates may be permitted to settle thoroughly and 50 ml. pipetted off for titration.

Cool the solution. Add 5 ml. potassium iodide solution. Titrate with N/10 sodium thiosulphate using starch solution as indicator as the end-point is approached.

1 ml. N/10 sodium thiosulphate $\equiv$ 0·001734 gram chromium.

Chromium $\times$ 1·4614 $\equiv$ Cr_2O_3.

Cobalt.

Occurrence.—There are a few small deposits of cobalt ore in the Transvaal. The better known deposits are in the Middelburg district and near Balmoral station. The cobalt is found as smaltite ($CoAs_2$).

Detection.—Borax bead test—deep blue. Microcosmic bead test—blue. On charcoal with powdered charcoal and soda—residue feebly magnetic.

Method of Assay.

Required.—Nitroso-beta-napthol solution. 10 grams of the salt to 100 ml. acetic acid.

Discussion.—The ore is decomposed by a mixture of strong nitric and hydrochloric acids. After fuming with sulphuric acid and diluting, the insolubles are filtered off.

After the removal of the metals, precipitated by hydrogen sulphide in acid solution and the removal of the iron group by precipitation with zinc oxide, the cobalt is precipitated by the nitroso-beta-napthol reagent ($C_{10}H_6O(NOH)$). The precipitate is cobalti-nitroso-beta-napthol ($CoC_{10}H_6O(NO)_3$) which on ignition decomposes to cobaltosic oxide (Co_3O_4).

The precipitate is very voluminous and for this reason not more than 0·1 gram of cobalt should be present in the precipitation. As the precipitate is insoluble in hydrochloric acid, any nickel which is present is dissolved out of the precipitate by washing with this acid.

Decomposition.—Weigh out an amount of the finely ground sample estimated to contain not more than 0·25 gram cobalt. Digest in a beaker with 10 ml. strong nitric acid and 5 ml. strong hydrochloric acid. Boil until nitrous fumes are driven off. Cool and add 10 ml. strong sulphuric acid. Boil until fumes of sulphur trioxide are given off.

Separation and Determination.—Cool and dilute to 100 ml. Boil until soluble salts dissolve. Filter and wash with hot water.

Pass hydrogen sulphide into the warm filtrate for 30 minutes. Filter off the sulphides, washing with hydrogen sulphide water. Boil the filtrate until the hydrogen sulphide is expelled. Add 3 ml. bromine water and boil off the excess bromine.

Wash the solution into a 500 ml. graduated flask and dilute to about 300 ml. Add an emulsion of zinc oxide while swirling the flask, until all iron is precipitated and a slight excess of zinc oxide is present. Make up to 500 ml. and allow to settle. Draw off 200 ml. portions of the clear, supernatant liquid (two-fifths of the original sample) in 600 ml. beakers. Add 6 ml. strong hydrochloric acid. Dilute to 300 ml. and boil.

Add nitroso-beta-napthol solution in the proportion of 2 ml. for every 0·01 gram cobalt presumed to be present. That is, 20 parts of the salt to each part of cobalt. Boil for two minutes and allow the bright red precipitate to settle.

Filter through an ashless paper. Wash the beaker out with hot 1 : 1 hydrochloric acid. Wash the precipitate 5 times with the same acid, alternating with hot water. Finally wash with hot water until the filtrate is free of acid.

Dry the paper and residue in a weighed procelain crucible. Ignite gently until the carbonaceous matter is burnt off and then at 800°C. (bright red heat). Weigh the residue as Co_3O_4.

$$Co_3O_4 \times 0{\cdot}7342 = Co.$$

COPPER.

Occurrence.—The chief deposits are at Messina and in Namaqualand. There are many other small occurrences in South Africa. Copper is also recovered as a by-product of gold mines in the Pilgrim's Rest and Carolina districts. The chief ores are chalcopyrite ($CuFeS_2$) and bornite (Cu_3FeS_4). It also occurs as malachite ($CuCO_3.Cu(OH)_2$), azurite ($2CuCO_3.Cu(OH)_2$). cuprite (Cu_2O), chrysocolla ($CuSiO_3.2H_2O$), covellite (CuS) and as native copper.

