nium salts remained in the precipitates to modify the effects of the acids so that little difference existed between hydrochloric and nitric acids. The magnitude of the difference between perchloric and other acid solutions is striking. The effectiveness of small concentrations of ammonium salts indicates the importance of thoroughly removing the wash solution after the final centrifugation of the calcium oxalate precipitate. A volume of 0.04 ml. (about 2 drops) of the 1% ammonium oxalate solution diluted to 25 ml. (the final volume for flame photometry) results in a solution $0.0002N$ in ammonium ion.

Previous work (*1*) stated that ammonium ion (from 1.8 to 36 p.p.m.) had no effect on the calcium emission of a diluted serum to which sufficient sodium had been added to bring the level to 5 meq. per liter. In the same work, samples in which the calcium was first separated as the oxalate were prepared for flame photometric analysis by the addition of 5 meq. per liter of sodium in order to use the same standard solutions, and no unusual effects were observed. Apparently the modifying effects of the various other ions and protein in the diluted serum and the large amount of added sodium in the separated calcium oxalate solution masked the phenomena noted in this work, where the system was kept as pure as possible. Magnesium in quantities up to 10 times the calcium content had no effect in the present work.

The data clearly show that, during the preparation of serum samples for the flame photometric determination of calcium, certain unavoidable errors are introduced which affect the total flame emission. From a practical standpoint it is possible to make a simple correction which consolidates both the solubility loss and the effect of ionic impurities.

Two standards each containing 100 γ of calcium are included with each group of sera or ultrafiltrates and carried through the precipitation and separation procedures. The flame photometer is standardized with a solution prepared by diluting the standard calcium solution to a concentration of 4 p.p.m. with distilled water. For 35 of the 100-γ samples treated exactly the same as the sera, the flame photometer readings were $92.3 \pm 1.7\%$ of the reading obtained from the standard solution. The true calcium contents of the sera and ultrafiltrates can then be calculated from the flame photometric value multiplied by 1.083. This method provides an exact standard for comparison because each solution is essentially pure calcium oxalate dissolved in the same quantity of hydrochloric acid.

Although small quantities of several ions added to a pure system produced unusual and appreciable effects, the nonadditive nature of these effects made it difficult to predict the net result of a mixture of different ions on the flame emission of calcium. By keeping the additions to the solutions for flame photometry to a minimum, a maximum sensitivity to small changes in calcium concentration was obtained and unnecessary complications were avoided. The technique of using a spectroscopic buffer was considered but not used, and only the acid necessary to dissolve the calcium oxalate was added.

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Volumetric Determination of Sulfate by Titration of Excess Lead Nitrate with Potassium Chromate Using Siloxene Indicator

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▶Sulfur in solution as sulfate is precipitated with a large excess of carefully measured standard lead nitrate solution. The excess lead is then titrated in a dark chamber with standard potassium chromate. The sudden change in potential at the end point causes siloxene indicator to emit light, which is measured by a multiplier photometer. This new method makes possible the accurate determination of sulfur in less than 2.5 hours. Unknown samples, differing in sulfur content from the standard samples by as much as 10%, have yielded good results. Larger differences have not yet been investigated.

The conventional gravimetric determination of sulfur as barium sulfate is time-consuming and often subject to considerable error because of coprecipitation and loss of precipitate. In the method discussed here, the sulfate to be determined is precipitated as lead sulfate by the addition of a measured amount (known to be in excess) of standard lead nitrate solution. The excess lead is then titrated in a dark chamber (*8*, *10*) with standard potassium chromate. The end point is reached when the lead has been quantitatively precipitated. The sudden increase of chromate in the solution at this point brings about an increase in the potential, which causes the siloxene indicator (*9*, *11*) to emit light. The light is measured with a photometer and thus marks the end point of the titration.

Chromate concentration and pH are factors in determining potential. For the quantitative precipitation of lead, the desirable pH range is 1.9 to 3.0 (*11*). A pH of about 2.85 was used in this work.

