

PROGRESS REPORT NO. 12

CONTROL INDICES AND ANALYTICAL PROCEDURES

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SUMMARY

The amperometric titration of sulfate ion with lead nitrate at -1.2 volts versus the saturated calomel electrode, using a dropping mercury cathode, offers a rapid and simple method for the determination of sulfate in a mixed inorganic salt solution. The method is capable of an accuracy of better than 0.7 percent in pure sulfate solution, and may be applied without preliminary treatment to solutions of dissolved 347 stainless steel containing in addition magnesium and nitrate ions, to yield results accurate to 3 percent.

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SUMMARY OF RESULTS

ANALYTICAL PROCEDURE STUDIES

III. DETERMINATION OF ANALYTICAL PROCEDURES

FOR IRON, CHROMIUM, SULPHATE AND NITRATE

IN A MIXED INORGANIC SALT SOLUTION

A. Objective and Implementation

The objective of the present investigation was to develop an accurate and rapid procedure for the determination of sulfate in a mixed inorganic salt solution of composition specified by the sponsoring agency.

The composition of the mixed inorganic salt solution is specified by its method of preparation as follows: dissolve 18.0 grams of 347 stainless steel in 277 ml of 6M sulfuric acid solution and add 3.1 grams of MgO and 102 ml of 15M nitric acid. The final volume obtained is thus close to 400 ml. In preparing such a stock sample solution an attempt was made to have a final volume of 500 ml; the following ingredients were added: 350 ml concentrated sulfuric acid, 22.5 grams of 347 stainless steel, 3.9 grams of magnesium oxide and 130 ml of concentrated nitric acid. On the basis of this composition and of the typical composition of 347 stainless steel (page 3 of Progress Report No. 1, June, 1953), the ionic composition of the stock sample solution would approximate the following:

Fe (III)	0.54M	SO ₄ ⁼	4.16M
Cr (probably III)	0.15M	NO ₃ ⁻	3.82M
Ni (II)	0.08M	P (if dissolved)	0.006M
Mn (II)	0.016M		
Cb (if dissolved)	0.004M	H ⁺ (based on ionic	
Mg (II)	0.18M	balance)	9.5M

A review of the existing methods for the determination of sulfate yielded several possibilities.

The nephelometric determination of sulfate is rapid, but the accuracy is low. Titration of sulfate with standard barium solution using THQ as indicator according to well-known procedures is also rapid, but the method requires a very experienced operator to detect the color change at the equivalence point. Reduction of sulfate to sulfide with hypophosphorus acid and determination of sulfide is subject to serious errors, as the reactions are not strictly stoichiometric.

The amperometric titration of sulfate with lead nitrate^{1,2,3} seemed most feasible as an accurate and rapid method, since no serious interferences could be foreseen in the sample system specified.

B. Experimental Procedure

Chemicals and Reagents. The chemicals and reagents used were prepared as follows:

6M sulfuric acid solution: 336 ml of concentrated sulfuric acid (sp. gr. 1.84) was diluted to 1 liter.

Sodium hydroxide solution: 0.5 M sodium hydroxide was used.

Methyl red indicator: A 0.1 percent solution of methyl red was used as the indicator.

347 stainless steel: This is the material in the form of hollow metal rods, supplied by the resident representative of the American Cyanamid Company, that was used for the density measurements of stainless steel solutions described in Progress Report No. 2, August, 1953. These rods were cleaned by first drawing acetone through them by means of suction and then clean dry air. The rods were cut into lengths of about 3 cm, and were completely immersed in acetone and then in ether. Clean dry air was allowed to evaporate most of the ether; final drying

was achieved by placing the metal briefly (about 3 minutes) in an oven at 110°C.

Nitrogen: Commercial oil-pumped nitrogen (Linde) was purified further by passing it successively through washing bottles filled with alkaline pyrogallol solution, sulfuric acid, and water.

All other chemicals were of reagent or CP quality grade, and were used without further purification.

Solutions. The solutions used in the experimental work were prepared according to the following specifications:

Lead nitrate standard: 29.0558 grams of solid, dry reagent-grade lead nitrate was diluted to 1 liter with distilled water to give a 0.08772M solution.

Potassium sulfate standard: 3.3103 grams of solid, dry reagent-grade potassium sulfate was diluted to 1 liter with distilled water to give a 0.01900M solution (Solution 1).

Sulfuric acid standard: 10.00 ml of the 6M sulfuric acid solution was diluted to 2 liters to give a solution which was 0.03M in sulfate (Solution 2).

Mixed inorganic salt solution: 22.5116 grams of the 347 stainless steel rods were weighed into a 1000-ml round-bottom flask with a standard-taper neck to which was fitted a 300-mm reflux condenser; 350 ml (measured out in 50-ml portions with a pipette) of 6M sulfuric acid were added and the mixture was heated in a water bath at approximately 80°C for 3 hours. The temperature was then lowered to approximately 60°C and the mixture allowed to react overnight. At the end of this time, solution was assumed to be complete, as no evidence of hydrogen bubbles was observed; 3.9 grams of magnesium oxide, MgO, and 130 ml of 15M concentrated nitric acid were then added. The final volume was brought up to 500 ml with a small volume of distilled water; 10.00 ml of this solution diluted with water to 2000 ml gave a solution which was 0.02M in sulfate ion (Solution 3).