Detection.—Flame test—sky blue with hydrochloric acid, emerald green with nitric acid. Borax and microcosmic bead tests—oxidising flame, blue; reducing flame, opaque red. On charcoal with soda—red spongy mass.

Method of Assay.

Required: Standardized N/10 sodium thiosulphate. Potassium iodide solution 50 grams to 100 ml. water.

Discussion.—In the long iodide method, the ore is decomposed by a mixture of nitric and hydrochloric acids. These acids are removed by evaporating with sulphuric acid. After dilution, the copper is precipitated as sulphide by means of sodium thiosulphate.

The copper sulphide, which may have arsenic precipitated with it, is ignited to the oxide. After dissolution in nitric acid, bromine is used to oxidize any arsenic which may remain after the ignition.

$$H_3AsO_3 + Br_2 + H_2O = H_3AsO_4 + 2HBr.$$

This prevents the arsenic reacting with the iodine later.

The mineral acids are neutralized with ammonium hydroxide and finally, an acetic acid solution of the copper is obtained. It is important to boil off the excess ammonia as a large amount of ammonium acetate slows the titration reaction. The assay is given a final boiling to ensure the complete removal of oxidising agents which would otherwise cause an indefinite end-point.

The assay is cooled to prevent the volatilization of iodine when potassium iodide is added.

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 4KC_2H_3O_2 + I_2 \quad . . \quad . . \quad . . \quad (1)$$

The liberated iodine is titrated with sodium thiosulphate.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \quad . . \quad . . \quad . . \quad . . \quad (2)$$

From equations (1) and (2):—

$$2Cu \equiv I_2 \equiv 2Na_2S_2O_3.$$

1 ml. N/10 thiosulphate $\equiv 0{\cdot}006357$ gram copper.

Decomposition.—Weigh out $0{\cdot}5$ gram of the finely powdered ore (or an amount estimated to contain about $0{\cdot}2$ gram copper). Heat in a 300 ml. Phillips beaker with 10 ml. strong hydrochloric acid and 5 ml. strong nitric acid. Add further acid, as required, to keep dissolved salts in solution. Cool and add 8 ml. strong sulphuric acid and, to get rid of nitric acid, evaporate until fumes of sulphur trioxide are evolved.

Separation and Determination.—Cool and dilute to 25 ml. Boil for five minutes to get the anhydrous ferric sulphate into solution. Filter and wash. Boil the filtrate. Then run in from a burette sufficient 20 per cent sodium thiosulphate to precipitate all the copper sulphide. Complete

precipitation is indicated when a white precipitate begins to form. Boil to coagulate the precipitate. Then filter and wash. (The conventional method of precipitating the copper with hydrogen sulphide is much more troublesome.)

Ignite the filter paper and copper sulphide in a small porcelain crucible at a dull red heat (400—500°C.). Cool and add 15 ml. 1 : 1 nitric acid. Warm the crucible on a hot plate. When all the copper oxide has dissolved, wash into a beaker. Add 5 ml. saturated bromine water and boil down to about 5 ml.

Cool and dilute with 50 ml. water. Add 1 : 1 ammonium hydroxide until slightly in excess. A deep blue colour is produced. Boil off the excess ammonia and add 5 ml. glacial acetic acid and boil again.

Cool to room temperature. Add 6 ml. potassium iodide solution. Use in the proportion of 2 ml. of potassium iodide for every 0·07 gram copper present. Do not use less than 2 ml. Titrate immediately with N/10 sodium thiosulphate using starch solution as indicator as the end-point is approached. See that a slight excess of potassium iodide is present.

1 ml. N/10 sodium thiosulphate = 0·006357 gram copper.

Short Iodide Method.—Where great accuracy is not required, the method may be simplified as follows:—

Proceed as above until the dilution of the sulphuric acid is reached. Now neutralize with ammonium hydroxide. Add 5 ml. glacial acetic acid and 2 grams sodium fluoride or sufficient to discharge the colour produced by the iron present. Boil for two minutes and cool to room temperature. Add the potassium iodide and titrate as above.