PREPARATION AND PROPERTIES OF INDICATOR

A comparison of photometer readings obtained in preliminary experiments

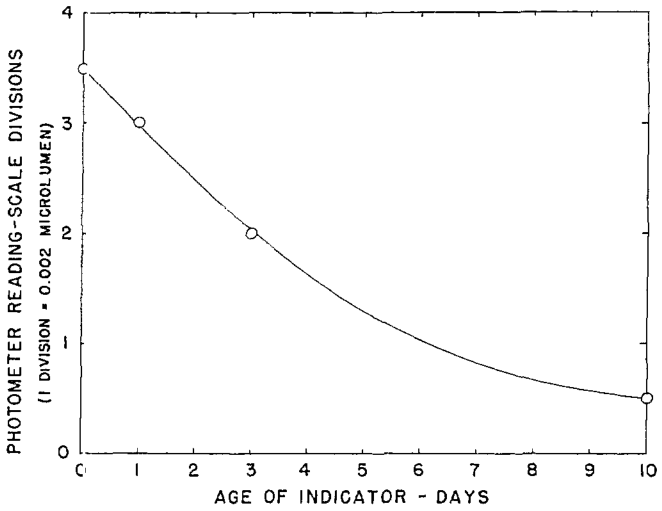

Figure 1. Mean light emission at end point *vs.* age of indicator

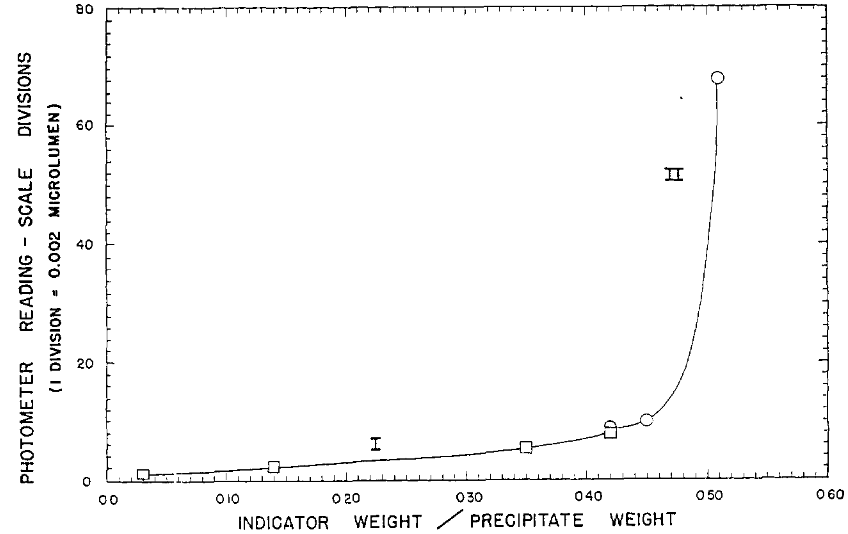

Figure 2. Mean light emission at end point vs. indicator-precipitate weight ratio

showed variations in the amount of light with the amount and age of the indicator. These factors were studied systematically, together with other factors which might affect the photometer reading at the end point, such as method of preparation of the indicator and indicator-precipitate weight ratio.

The main steps in the preparation of the indicator are: pulverizing the calcium silicide; treatment with hot hydrochloric acid; treatment with hot water; and washing, decantation, and drying.

When calcium silicide is treated with hydrochloric acid at elevated temperature, chlorine substitution in siloxene [$(Si_6H_6O_3)_n$] results. Subsequent treatment with water at elevated temperature replaces most of the chlorine with hydroxyl (*1, 2, 4, 6*). The treatment at elevated temperature, either with acid or with water, also introduces oxygen into some of the six-membered silicon rings. A limited amount of heat and water treatment should improve the light-giving properties of the product. (*1–7, 12*). Excessive heat treatment, which causes oxygen to enter too many six-membered silicon rings, yields a product which has diminished light-giving properties (*1–3, 5*).

Preparations were carried out which were identical in all respects, except for variations in water and heat treatments and the fineness of the calcium silicide. This work was done with technical calcium silicide obtained from the Electro-Metallurgical Co., Alloy, W. Va. The results indicated that intermediate heat treatment yields the best product, and that 100-mesh calcium silicide is preferable to larger particle size. The following method was adopted for the preparation of the indicator.

Three grams of 100-mesh calcium silicide was treated with 30 ml. of 12*M* hydrochloric acid in a 600-ml. beaker. (A 4-gram portion of calcium silicide may also be used.) The mixture was stirred until the first vigorous reaction subsided, when 15 ml. of 12*M* hydrochloric acid was added and the mixture boiled for exactly 5 minutes. Then 100 ml. of boiling water was added and boiling was continued for 10 minutes. Additional boiling water was added from time to time to keep the volume constant.

