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ORNL-TM- 472

COPY NO. - 2

DATE - April 1, 1963

DETERMINATION OF TRACES OF IRON(III) IN NaF-LiF-KF-UF₄ WITH THIOCYANATE

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JWM-4

ABSTRACT

DETERMINATION OF TRACES OF IRON(III) IN NaF-LiF-KF-UF₄
WITH THIOCYANATE

A direct spectrophotometric determination of iron(III) in NaF-LiF-KF-UF₄ was developed in which the sample is dissolved in H₃PO₄-H₂SO₄-H₃BO₃ solution. Potassium thiocyanate is added to form the iron(III)-thiocyanate complex, which is then extracted with isobutyl alcohol. The phosphoric acid concentration must be maintained above 8 M to prevent reduction of iron(III) by uranium(IV) during dissolution of the sample. The coefficient of variation for the method was three per cent for the range of 0.25 to 1.5 mg of iron(III) per gram of sample.

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Purpose.

To establish conditions for the dissolution of mixtures of alkali metal fluoride salts containing uranium and iron without altering the oxidation states of the ions involved, and to determine the concentration of iron(III).

Introduction

A polarographic study of the reaction of iron(III) and uranium(IV) in various media showed that uranium(IV) was quantitatively oxidized by iron(III) in dilute sulfuric acid solution, but that it did not react in solutions of phosphoric acid above 8 M (JWM-3). This observation is in agreement with findings by Baes¹ who reported that the iron(II)/(III) couple exhibits a phosphoric acid concentration dependence opposite to that of the uranium(IV)/(VI) couple and that the formal electrode potentials of the two systems are the same in 2.4 M phosphoric acid.

If solid samples containing uranium(IV) and iron(III) are dissolved in a solvent of acid concentration greater than 2.4 M phosphoric acid, the iron(III) will theoretically remain in the trivalent state. Under these conditions the iron is reduced at such a negative potential that a polarographic determination is difficult. The presence of small amounts of uranium(VI) would interfere with the ultraviolet absorption method² for the determination of iron(III). Even though it has many disadvantages, the application of the thiocyanate method for the determination of iron is possible under these conditions.

Experimental

1. Preliminary Tests

A solution was prepared containing UCl₄ (500 µg/ml as U), NaF (500 µg/ml as F), and FeNH₄(SO₄)₂·12 H₂O (10 µg/ml as Fe) in 8 M H₃PO₄ and 1 N H₂SO₄. Aliquots of 5 ml were transferred to 25-ml volumetric flasks, varying amounts of potassium thiocyanate were added, and the flasks made to volume with water. The absorbance of the solutions at 460 mµ ranged from 0.410 for solutions with 4 g of thiocyanate added to 1.25 for solutions with 12 g added. Readings were repeated at 5-minute intervals. All the solutions faded rapidly with an average loss of intensity of 1.5 per cent per minute. In addition, the solutions containing higher concentrations of thiocyanate became turbid.

2. Extraction with Organic Solvents

In order to avoid the difficulties encountered in measuring the absorbance of the aqueous solutions, several solvent extraction techniques were tested. The method of Stokes and Cain³ which is based on extraction of the iron(III)-thiocyanate with a mixture of amyl alcohol and ether, and the method of Thompson⁴, based on extraction with isobutyl alcohol, were tried. Results by these methods were far better than those obtained by measurement of absorbancies of the aqueous solutions. The colored complex remained stable in the organic solvents for several hours and no turbidity was observed. The isobutyl alcohol extraction method was more convenient and was selected for further work.

3. Effect of Addition of Aluminum Salts

Wirth⁵ reported a more sensitive thiocyanate method for iron in the presence of phosphate based on the addition of aluminum salts to complex the phosphate ions. Iron-free solutions of aluminum nitrate, chloride, and sulfate were prepared and added to solutions containing uranium(IV) and iron(III) in 8 M phosphoric acid solution. No increase in absorbance was observed upon addition of aluminum chloride or sulfate prior to color development with potassium thiocyanate. Addition of aluminum nitrate did enhance the color, but erratic results were obtained and a yellow precipitate of polymeric thiocyanic acid frequently formed. Efforts to increase the sensitivity of the method by addition of aluminum salts were abandoned.