In the short iodide method, a larger excess of potassium iodide is necessary.

This is probably due to the larger excess of salts in the final solution tending to slow the reaction.

Iron.

Occurrence.—There are extensive deposits of iron ore in the Pretoria, Rustenburg, Postmasburg and Messina districts, and in the Tugela Valley, Natal. The common ores are haemitite (Fe_2O_3), magnetite ($FeO.Fe_2O_3$), siderite ($FeCO_3$). Simonite ($Fe_2O_3.nH_2O$) and marcasite, a a form of pyrite, (FeS_2) are also found.

Detection.—Borax bead test—oxidizing flame, yellow when hot, colourless when cold; reducing flame, bottle green. Microcosmic bead test—oxidizing flame, colourless to brownish red; reducing flame, reddish. On charcoal with soda—residue strongly magnetic.

Method of Assay.

Required: Standardized N/10 potassium permanganate.

Stannous chloride solution. Dissolve 60 grams stannous chloride in 600 ml. strong hydrochloric acid and dilute to 1 litre. Keep in a stoppered bottle with a stick of pure tin in the solution.

Mercuric chloride solution. Make a saturated solution in hot water. Cool and filter.

Manganese sulphate solution. Dissolve 80 grams manganese sulphate in 875 ml. water. Add 165 ml. phosphoric acid syrup and 160 ml. strong sulphuric acid.

Discussion.—Solution of the ore is obtained by hydrochloric acid aided by stannous chloride. In chrome iron ore, the iron is re-precipitated with ammonium hydroxide to remove the nickel from the crucible. The green colour of the nickel would obscure the reduction of the iron later.

The iron is reduced by stannous chloride.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The excess stannous chloride is oxidized by the mercuric chloride.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

A large excess of stannous chloride must be avoided in the first place or the reaction:—

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg$$

takes place. The finely divided mercury discolours the liquid. The reduced iron is titrated with potassium permanganate.

Sulphuric and phosphoric acids present during the titration make the end-point sharp. Manganese sulphate prevents the hydrochloric acid acting on the permanganate with the liberation of chlorine.

Since both hydrochloric and sulphuric acids are present in the titration, the reactions may be represented by:—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

$$5FeCl_2 + KMnO_4 + 8HCl = 5FeCl_3 + KCl + MnCl_2 + 4H_2O$$

The ratio between the iron and permanganate is the same in each case, i.e. 5 : 1. Since the equivalent weight is $\frac{1}{5}$ of the molecular weight of permanganate, 1 ml. N/10 permanganate $\equiv$ 0·005584 gram iron.

Decomposition.—Treat 0·5 gram of the finely powdered ore with 15 ml. 1 : 1 hydrochloric acid and 2·5 ml. stannous chloride solution. Boil gently until completely decomposed.

(For chrome iron ores, proceed as in the chromium assay but use a nickel crucible. Remove the excess sodium peroxide. Add ammonium hydroxide and filter. Wash with hot water. Take up the precipitate in hydrochloric acid, re-precipitate with ammonium hydroxide and filter. Wash with hot water. Re-dissolve the residue in hydrochloric acid. Proceed with this solution.)

Separation and Determination.—To the hot solution run in stannous chloride from a burette until the iron is reduced. Avoid a large excess. The reduction is indicated by the disappearance of the greenish yellow colour.

Have ready a 600 ml. beaker containing 8 ml. manganese sulphate solution. Wash down the sides of the beaker containing the iron and add 5 ml. of mercuric chloride solution while stirring. Wash into the 600 ml. beaker and titrate with N/10 potassium permanganate.

1 ml. N/10 permanganate $\equiv$ 0·005584 gram iron.

Lead.

Occurrence.—There are numerous deposits of lead ore in South Africa, but none is of any great importance. The main deposits are in the Lydenburg, Rustenburg and Zeerust districts. The lead is found chiefly as galena (PbS) but also as oxidised products, cerussite ($PbCO_3$), anglesite ($PbSO_4$), and also as pyromorphite ($3Pb_3P_2O_8.PbCl_2$).