The mixture was allowed to settle for 0.5 minute to permit the silicon and ferrosilicon impurity to sink to the bottom of the beaker. The suspension of less dense siloxene indicator was then decanted onto two thicknesses of filter paper in a Büchner funnel. Care was taken to prevent the gray particles of silicon and ferrosilicon from reaching the filter.

The yellow siloxene indicator was washed four times with cold water, three times with alcohol, and three times with ether. It was then spread out on a sheet of paper and dried for 10 minutes in a dark, ventilated location. It was stored in a brown, glass-stoppered bottle; each batch was used within several hours of preparation.

PROCEDURE

The sample was dried to constant weight at 100° C. Portions were weighed into 100-ml. beakers and dissolved in about 10 ml. of water. A 30.00-ml. portion of 0.2000*M* lead nitrate solution was added from a buret and the pH was adjusted to 2.85 by the addition of nitric acid. (pH was measured with a Beckman H-2 pH meter.) Then 75 mg. of siloxene indicator was added. The titration was carried out with 0.2000*M* potassium chromate in a dark chamber titrator (*10*) attached to a Photovolt multiplier photometer 520-A (Photovolt Corp., New York, N. Y.) (*11, 13*). The swift movement of the needle on the No. 3 scale to a predetermined value was taken as the end point.

The photometer reading at the end point was determined by titration of a known sulfate sample in the same manner as for unknown samples; the photometer reading was taken when the stoichiometric point was reached.

Except for variations in the age and amount of indicator used, this procedure was used for all the samples described in this work.

VARIABLES

Age of Indicator. Indicator prepared from approximately 100-mesh calcium silicide was used in 600-mg. portions in a series of titrations in which 7.500 ml. of 0.3000*M* potassium sulfate was treated with 22.50 ml. of 0.2000*M* lead nitrate and titrated with 22.50 ml. of 0.1000*M* potassium chromate. The pH at the start of each titration was 2.85. The titrations, in duplicate, were extended over a period of 10 days.

The plot of average light emission, recorded on the No. 3 scale of the photometer, *vs.* the age of the indicator in days (Figure 1) clearly shows that the light emission diminishes with the age of the indicator. Use of larger portions of indicator may counteract this effect to some extent.

Indicator-Precipitate Weight Ratio. In considering the effect of the weight of the indicator on the light recorded at the end point, the screening effect of the precipitate must be taken into account. This effect may be due in part to the blocking of light from the pickup unit of the photometer, as well as to the formation on the surface of the indicator of a layer impervious to the solution. The screening effect depends to a large extent on the amount of precipitate relative to the amount of indicator used.

It should be borne in mind, however, that the composition of the precipitate may be important under some conditions, owing to unequal screening effects of lead sulfate and lead chromate.

Titrations were carried out which gave the same weight and composition of precipitate, using one batch of indicator in varying amounts from 50 to 600 mg. The resulting values for indicator-precipitate weight ratio, together with the corresponding deflections at the end point, are plotted in curve I, Figure 2. Similar titrations with a second batch of indicator were used to extend the weight ratio to a value of 0.514 (curve II).

Titrations of unknown samples, carried out with ratios between 0.03 and 0.3, yielded good results provided the sulfur content of the known samples was close to that of the unknown samples. This was the case for the titrations shown in Table II. However, when there was considerable difference in the sulfur content of known and unknown samples, errors of as much as 9.0 p.p.t. were encountered. The difference in screening effect of lead sulfate and lead chromate apparently becomes important when a very feeble light is recorded.

When the value of the ratio was between 0.30 and 0.45, good results were obtained in the titration of unknown samples, even when the sulfur content differed in either direction from that of the known sample by approximately 10%. Substantially greater differences have not as yet been studied, nor have titrations of unknown samples been carried out with ratios greater than 0.45.

For the results given in the first part of Table I, a ratio of 0.45, considered the most favorable used thus far, was employed. This ratio corresponds roughly to 27 mg. of indicator for each 1 ml. of $0.2M$ lead nitrate when the sulfate present is equivalent to approximately half the lead. An end point of 9.3 scale divisions was used, based on the titration of four known samples containing 9% less sulfur than the unknown samples.