4. Sample Dissolution

Six representative samples of NaF-KF-LiF-UF₄ were obtained. The uranium content varied from 11.1 to 13.9 per cent. Various mixtures of acids were tried with phosphoric acid concentration maintained at about 8 M. The following solvent was found to be the most satisfactory: Dissolve 5 g of boric acid in 600 ml of water, add 200 ml of concentrated phosphoric acid and 100 ml of concentrated sulfuric acid. Use 90 ml to dissolve one gram of sample. One gram portions of all samples tested dissolved in 90 ml of the acid mixture at room temperature in 10 to 15 minutes to produce a crystal clear solution.

5. Preparation of Calibration Curves

Approximately 1 g samples were weighed accurately and transferred to 125-ml glass-stoppered flasks. Ninety ml of acid solvent was added and the mixture stirred until the sample dissolved. Each solution was transferred quantitatively to a 100-ml volumetric flask and diluted to volume with water. Aliquots of 5 ml were transferred to 25-ml volumetric flasks and known quantities of iron(III) added. One, 2, 3, or 5 ml of thiocyanate solution (1 g/ml) were pipetted into each flask, the flask diluted to volume immediately and quickly transferred into a 60-ml separatory funnel containing 25 ml (measured by a pipet) of re-distilled isobutyl alcohol. The funnels were

shaken for one minute. After the addition of thiocyanate, each sample was carried through the extraction step before starting the next sample. After the layers separated, the aqueous portion was drawn off, the funnel shaken lightly to remove water droplets on the walls, and allowed to stand for 10 minutes. The last bit of water was then drawn off and the solvent collected in a 50-ml glass-stoppered flask. The solution was allowed to stand for 2 hours, then 100 mg of anhydrous sodium sulfate was added. The absorbance of the solution was measured at 485 m μ against a reference solution which had no iron added. A plot of absorbance vs iron concentration gave a series of straight lines the slopes of which were a function of the amount of thiocyanate added. See Table I and Figure 1.

6. Study of Rate of Reduction of Fe(III) by U(IV) in 8.8 N Phosphoric Acid Solution Containing Fluoride

A 0.9782 g sample of NaF-KF-LiF-UF₄ (13.9 per cent U as UF₄) was dissolved in 90 ml of stock acid solvent and 1.0 mg of iron(III) solution added. Five-ml aliquots were taken at 0, 0.5, 1.5, and 3.0 hour intervals. Three ml of thiocyanate solution were added to each and the volumes made to 25 ml. The solutions were extracted with isobutyl alcohol and absorbancies read against a reference solution prepared in a similar manner. Results are given in Table II.

7. Evaluation of the Method

The following procedure was established for evaluation of the method.

Weigh two samples (approximately 1 g each) of a given alkali metal fluoride mixture. Transfer the samples to 125-ml glass-stoppered flasks. Add 90 ml of stock acid solvent to one flask and 90 ml of solvent plus a known amount of iron(III) to the second flask. Stir without heating until samples are dissolved (10 to 15 minutes).

Transfer the solutions to 100-ml volumetric flasks and make to volume with water. Transfer a 5-ml aliquot of the sample containing no added iron to a 25-ml volumetric flask for use as reference solution. Transfer several 5-ml aliquots of the second solution to 25-ml volumetric flasks for the iron determination. Refer to the calibration curves and choose a suitable sensitivity range. Pipet a suitable amount of thiocyanate solution into each flask, make to volume, and extract with isobutyl alcohol as described above. After each addition of thiocyanate, complete the extraction before proceeding to the next sample. After transferring the alcohol in solutions to dry flasks, allow to stand two hours, add 100 mg of anhydrous sodium sulfate and measure the absorbance against the reference solution. Refer to the appropriate calibration curve to determine the iron concentration.

Two series of tests were run. In the first series, 0.25 to 1.5 mg of iron(III) was added to approximately 1-g samples of fluoride salts. Since iron concentrations in the final solutions varied from 0.5 to 3.0 $\mu\text{g/ml}$, three g of thiocyanate reagent was added for color development. In the second series, 0.1 to 0.2 mg of iron(III) was added giving 0.2 to 0.4 $\mu\text{g/ml}$ in the final solutions and 5 g of thiocyanate was added for color development. The second series was run with solvent that had been recovered from previous runs and the results were somewhat erratic. Results are given in Table III.