Detection.—On charcoal—incrustation dark yellow when hot, yellow when cold. With potassium iodide—incrustation brilliant yellow. With soda—soft bead, marks paper.

Method of Assay.

Required: Ammonium molybdate solution. 9 grams per litre. See standardization below.

Tannin solution. 0·5 gram per 100 ml. water.

Discussion.—The ore is digested with hydrochloric and nitric acids. These acids are displaced by evaporating with sulphuric acid.

On diluting the sulphuric acid solution, the lead is precipitated as lead sulphate. This is filtered off together with any silica present. Ammonium acetate converts the lead sulphate to the soluble acetate.

$$PbSO_4 + 2NH_4C_2H_3O_2 = Pb(C_2H_3O_2)_2 + (NH_4)_2SO_4.$$

The lead acetate is titrated with ammonium molybdate, using tannin solution as an external indicator.

$$Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 = PbMoO_4 + 2NH_4C_2H_3O_2.$$

The solid ammonium molybdate varies in formula from $(NH_4)_2MoO_4.4H_2O$ to $(NH_4)_6Mo_7O_{24}.4H_2O$. Hence the lead value cannot be calculated from the formula and standardization is necessary.

Decomposition.—Weigh out 1 gram of the finely powdered ore. Digest in a beaker on a hot plate with 20 ml. strong hydrochloric acid. Add 10 ml. strong nitric acid. When action ceases, cool and add 5 ml. strong sulphuric acid. Boil until fumes of sulphur trioxide are produced. Cool and dilute to 100 ml. Boil to ensure that any soluble sulphates are in solution. Allow to stand for one hour.

Separation and Determination.—Filter by decantation, washing well with 1 per cent sulphuric acid. Place the beaker containing the washed precipitate beneath the filter paper. Puncture this and wash the precipitate which is on the paper through using a hot, strong solution of ammonium acetate. Boil the ammonium acetate until all the lead sulphate has dissolved. To this solution then add 5 ml. of glacial acetic acid, dilute to 200 ml., heat to boiling and titrate with the ammonium molybdate solution. Use drops of tannin solution on a spot plate as an external indicator. An excess of molybdate produces a yellow brown colour with the tannin.

1 ml. ammonium molybdate = 0·01 gram lead approximately.

Standardization of Ammonium Molybdate: 0·3 gram of pure lead is dissolved in dilute nitric acid, fumed with sulphuric acid and treated precisely as in the ore. Since it may require up to 1 ml. of the ammonium molybdate in excess to produce the colour with the tannin, it is advisable to adjust the weight of lead foil taken, so that approximately the same amount of ammonium molybdate is used for the standardization and the assay.

Gravimetric Method.—Proceed as in the molybdate method until the lead acetate filtrate is obtained. To this add 5 ml. concentrated sulphuric acid, and boil down to fumes of sulphur trioxide. Cool and dilute to 100 ml. Add 100 ml. methylated spirits and allow to stand for one hour.

Filter through a weighed Gooch crucible, using asbestos as a filter. Wash with 1 per cent sulphuric acid and finally with alcohol. Dry in a steam oven and ignite at a dull red heat (400—500°C.). Weight of $PbSO_4 \times 0·6832 = Pb$. The methylated spirits aids in precipitating the sulphate completely.

MANGANESE.

Occurrence.—There are extensive deposits of manganese minerals in the Postmasburg district. The ore is found as a mixture of manganite ($Mn_2O_3.H_2O$), braunite ($3Mn_2O_3.MnSiO_3$) and psilomelane ($MnO_2.nH_2O$). Pyrolusite and polianite (MnO_2) are also found. There are other deposits in South Africa at Krugersdorp, Pretoria, Piet Retief, Waterburg, Vryheid and in the Cape Peninsula which have so far proved uneconomical.

Detection.—Borax bead and microcosmic bead tests—oxidizing flame, reddish violet; reducing flame, colourless. Soda bead test—oxidizing flame, bluish green, opaque when cold.

Method of Assay.

Required: Standardized N/10 potassium permanganate.

