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PROGRESS REPORT NO. 16

CONTROL INDICES AND ANALYTICAL PROCEDURES

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## SUMMARY

The individual procedures for the amperometric titration of sulfate, the photometric determination of nitrate, and the polarographic determination of chromium and iron, which have been described in Progress Report Nos. 12, 13, and 15, respectively, have been combined for this report into a systematic procedure for the analysis of the mixed inorganic salt solution originally specified.

Suggestions are presented for possible analytical methods to cover some analytical determinations such as that of tin, which are desired to supplement the methods originally proposed.

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SUMMARY OF RESULTS

ANALYTICAL PROCEDURE STUDIES

III. DETERMINATION OF ANALYTICAL PROCEDURES FOR

IRON, CHROMIUM, SULFATE AND NITRATE

IN A MIXED INORGANIC SALT SOLUTION

A. Objective and Implementation

The objective of the present investigation was to develop rapid procedures for the determination of sulfate, nitrate, iron, and chromium in a mixed inorganic salt solution of a composition specified by the sponsoring agency.

The composition of mixed inorganic salt solution is specified by its method of preparation as follows: 18.0 grams of 347 stainless steel are dissolved in 277 ml of 6M sulfuric acid solution and 3.1 grams of MgO and 102 ml of 15M nitric acid are added. 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 MgO 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 <sub>4</sub> <sup>=</sup>	4.16M
Cr (probably III)	0.15M	NO <sub>3</sub> <sup>-</sup>	3.82M
Ni (II)	0.08M	P (if dissolved)	0.006M
Mn (II)	0.016M		
Cb (if dissolved)	0.004M	H <sup>+</sup> (based on ionic	9.5M
Mg (II)	0.18M	balance)	

Methods have been proposed on the basis of work described in the following technical progress reports:

- Progress Report No. 12: Amperometric titration of sulfate,  
 Progress Report No. 13: Photometric (colorimetric) determination of nitrate, and  
 Progress Report No. 15: Polarographic determination of chromium and iron.

The details of the methods, including preparation of necessary reagents, are given in the reports just cited. The following sections present modified versions of the methods suitable for direct use in analyzing samples of the general type of the mixed inorganic salt solution specified.

Sample calculations have not been provided, since the main factors in such calculations are the dilutions involved, which in actual practice may be altered to suit the sampling and manipulative techniques which have to be used.

#### B. Determination of Sulfate

Standard Solution. Dilute 26.50 to 33.12 grams of dried reagent-grade lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] to 1 liter to give a standard solution which is 0.0800 to 0.1000 molar in lead.

Analytical Procedure. Dilute the sample of the mixed inorganic salt solution 1:100 with distilled water, e.g., dilute 10.00 ml to 1000 ml.

Transfer 10.00 ml of the diluted sample solution to the amperometric titration cell, e.g., a 150-ml beaker, and add 10 ml of water. Add, with stirring or agitation (e.g., nitrogen bubbling), 0.5M sodium hydroxide solution until the color of colloidal ferric hydroxide is just barely perceptible, then add one drop of 0.1% methyl red and 5 ml of alcohol. Fit the cell to the cell-head, e.g., a rubber stopper, containing a dropping-mercury electrode, a saturated calomel electrode, nitrogen inlet tubes, and the buret outlet.

Remove the oxygen from the solution by purging with nitrogen for about 10 minutes. Then add standard lead nitrate solution in 0.5-ml increments with nitrogen bubbling after each addition. Read the current as soon as it has become constant, i.e., 1 to 2 minutes after each addition, at a potential of -1.20 v vs S.C.E. Maintain the nitrogen atmosphere over the solution during the titration.

Plot the points obtained (current vs volume of titrant) and draw two straight lines through them in the usual manner. The intersection of the two points corresponds to the equivalence point.

### C. Determination of Nitrate

Preparation of Calibration Curve. Dilute a standard potassium nitrate solution (4.60 grams of dried reagent-grade  $\text{KNO}_3$  per liter) to 5:5, 4:5, 3:5, 2:5, 1:5, and 0:5 by adding accurately measured amounts to volumetric flasks and diluting to volumes; e.g., dilute to a final volume of 50 ml in 50-ml volumetric flasks 0, 10, 20, 30, 40, and 50 ml of the standard nitrate solution.

Develop the color in samples of each of the known nitrate solutions and perform the photometric measurement as indicated in the following section.

Analytical Procedure. Dilute the sample of the mixed inorganic salt solution 1:100 with distilled water; e.g., dilute 10.0 ml to 1000 ml.

Add to a 50-ml beaker by means of pipettes 1.0 ml of water and 2.00 ml of the diluted nitrate-containing sample solution. Cool the beaker and its contents in an ice bath; add 1 ml of ferrous iron reagent solution while continuously swirling the beaker in the ice bath. Then very slowly add 25 ml of 15M sulfuric acid (total addition time of about 3 to 5 minutes) while continuously swirling the beaker. Remove the beaker from the ice bath, stir its contents with a glass rod, and transfer a portion of the solution to the filter photometer (colorimeter) cell for measurement. For comparison, to determine the  $I_0$  value, use a blank containing all the reagents but no test solution. Use a 430-m $\mu$  filter, preferably of the interference type.

