and all results (Table I) were within ±3% of the required values. Absorbances recorded in Table I are the means of the average absorbances of each sample. They approximate closely the absorbances reached in the Liebermann-Burchard reaction after 32 minutes.

That the absorbances are not interfered with by the presence of the aliphatic wool wax alcohols is shown by the third experiment in which known amounts of cholesterol and triterpenols were added separately to whole wool wax unsaponifiables. In each case the results for total cholesterol and triterpenols were within the limits of experimental error recorded for the pure substances. The smallest amounts of cholesterol and triterpenols in an aliquot used for analysis were 60γ and 30γ, respectively. The 60γ of cholesterol is probably the smallest amount that can be estimated to the reported accuracy, but with triterpenols satisfactory results should be possible with 10γ.

ACKNOWLEDGMENT

The author is grateful to the Dairy Research Section of C.S.I.-R.O. for the use of the Unicam spectrophotometer.

LITERATURE CITED

(1) Delsal, J. L., *Bull. soc. chim. biol.*, **26**, 239 (1944).
(2) Drake, N. L., and Jakobsen, R. P., *J. Am. Chem. Soc.*, **57**, 1570 (1935).
(3) Latarjet, R., and Husson, A., *Compt. rend. soc. biol.*, **125**, 683 (1937).
(4) Lederer, E., and Tchen, P. K., *Bull. soc. chim. biol.* **27**, 419 (1945).
(5) McGhie, F. J., "Contributions to the Chemistry of the Sterols," Thesis, University of London, 1947.
(6) Schoenheimer, R., and Sperry, W. M., *J. Biol. Chem.*, **106**, **745** (1934).

RECEIVED for review April 28, 1953. Accepted June 24, 1953.

Siloxene as a Chemiluminescent Indicator in Chromate Titration for Determination of Lead

FREDERIC KENNY AND R. B. KURTZ
Hunter College, New York, N. Y.

THE present authors have used siloxene (*1*) as a chemiluminescent indicator in an oxidation-reduction titration (*2*), but it has not been employed heretofore as an indicator in a precipitation reaction.

Siloxene can be used as a chemiluminescent indicator in an accurate volumetric determination of lead, using a multiplier photometer (*4*). Only a few minutes are required for each analysis. The lead is precipitated as lead chromate by titrating the solution containing lead(II) with standard potassium chromate solution in accordance with the equation,

$$Pb^{++} + CrO_4^{--} \rightarrow PbCrO_4$$

In this first application of siloxene indicator to a precipitation reaction a minute excess of dichromate in the presence of H_3O^+ can be made to produce an oxidation potential of the proper value to cause the indicator to emit light at or near the stoichiometric point. The present authors have shown (*2*) that this value is approximately 1.17 volts.

Since for the system

$$6e + 14H_3O^+ + Cr_2O_7^{--} \rightleftarrows 2Cr^{+++} + 21H_2O$$

the potential is given by:

$$e = \frac{0.0591}{6} \log \frac{a_{Cr_2O_7^{--}} \times a^{14}_{H_3O^+}}{a^2_{Cr^{+++}}} + e^\circ$$

the pH is seen to be a factor in the potential obtained.

In order to establish a suitable pH range, portions of distilled water to which indicator was added were adjusted to values of pH from 1 to 8 by means of nitric acid or ammonia. The pH was measured in each case by means of a glass electrode, saturated calomel electrode, and Beckman H-2 pH meter. The beaker containing the solution under investigation was placed just above the shutter of a dark-chamber titrator (*3*). The photomultiplier tube of a Photovolt multiplier photometer 520-A was placed just below the shutter. One drop of 0.1000 *M* potassium chromate was added to the beaker and the reading was taken on the No. 3 scale, on which one unit is equivalent to 0.002 microlumen. The 1-drop excess of potassium chromate corresponds to an error of about 1.3 parts per 1000 in the volume of potassium chromate required in subsequent titrations of lead.

The results of these measurements, given in Figure 1, indicate that for decisive end points the pH value should not be much greater than 3.