Discussion.—After complete decomposition of the ore by treatment with hydrochloric acid, followed by nitric acid, the manganese is obtained in solution as manganese sulphate by fuming with sulphuric acid. The iron present is precipitated by the addition of an emulsion of zinc oxide and the manganese is determined by titration with standard potassium permanganate. The titration is conducted at a temperature of at least 80°C. and is continued until a permanent permanganate colour pervades the supernatant liquid. When the clear solution is titrated with potassium permanganate the main reaction is:—

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

In the presence of other metals, e.g. zinc, manganates are formed.

$$6MnSO_4 + 5ZnSO_4 + 4KMnO_4 + 14H_2O = 5(ZnH_2O_2.2MnO_2) + 4KHSO_4 + 7H_2SO_4.$$

However, the ratio of manganese to potassium permanganate remains the same at $3Mn \equiv 2KMnO_4$, from which the manganese value is calculated.

Decomposition.—Weigh out an amount of the finely powdered ore estimated to contain about 0·2 gram manganese. Treat in a beaker on a hot plate, first with 10 ml. strong hydrochloric acid and then with 5 ml. strong nitric acid. When decomposition is complete, boil down with 7 ml. strong sulphuric acid until fumes of sulphur trioxide are produced.

Separation and Determination.—Cool and add 25 ml. water and 2 ml. bromine water. Boil until anhydrous ferric sulphate has dissolved and the excess bromine has been driven off.

Wash the mixture into a 500 ml. graduated flask and dilute to about 300 ml. Add an emulsion of zinc oxide, while agitating the flask, until the iron is precipitated and a slight excess of zinc oxide remains. Make up to the 500 ml. mark and allow to settle.

Pipette off 100 ml. portions (representing $\frac{1}{5}$ of the original assay) of the supernatant liquor. Heat nearly to boiling point and titrate with N/10 potassium permanganate. During the titration a dark precipitate is formed. It is necessary to agitate the solution, allow the precipitate to settle, and examine the supernatant liquid for the pink end-point. The precipitate may be induced to settle more rapidly by adding 2—3 drops of nitric acid. The assay must be kept near boiling point during the titration.

1 ml. N/10 potassium permanganate ≡ 0·001648 gram manganese.

MERCURY.

Occurrence.—Two small deposits of cinnabar (HgS) are known in South Africa. One is near Hectorspruit in the Eastern Transvaal, the other in the Pretoria district near Premier Mine.

Detection.—Closed tube test—metallic globules or black sublimate. With soda—sublimate of metallic globules. With potassium iodide on charcoal—incrustation and greenish yellow fumes.

Method of Assay.

Discussion.—The mineral is decomposed by heating it in contact with metallic iron thus liberating the vapour of mercury which condenses readily on, and amalgamates with, the cool surface of a gold or silver cover.

$$HgS + Fe = FeS + Hg.$$

Constant attention is needed in order to ensure a cooling condition on the top of the cover.

Decomposition and Determination.—Mix 0·2 gram of the finely powdered ore (up to 5·0 grams for low-grade ore) with 1—10 grams of iron filings in an iron, nickel or porcelain crucible. Sprinkle 1 gram of filings over the mixture. Fit the crucible into a hole in an asbestos sheet so that the bottom half of the crucible protrudes.

A silver or gold foil lid is made to fit the crucible. The lid should have a hollow in the centre in which a pool of water can be maintained; or, better still a thin brass condenser, through which cold water circulates is clamped on the lid.

Clean the lid, heat in a bunsen flame, cool and weigh. Place the lid on the crucible and carefully heat the lower portion of the crucible with a bunsen burner. Regulate the heat so that the lid does not reach the temperature of boiling water. The asbestos sheet will materially help in preventing the lid from being overheated. Continue the heating for 15-30 minutes.

When the operation is considered complete, allow the apparatus to cool. Remove the lid, which now has the mercury amalgamated on it. Wash the lid in alcohol, dry in a warm atmosphere and weigh. The increase in weight is the weight of the mercury in the sample.

MOLYBDENUM.