The color comparison should be performed between 15 and 30 minutes after the addition of the color-producing reagents to the diluted sample solution.

D. Determination of Chromium

Preparation of Standard Curve. Dissolve about 0.15 gram (weighed to four significant figures) of reagent-grade potassium dichromate in water and dilute to 500 ml in a volumetric flask. Prepare dilutions of this solution to cover the range of chromium concentration expected in the samples to be analyzed. Analyze these solutions polarographically as described in the next section, starting with the second paragraph on preparation of the cell-test solution.

Analytical Procedure. Transfer a 5.00-ml aliquot of the sample mixed inorganic salt solution to a 400-ml beaker. Add 200 ml of water, 2.5 ml of concentrated sulfuric acid, and a few clean glass beads. Heat the resulting solution to the boiling point. Add one drop of 0.5M silver nitrate solution and 2 grams of ammonium persulfate. Continue boiling for 10 minutes in order to decompose the persulfate. Cool the solution, transfer it to a volumetric flask and dilute it to 500 ml.

Transfer a 5.00-ml aliquot to a 100-ml volumetric flask, add 50 ml of 1.6M potassium hydroxide solution and 0.5 ml of 1% gelatine solution and mix well. Dilute the solution to the 100-ml volume, mix well, and allow the precipitate to settle. Transfer a portion of the nearly clear supernatant liquid to the polarographic cell. Bubble nitrogen through the solution for 10 minutes. Determine the current-potential curve over the range of -0.5 to -1.5 v vs S.C.E., maintaining a nitrogen atmosphere over the solution during electrolysis. Compare the current increment due to the sample to the standard-series curve.

E. Determination of Chromium and Iron

Preparation of Standard Solution. Dissolve 0.1800 gram of pure ferric oxide or the equivalent amount of another pure ferric compound in 3.5 ml of 6M sulfuric acid with heating. Add 1.3 ml of concentrated nitric acid and 20 ml of water; heat the solution to the boiling point and keep it boiling for several minutes. Then cool and transfer to a 500-ml volumetric flask in which 0.1200 gram of reagent-grade potassium dichromate has been placed. Mix and dilute to the 500-ml volume and mix again.

Analytical Procedure. Transfer a 5.00 ml aliquot of the sample mixed inorganic salt solution to a 400-ml beaker. Add 200 ml of water and then 2.5 ml of concentrated sulfuric acid and a few clean glass beads. Heat the resulting solution to the boiling point and add one drop of 0.5M silver nitrate solution and 2 grams of ammonium

persulfate. Continue boiling for 10 minutes in order to decompose the persulfate. Cool the solution and dilute it to 500 ml after transfer to a volumetric flask.

Add 30 ml of 10M potassium hydroxide solution and 3.6 grams of mannitol to a 100-ml volumetric flask. Add a 5.00-ml aliquot of the oxidized sample solution and dilute to volume. Mix well and transfer a portion of this solution to the polarographic cell. Bubble nitrogen through the solution for 10 minutes. Determine the current-potential curve for the range of  $-0.4$  to  $-1.6$  v vs S.C.E., while maintaining a nitrogen atmosphere over the solution.

Repeat the procedure of the previous paragraph, adding in addition to the 5.00 ml of oxidized mixed inorganic salt sample solution 2.00 to 3.00 ml of the standard chromium and iron solution.

Proportionate the chromium (first-wave) and iron (second-wave) currents for the two solutions and calculate the chromium and iron contents of the original sample.

Notes on the Polarographic Procedure. The drop-time for the capillary used should be between 6 and 7 seconds for satisfactory results.

The capillary should be cleaned between runs by immersion in 1:1 nitric acid (at room temperature) for about 1 minute, followed by thorough rinsing with distilled water.

#### F. Other Desired Determinations

Determinations of Tin. An approach to the polarographic determination of tin in solutions containing high concentrations of aluminum, fluoride, hydrogen, and zirconium ions has been indicated on page 6 of Progress Report No. 7, September, 1953.

The determination of tin in a solution similar to the mixed inorganic salt solution may need further consideration.

The original components of the sample solution would interfere with some of the amperometric titration methods suggested in the literature for tin.

Determination of Fluoride. The direct determination of total fluoride in a solution also containing aluminum, chromium, hydrogen, nitrate, and zirconium ions seems rather difficult, although it may be possible to determine the fluoride with satisfactory accuracy without a preliminary separation of the fluoride by a Willard and Winter distillation.



Consideration might be given to purging the solution of metal ions by diluting to a given volume while adjusting to pH 8 (ammonia buffer), removing a clear portion of the supernatant liquid, and analyzing the latter for fluoride content by a polarographic or photometric procedure. The possibility of basic fluoride salts precipitating may vitiate this approach. A similar approach is to attempt removal of all the metals present by a simple extraction procedure using either a single or a mixture of suitable complexing agents.

The determination of the fluoride is possible; the critical factors are the manipulation and time required to obtain results of the desired accuracy.

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