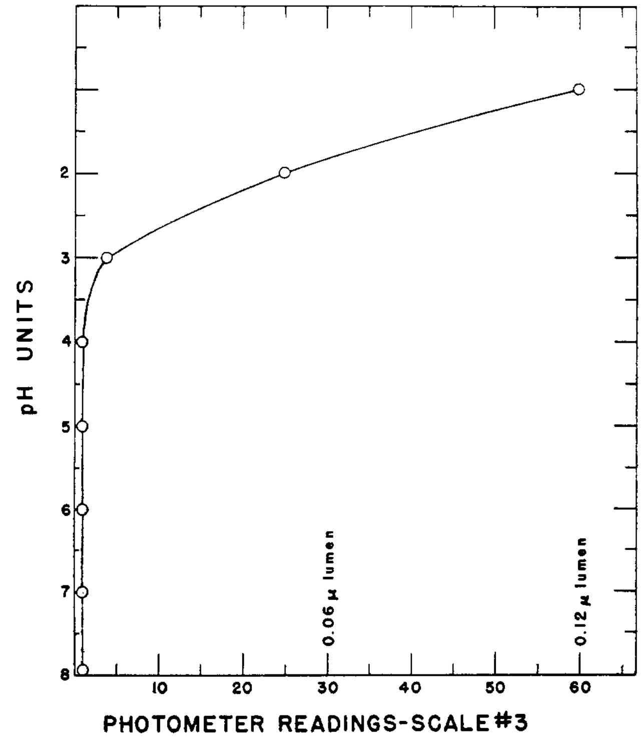

Figure 1. Photometer Readings at pH Values between 1 and 8

For a 1-drop excess of 0.1000 *M* K_2CrO_4, using siloxene indicator

In order to verify this point and also to establish a lower limit for pH, 30.00-ml. portions of 0.1000 *M* lead nitrate were titrated with a 0.1000 *M* potassium chromate at a variety of pH values between 1.3 and 5.2. A decisive motion of the needle of the photometer was taken as the end point. The samples were stirred by a motor inside the dark chamber. The lead nitrate solution used was prepared from 41.4426 grams of chemically pure lead which was dissolved in nitric acid, evaporated nearly to dryness, and carefully diluted to 2000.0 ml. at 26°. The potassium chromate solution was prepared from 38.8410 grams of Merck's C.P. potassium chromate dissolved and diluted to 2000.0 ml. at 26°. The solutions were used at substantially the same temperature at which they were prepared.

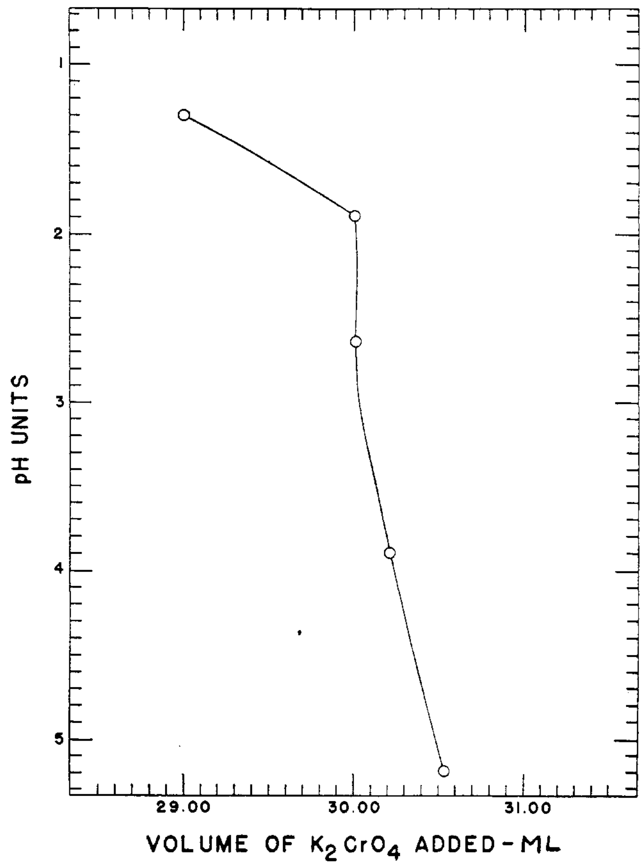

Figure 2. Volumes of Potassuim Chromate Solution Required to Titrate 30.00 Ml. of 0.1000 *M* Lead Nitrate Solution