Occurrence.—The chief mineral is molybdenite (MoS_2) which is found associated with numerous small deposits of cassiterite in the Transvaal, the most important being in the Waterburg area. Molybdenum is also known to occur in Natal in the Hlatimbe Valley and near Stellenbosch in the Cape Province. The minerals molybdite (MoO_3), molybdic ochre ($Fe_2O_3.3MoO_3.nH_2O$) and molybdenite (MoS_2) are also found in small quantities.

Detection.—Microcosmic bead test—oxidizing flame, bright green: reducing flame, green. On charcoal—oxidizing flame, incrustation yellow when hot, yellow to colourless when cold; reducing flame, incrustation blue.

Method of Assay.

Required: Saturated ammonium acetate solution. Lead acetate solution —40 grams lead acetate, 10 ml. glacial acetic acid per litre.

Discussion.—The ore is fused with a mixture of sodium carbonate and sodium hydroxide. After dissolving the melt, ferric hydroxide is filtered off. The ferric hydroxide is dissolved and re-precipitated and again filtered off.

The filtrate is acidified with hydrochloric acid. The molybdenum is now in the form of H_2MoO_4.

Ammonium acetate is added to destroy the free hydrochloric acid. The solution is acidified with acetic acid and the molybdenum is precipitated as lead molybdate by the addition of lead acetate.

$$Pb(C_2H_3O_2)_2 + H_2MoO_4 = PbMoO_4 + 2HC_2H_3O_2.$$

The lead molybdate is filtered off and ignited at 400°C. to constant weight.

If tungsten is present, the ignited precipitate is dissolved in hydrochloric and nitric acid and evaporated almost to dryness. After adding more hydrochloric acid and filtering off the tungstic oxide, the molybdenum is re-precipitated from the filtrate by ammonium acetate, acetic acid and lead acetate as above.

$$\text{Weight of } PbMoO_4 \times 0{\cdot}2613 = \text{Mo}.$$

Decomposition.—Weigh out 1 to 2 grams of the finely powdered ore and mix in an iron crucible with 5 grams sodium carbonate and 2 grams sodium hydroxide. Heat gently at first to avoid spattering, and then strongly until a clear fusion is obtained.

Separation and Determination.—Dissolve the melt in 200 ml. water in a beaker. Remove and rinse off the crucible. Filter off and wash the ferric hydroxide precipitate with hot water.

Remove the funnel to another beaker, puncture the paper and wash the precipitate through with the minimum quantity of 1 : 1 hydrochloric acid. After washing with water re-precipitate the iron with sodium hydroxide. Boil and filter into the original filtrate. Wash well with hot water.

Acidify the filtrate with hydrochloric acid, adding sufficient to dissolve any molybdic acid which may separate. Add 5 ml. glacial acetic acid and 5 ml. ammonium acetate solution.

Boil and add lead acetate solution from a burette until the milky solution starts to clear. Allow to settle and add a few drops of the lead acetate to see if the precipitation is complete. Avoid a large excess of lead acetate.

Warm on a steam bath for 20 minutes. Filter and wash with water by decantation through an ashless filter paper. Dry and ignite at 400°C. (dull red heat) to constant weight.

If any tungsten is present dissolve the ignited precipitate in the minimum of hydrochloric acid. Add 2 ml. strong nitric acid and evaporate nearly to dryness. Add 150 ml. 20 per cent hydrochloric acid, boil, filter and wash with water. Re-precipitate the molybdenum from the filtrate with ammonium acetate and acetic acid, etc., as above.

$$\text{Weight of } PbMoO_4 \times 0{\cdot}2613 = \text{Mo}.$$

NICKEL.

Occurrence.—Nickel occurs mainly as pentlandite (2FeS.NiS) which is found associated with chalcopyrite and pyrrhotite in nearly all deposits of these sulphides in South Africa. The most notable deposits are in the Rustenburg district.

Detection.—Borax bead test—oxidizing flame, reddish brown when cold; reducing flame, opaque grey. Microcosmic bead test—oxidizing flame, yellow when cold; reducing flame, reddish yellow.

Method of Assay.

Required: Dimethylglyoxime solution. 1 gram per 100 ml. alcohol.

Discussion.—The ore is dissolved in aqua regia, however, if silicates are present in the ore, fusion with sodium carbonate may be necessary. The melt is dissolved in hydrochloric acid.