For the results in the second part of Table I, a ratio of 0.42 was used. An end point of 8.4 scale divisions was used, based on the titration of four known samples containing 11% more sulfur than the unknown samples.

Table I. Titration of Pure Potassium Sulfate[a] with Potassium Chromate Using 600 Mg. of Siloxene Indicator

Potassium Chromate, $0.1000M$, Ml.	Sulfur Trioxide Found, %	Deviation, P.P.T.
Conditions: Indicator-precipitate weight ratio, 0.45; 0.4182 gram of pure potassium sulfate; 22.0 ml. of $0.2067M$ lead nitrate		
21.45	45.98	2.2
21.48	45.94	1.3
21.50	45.91	0.7
21.61	45.70	3.9
Av.	45.88	2.0
Std. dev., 2.7 p.p.t.; error, 1.3 p.p.t.		
Conditions: Indicator-precipitate weight ration, 0.42; 0.3485 gram of pure potassium sulfate; 21.77 ml. of $0.2067M$ lead nitrate		
25.20	45.48	6.1
25.02	45.91	3.3
25.01	45.91	3.3
25.09	45.74	0.4
Av.	45.76	3.2
Std. dev., 4.3 p.p.t.; error, 3.9 p.p.t.		

[a] Contains 45.94% sulfur trioxide.

The indicator-precipitate weight ratio and the age of the indicator were further studied in a series of experiments with a soluble sulfate salt mixture, which contained 42.48% sulfur trioxide when analyzed by the traditional barium sulfate precipitation method.

The first set of four samples was titrated in the presence of 75 mg. of siloxene indicator, which was used on the same day it had been prepared. The end point, determined by titrating a known sulfate sample, was 0.5 scale division on the No. 3 scale.

The same batch of indicator was used 1 day after it had been prepared to titrate a second set of four unknowns and one known sample. The procedure was otherwise the same as for the first set, except that 150-mg. portions of the indicator were used. The titration of the known sample again gave an end point of 0.5 scale division.

A third set of titrations was carried out with 225 mg. of indicator, used on the same day it was prepared. The end point was determined for this amount of indicator by titrating four known samples. The average reading on the No. 3 scale for these four samples was 4.4 divisions.

The results of all these experiments are given in Table II.

Table II. Titrations of Sulfate Salt Mixture[a] with Potassium Chromate

Sample, Grams	Potassium Chromate, $0.1000M$, Ml.	Sulfur Trioxide, %	Deviation, P.P.T.
Conditions: 75 ml. of siloxene indicator,[b] used on day of preparation; 30.00 ml. of $0.2000M$ lead nitrate.			
0.5662	29.96	42.36	1.76
0.5645	30.05	42.62	3.03
0.5668	29.93	42.28	1.27
0.5659	29.97	42.40	0.47
	Av.	42.42	1.63
Std. dev., 2.2 p.p.t.; error, 1.4 p.p.t.			
Conditions: 150 mg. of siloxene indicator,[b] 1 day old; 30.00 ml. of $0.2000M$ lead nitrate			
0.5652	30.01	42.51	0.70
0.5650	29.70	42.52	0.90
0.5655	29.80	42.47	0.23
0.5657	29.86	42.44	0.94
	Av.	42.48	0.69
Std. dev., 0.9 p.p.t.; error, 0 p.p.t.			
Conditions: 225 mg. of siloxene indicator,[c] used on day of preparation; 30.00 ml. of $0.2000M$ lead nitrate.			
0.5658	30.00	42.45	1.2
0.5650	30.07	42.51	0.2
0.5647	29.63	42.54	0.9
0.5640	30.60	42.57	1.6
	Av.	42.50	0.98
Std. dev., 1.2 p.p.t.; error, 0.47 p.p.t.			

[a] Contains 42.48% sulfur trioxide by barium sulfate method.
[b] Same batch of indicator.
[c] Different batch of indicator.

SUMMARY

By this method sulfate can be titrated in a water-soluble sample with a high degree of accuracy and precision, even when a very feeble light emission is obtained at the end point, provided the indicator is standardized against a standard having a sulfate content that differs only slightly from that of the unknown.

The accuracy and precision are good when the light emission gives a photometer reading at the end point between 4 and 10 divisions on the No. 3 scale (0.008 to 0.02 μlumen) when the sulfate content of the standard differs from that of the unknown by as much as ±10%.