At pH values between 1.30 and 5.20, using siloxene indicator

The results of the titrations, shown in Figure 2, indicate that the best pH range is between 1.9 and 3.0. At pH values below 1.9 appreciable light is emitted prior to the stoichiometric point. The high value of the potential at the end point in solutions of low pH results largely from the high value of $a_{H_3O^+}$. However, increased solubility of lead chromate in these solutions may contribute to the high potential. Furthermore, transformations in the indicator in the presence of protons may increase the light-emitting property at a given potential. At pH values above 3.0 the potential is not high enough to cause the indicator to emit appreciable light at the stoichiometric point. The pH can be adjusted with a pH meter or with a pH indicator, but it must be done prior to adding siloxene, as excess base might destroy the siloxene.

In order to determine the effect on the end point of variations in the amount of indicator used, portions of the lead nitrate solution at pH values between 1.9 and 3.0 were titrated, using varying weights of indicator. The results show that variation of the weight of the indicator between 0.02 and 0.08 gram has no appreciable effect on the end point. Weights between these limits were used in subsequent titrations.

In order to determine the accuracy and precision of this method of determining lead, a series of titrations was carried out in which the pH was between 1.9 and 3.0 and the weight of indicator was between 0.02 and 0.08 gram. The results, given in Table I, yield a precision expressed as the average deviation of a single observation of 1.3 parts per 1000 and an accuracy of 0.7 part per 1000.

In order to determine the extent of interference of a variety of metals in the foregoing method for determining lead, a series of titrations was carried out in which the added metal ion had the same concentration as the lead in the solution. The results are shown in Table II, and indicate that any error introduced by the presence of one of the six metals employed is 3 parts per 1000 or less.

Table I. Titration of Lead Nitrate with Potassium Chromate

Titration of 30.00 ml. of 0.1000 *M* $Pb(NO_3)_2$ with 0.1000 *M* K_2CrO_4 at pH values between 1.9 and 3.0 and indicator weights between 0.02 and 0.08 gram. Siloxene indicator and a Multiplier photometer were used.

Volume of K_2CrO_4, Ml.	Average Deviation, Ml.
30.04	0.06
30.00	0.02
29.91	0.07
30.00	0.02
30.00	0.02
29.89	0.09
30.00	0.02
29.99	0.01
29.98	0.00
29.85	0.13
29.89	0.09
29.96	0.02
30.02	0.04
29.99	0.01
30.05	0.07
30.07	0.09
Mean 29.98	0.04

The depth of color of the lead chromate precipitate makes the use of an ordinary redox indicator impossible. The siloxene, however, functioned satisfactorily in spite of the precipitate.

Table II. Interference of Metals

Ml. of 0.1000 *M* K_2CrO_4 solution required to titrate 30.00 ml. of 0.1000 *M* $Pb(NO_3)_2$ solution which was approximately 0.1 *M* with respect to an additional metal ion, using siloxene indicator and Multiplier photometer.

	Additional Metal Ion					
	Mn^{++}	Ni^{++}	Fe^{+++}	Zn^{++}	Ca^{++}	Mg^{++}
	30.09	30.08	30.03	30.10	30.01	29.92
	30.10	30.09	29.97	30.08	30.03	29.96
Mean	30.09	30.08	30.00	30.09	30.02	29.94

The method outlined in this paper affords a rapid and accurate means of determining lead in highly colored solution and in solutions containing high concentrations of manganese, nickel, iron, zinc, calcium, and magnesium. Work on titrations of lead in solutions containing metal ions other than those listed here, including tin, antimony, and bismuth, is in progress and will be reported later.

LITERATURE CITED

(1) Emeleus, H. J., and Anderson, J. S., "Modern Aspects of Inorganic Chemistry," p. 315, New York, D. Van Nostrand Co., 1939.
(2) Kenny, F., and Kurtz, R. B., ANAL. CHEM., **22**, 693 (1950).
(3) *Ibid.*, **24**, 1218 (1952).
(4) Photovolt Corp., New York, N. Y., "Operating Instructions for Multiplier Photometer 520-A."

RECEIVED for review February 4, 1953. Accepted May 19, 1953.