The repeated process of adding hydrochloric acid, evaporating and baking, converts the nickel to the chloride, removes the nitric acid and dehydrates the silica. A hydrochloric acid solution is finally obtained.

Antimony, arsenic and copper are precipitated as sulphides by hydrogen sulphide. Bromine ensures that the iron is oxidized and tartaric acid keeps it in solution. Similarly, ammonium chloride keeps the manganese and zinc in solution.

In the precipitation with dimethylglyoxime, hydrochloric acid is liberated. Hence an excess of ammonium hydroxide is necessary.

$$(C_4N_2O_2H_8)_2 + NiCl_2 = (C_4N_2O_2H_7)_2Ni + 2HCl$$

Decomposition.—Weigh out a portion of the finely powdered sample, estimated to contain not more than 40 mg. of nickel. Treat in a beaker on a hot plate with 10 ml. aqua regia. Evaporate to dryness. Cool and add 10 ml. strong hydrochloric acid. Evaporate to dryness and bake. Cool and add 5 ml. hydrochloric acid and 100 ml. water. Boil until all soluble salts are in solution.

Separation and Determination.—Pass hydrogen sulphide through the hot solution for 30 minutes. Filter and wash with hydrogen sulphide water. Boil the filtrate until all hydrogen sulphide is driven off. Add 2 ml. bromine water and boil off the excess bromine. Add 2 grams tartaric acid and 2 grams ammonium chloride. Make slightly alkaline with ammonium hydroxide. If the solution becomes cloudy, add ammonium chloride until it clears.

Heat nearly to boiling. Add 3 ml. dimethylglyoxime solution for every 4 mg. nickel presumed present, and then a slight excess. Add ammonium hydroxide, if necessary, to maintain distinct alkalinity. Allow to settle in a warm place for 1½ hours.

Filter through a weighed Gooch crucible, using asbestos as a filter. Wash well with hot water. Dry in an oven at 110°-120°C. to constant weight.

$$(C_4N_2O_2H_7)_2Ni \times 0{\cdot}2031 = Ni.$$

TIN.

Occurrence.—Cassiterite (SnO_2) is practically the only important ore of tin found in South Africa. Deposits of note are in the Potgietersrust, Warmbaths and Nylstroom areas. Tin is also found in the Cape, Natal and Swaziland.

Detection.—On charcoal—incrustation yellow when hot, pale or colourless when cold. With cobalt nitrate—incrustation blue-green. With soda—tin white bead, malleable, soft, does not mark paper.

Method of Assay.

Required: Standardized N/10 iodine solution.

Discussion.—The sample of tin ore is fused with sodium peroxide, the melt extracted with water and acidified with hydrochloric acid. The tin, which is now in solution as stannic chloride is reduced to the stannous state by suspending in the solution a roll of nickel foil, and boiling. After complete reduction, a few pieces of marble are added so that cooling may take place in an atmosphere containing no oxygen.

The assay is cooled rapidly under the tap to between 20 and 25°C. and the stannous chloride is quantitatively re-oxidized by titration with standard iodine using starch as indicator.

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI.$$

Tungsten, if present, forms a blue precipitate when the assay is reduced and may mask the end-point. Bismuth is also precipitated as metal and will react with the iodine. Both these metals, if present, must be filtered off and the assay again submitted to the reducing treatment with nickel.

Titanium may be removed by fusing the sample first with potassium bisulphate or potassium pyrosulphate. On leaching the melt, the titanium is dissolved out and the insoluble residue, containing the tin is then fused with sodium peroxide.

Decomposition.—Weigh out 0·5 to 2 grams of the finely powdered ore and mix with 8 grams sodium peroxide in an iron crucible. Fuse, gently at first, and when the melt is tranquil, heat strongly for a few minutes.

Reduction and Determination.—Cool the crucible to about 100°C. and place it in a porcelain dish containing 100 ml. water. Roll the crucible about until the melt has dissolved. Wash the crucible off carefully and wash the solution into a 500 ml. Erlenmeyer flask. Neutralize with strong hydrochloric acid. Add 50 ml. acid in excess and dilute to 200 ml.