The indicator becomes less sensitive with age and should be used within 2 or 3 days after preparation. The light recorded at the end point increases with an increase in the weight ratio of indicator to precipitate, and rises sharply beyond a value for this ratio of

0.45. The indicator-precipitate weight ratio which gave the best results thus far was 0.45, when a 10% difference exists between the unknown sample and the standard. This corresponds roughly to 27 mg. of indicator for each 1 ml. of 0.20M lead nitrate, when the sulfate present is equivalent to approximately half the lead. This result is obtained when the indicator is used on the day it was prepared. Somewhat larger amounts of indicator must be used on the second or third day.

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Determination of Mercury in Presence of Halides

Rapid Amperometric Titration

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An amperometric titration of the iodomercurate(II) ion with bis(ethylenediamine)copper(II) ion is described as a rapid method for the determination of divalent mercury in the presence of the halides. A systematic investigation of the variables, including solubility of the precipitate, was made. The use of sodium sulfite, an effective means for removing oxygen from the solution, greatly increases the simplicity of the titration. A constant error of approximately 5 p.p.t. is present in the titration, but is easily avoided by standardizing the reagent. The average deviation of the results in titrating from 0.02- to 0.06M mercury is 1.5 p.p.t. The titration is a rapid, accurate, and convenient way for determining mercury in the presence of thiocyanate, chloride, bromide, iodide, and similar complex formers.

THE USE of bis(ethylenediamine) copper(II) ion to precipitate the insoluble copper(II) ethylenediamine iodomercurate(II), [$Cu(en)_2HgI_4$, where en = ethylenediamine], was first reported by Spacu and Suciu (*13, 16*) as a reagent for the gravimetric determination of mercury. Bis(propylenediamine) copper (II) (*12*), the ferrous dipyridyl complex (*1*), and bis(ethylenediamine)palladium(II) (*15*) have also been employed in place of the bis(ethylenediamine)copper(II) ion. The use of bis(propylenediamine)copper(II) for determining mercury in organic compounds has recently been discussed by Walton and Smith (*14*), who also made a critical study of the earlier work. All of these methods presumably would be satisfactory in the presence of halides and other such complex formers, but they use the gravimetric approach and, therefore, would be somewhat slow and tedious when many samples are to be determined.

Spacu and coworkers have described a potentiometric (*11*) and a titrimetric method (*10*) for the determination of mercury based on the use of bis(ethylenediamine)–copper(II) nitrate reagent. The titrimetric method makes use of an outside indicator, which is rather cumbersome and slow, and the potentiometric method requires numerous potential measurements around the end point. In addition, a systematic investigation of the methods, including the effect of temperature on the solubility, the effect of concentrations of various reagents, and the range of concentrations in which the methods are most useful, was not made. Furthermore, the experimental details describing the work are somewhat sketchy and not clear.

The amperometric method for end point detection should be adaptable for this titration and should increase the speed with which the determination can be carried out. It should also be possible to determine smaller amounts of mercury using the amperometric method than with the potentiometric method. The results of a systematic investigation of the factors affecting the precipitation of mercury in the form of the iodomercurate(II) ion with bis(ethylenediamine)-copper(II) ion are reported here, as well as an amperometric titration based on this reaction. The method makes possible a rapid determination of mercury in the presence of the halides, thiocyanate, and similar complex formers.

EXPERIMENTAL

A Leeds & Northrup Type E Electrochemograph was used throughout the work, both for current voltage curves and for the titrations. Previous work has indicated the suitability of this instrument for quantitative current measurements (*9*). An external saturated calomel electrode was used as the reference electrode. In the beginning, this was connected to the polarographic cell by an agar bridge which was practically saturated with ammonium nitrate, but it was found later that the same results could be obtained with a bridge saturated with potassium chloride. For the polarographic investigations and for some of the titrations a single compartment polarizing cell similar to that described by Hume and Harris (*2*) was used as the electrolysis cell.

In those cases where temperature control was required, a water bath thermostated to 0.1° C. was used. Both a 5- and a 10-ml. microburet were employed for the titrations. In those titrations and polarographic investigations carried out in the absence of sulfite, oxygen was removed from the solutions by sweeping with a stream of pure nitrogen.

The bis(ethylenediamine)–copper(II) nitrate used for the titrations was prepared by weighing out the appropriate

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