Apparatus. The titrations were carried out in 150-ml beakers using a Sargent Ampot in conjunction with a dropping mercury electrode and a saturated calomel electrode. The beaker was fitted with a five-holed rubber stopper to accommodate the two electrodes, the buret, and the nitrogen inlet. A 10-ml buret graduated to 0.05 ml was used.

Procedure for Amperometric Titration of Sulfate. The following procedure is applicable to solutions such as 1, 2, and 3, described above.

If the solution is very acid, e.g., Solutions 2 and 3, the acid has to be largely neutralized by adding the necessary amount of 0.5M sodium hydroxide solution. In the case of Solution 2, the amount of the latter necessary to neutralize a given volume of the sample solution to methyl orange should be determined beforehand on a separate portion of the sample solution. The analytical procedure is then as follows.

A 25-ml sample of the solution is pipetted into a 150-ml beaker. In the case of solutions similar to Solution 2, the previously determined necessary amount of sodium hydroxide solution is added; in the case of samples similar to Solution 3, 0.5M sodium hydroxide solution is added until the color of colloidal ferric hydroxide is just barely perceptible.

A drop of 0.1 percent methyl red and 5 ml of alcohol are then added. The beaker is fitted to the stopper containing the nitrogen inlet, electrode, and buret. Oxygen is removed from the solution by passing nitrogen through the solution, about 10 minutes. Standard lead nitrate solution is then added in 0.5-ml increments with nitrogen bubbling after each addition. The current is read 1 to 2 minutes after each addition or as soon as it has reached a steady value, at a potential of -1.20 v vs. S.C.E. The points thus obtained yield two straight lines intersecting at the equivalence point when plotted in the conventional manner.

In plotting the experimental data (current vs. volume of titrant), it was found that the correction for the dilution due to the addition of the lead solution was negligible. However, if the volume of titrant is appreciable compared to the original volume being titrated, it may be advisable to correct for dilution by multiplying the current read at each point by $(V + v)/V$, where V is the original volume of the solution and v is the volume of titrant added up to that point.

C. Data Obtained and Interpretation

Typical data for titration of a pure sulfate solution (Solution 1) are given in Table I; the accuracy is very satisfactory for the titration in question.

The sulfate ion content of the mixed inorganic salt solution (Solution 3) was calculated from the results obtained on the amperometric titration of the pure sulfuric acid solution (Solution 2) (the three titrations averaged 0.03181M with an average error of 0.2 percent). The results for the inorganic salt solution (Table II) are of lower accuracy than those for the pure sulfate solution, although still well within the 5 percent limits set forth in the Analytical Procedure Studies outline. This lower accuracy is probably due to the effect of the various metal ions present on the solubility of the lead sulfate precipitate.

Suggestions for Further Study. It would obviously be desirable to improve the accuracy of the determination when applied to the salt solution. If the errors are due to the interference of the ions derived from the stainless steel, it might be possible to decrease this effect by further dilution of the sample solution. In such a case, it might be necessary to increase the alcohol content in order to decrease further the lead sulfate solubility. Another possibility would be to dilute a portion of the sample solution in a volumetric flask, to make the solution alkaline, to allow the precipitate to settle, and to remove a clear aliquot for titration; the latter would have to be neutralized prior to titration.

Use of an amperometric titration cell designed to permit continuous purging with nitrogen (Sargent No. S-29408) would decrease still further the short period of time required for the titration.

D. Literature Cited

1. Kolthoff, I. M., and Pan, Y. D., J. Am. Chem. Soc., 62, 3332 (1940).
2. Kolthoff, I. M., and Lingane, J. J., Polarography, vol. II, Interscience Publishers, New York, 1952, p. 917.
3. Hitchen, A., Can. Dept. Mines and Tech. Surveys, Mines Branch Topical Rept. No. TR-106/52, 10 pp. (1952); cf. Chem. Abstr., 47, 4247b (1953).

TABLE I
 AMPEROMETRIC TITRATION OF SULFATE
 IN POTASSIUM SULFATE SOLUTION

$\text{SO}_4^{=}$, molarity		
<u>Taken</u>	<u>Found</u>	<u>Error, %</u>
0.01900	0.01894	-0.3
0.01900	0.01886	-0.7
0.01900	0.01880	-1.0
	Average:	0.7

TABLE II
 AMPEROMETRIC TITRATION OF SULFATE
 IN MIXED INORGANIC SALT SOLUTION

$\text{SO}_4^{=}$, molarity		
<u>Taken*</u>	<u>Found</u>	<u>Error, %</u>
0.02226	0.02105	-5.3
0.02226	0.02181	-2.0
0.02226	0.02181	-2.0
	Average:	3.1

* As determined by amperometric titration of Solution 2.

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