Suspend a rolled piece of nickel foil (1 inch by 5 inches) in the solution, by means of a glass hook or silver wire attached to a bunsen valve, fitted into the neck of the flask. Heat to boiling and then allow to simmer gently. The solution will turn a light green colour. Continue the reduction for 40 to 60 minutes longer.

Remove from the hot plate. Cool somewhat and add a few marble chips. Remove the nickel foil and replace the bunsen valve. Cool rapidly under the tap. Add a little starch solution and titrate immediately with N/10 iodine.

1 ml. N/10 iodine = 0·005935 gram tin.

Alternate Method of Reduction.—To the solution obtained after the fusion of the ore, the extraction of the melt and the addition of the hydrochloric acid, a 1 inch square of $\frac{1}{16}$ inch aluminium sheet is added. It is not necessary to heat the solution.

Hydrogen is evolved briskly and the tin in solution is reduced to the stannous state. Other metals do not interfere and it is, therefore, unnecessary to remove them.

When reduction is complete the solution is colourless. A little of the aluminium should be allowed to remain at this stage. From very high grade ores a black precipitate of metallic tin may sometimes be observed. If present, the solution is boiled for 15 minutes and the metallic tin is re-dissolved.

The solution is allowed to cool in a neutral atmosphere, by introducing into the flask a stream of carbon dioxide from a generator or cylinder. When cool, a marble chip is added and the titration is carried out as above.

other than silica remains, fuse a fresh assay with sodium carbonate. Dissolve the melt in hydrochloric acid.

Separation and Determination.—Add 20 ml. 1 : 1 sulphuric acid and evaporate until fumes of sulphur trioxide are produced. Cool and dilute with 50 ml. water and boil to dissolve soluble salts. Add a strip of aluminium foil and boil for 20 minutes. Filter through a paper containing a piece of aluminium. Wash with hot water.

Boil the filtrate and pass hydrogen sulphide to precipitate any remaining copper, cadmium, or bismuth. Filter and wash with hydrogen sulphide water. Boil off the hydrogen sulphide from the filtrate and add 5 ml. bromine water. Boil off the excess bromine and add 7 grams ammonium chloride. Cool and make alkaline with ammonium hydroxide. Filter off the iron precipitate and wash with boiling water. Reserve the filtrate. Dissolve the precipitate in hydrochloric acid, add ammonium chloride and precipitate again with ammonium hydroxide. Filter, wash with boiling water and combine the filtrates.

Using a piece of litmus paper, neutralize the filtrate with hydrochloric acid. Add 3 ml. strong hydrochloric acid in excess. Dilute to 250 ml. and titrate hot with the potassium ferrocyanide solution. Use drops of uranium acetate on a spot plate as indicator. A brown colour is produced with an excess of potassium ferrocyanide.

Standardization of Potassium Ferrocyanide.—Prepare a solution of potassium ferrocyanide containing 22 grams per litre. Standardize as follows:—

Weigh out 0·5 gram of freshly ignited pure zinc oxide. Dissolve in 5 ml. strong hydrochloric acid. Dilute to 100 ml. Neutralize with ammonium hydroxide. Acidify with 3 ml. strong hydrochloric acid and titrate hot as in the assay.

$$ZnO \times 0{\cdot}8034 = Zn.$$

Calculate the amount of zinc per ml. of potassium ferrocyanide.

Alternative Internal Indicator.—Dissolve 5 grams diphenylbenzidine in sufficient sulphuric acid to give a green solution. Pour this into 40 ml. of water. Add drops of sulphuric acid to dissolve any reagent which may precipitate out during the dilution. Use 1 to 2 ml. of this indicator internally for each titration. The potassium ferrocyanide used must contain 0·22 gram of potassium ferricyanide per litre.

The indicator produces a blue violet colour in the presence of the ferricyanide ions. When the titration is complete, the free ferrocyanide ions produce a pale green colour.

Diphenylbenzidine cannot be used in the case of low percentage titrations unless a known quantity of standard zinc solution is added beforehand. The value of this addition would, of course, have to be deducted before the zinc content of the assay could be assessed.