Data

Table I

Data for Preparation of Calibration Curves for Determination of Iron(III) by Thiocyanate Method

1 cm cells
 Beckman Model DU spectrophotometer
 485 μ

<u>Weight of Sample in 100 ml, g</u>	<u>UF₄ in Sample, Per Cent U</u>	<u>KSCN Added, mg</u>	<u>Iron(III) Added to Aliquot, mg</u>	<u>Iron(III) Conc. in Final Soln, $\mu\text{g/ml}$</u>	<u>Absorbance</u>
0.9455	13.9	1	0.0	0.0	-
			0.02	0.8	0.020
			0.06	2.4	0.075
			0.10	4.0	0.132
0.8090	13.5	2	0.0	0.0	-
			0.05	2.0	0.173
			0.10	4.0	0.348
			0.15	6.0	0.505
0.7316	13.9	3	0.0	0.0	-
			0.03	1.2	0.159
			0.06	2.4	0.312
			0.09	3.6	0.497
0.8634	11.4	5	0.0	0.0	-
			0.0125	0.5	0.90
			0.025	1.0	0.186
			0.0375	1.5	0.290

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Table IIRate of Reduction of Iron(III) by Uranium(IV) in 8.8 M
Phosphoric Acid Solutions Containing Fluoride

<u>Time Iron(III) and Uranium Remained in Contact (Hours)</u>	<u>Absorbance 485 mμ</u>
0.0	0.260
0.5	0.256
1.5	0.248
3.0	0.250

Table IIIDetermination of Iron(III) Added to Mixtures of Alkali Metal
Fluoride Salts Containing UF₄5 g KCNS
1 cm cellsBeckman Model DU Spectrophotometer
485 m μ

<u>Added</u>	<u>Found mg</u>	<u>Average</u>	<u>Iron(III)</u>	
			<u>Coefficient of Variation mg</u>	<u>Per Cent</u>
<u>Series I</u>				
0.250	0.212 0.208 0.215	0.212	0.004	1.6
0.500	0.488 0.531 0.481	0.500	0.027	5.4
1.000	1.084 1.077 1.058	1.073	0.013	1.2
1.5	1.623 1.558 1.561	1.581	0.038	2.3
<u>Series II</u>				
0.100	0.085 0.092	0.0885	0.004	4.0
0.200	0.206 0.242 0.163	0.2037	0.039	19.3
			Over-all	2.6*

* Over-all value did not include Series II which was run with recovered solvent.

Conclusion

The thiocyanate method may be used for the determination of iron in 8 M phosphoric acid solutions containing fluorides provided a large excess of reagent is used and that conditions are carefully controlled. The colored complex was found to fade rapidly under these conditions but satisfactory results can be obtained by extraction with isobutyl alcohol immediately after addition of the thiocyanate reagent. Results obtained by reading absorbancies of the alcohol extracts immediately after extraction were high and erratic; however, consistent results were obtained by allowing the solutions to stand for two hours. It is believed that the high absorbance was caused by turbidity which disappeared upon standing.

Addition of aluminum salts was found to offer no improvement in the method.

Rapid and complete dissolution of the samples was effected by addition of boric acid to the phosphoric-sulfuric acid solvent mixture and did not interfere with the determination. It is essential that the phosphoric acid concentration never fall below 8 M. Any dilutions made prior to addition of thiocyanate will produce low results. When preparing calibration curves, solutions should be chosen of such concentrations that the total volume added to the 5 ml aliquots does not exceed 1 ml.

A reduction of iron(III) was observed in the phosphoric acid-fluoride medium, but the rate appeared to be very slow. It is necessary that samples be run as soon after dissolution as possible. A preliminary study indicated a loss of about 1 per cent per hour of contact between uranium(IV) and iron(III).

Tests were run on samples with 0.1 to 1.5 mg of iron added to approximately 1-g portions of alkali metal fluoride solids. Final solutions tested ranged from 0.2 to 3.0 μg iron(III)/ml. This appeared to represent the lower limits of iron which could be determined by the method; however, from the calibration curves presented, it is assumed that the method could easily be extended to higher concentrations.

Because of the many variables which affect the iron-thiocyanate determination, all volumes must be carefully measured and calibration curves must be checked when new reagents are prepared. Large volumes of stock solvents and reagent solutions should be prepared to reduce the frequency of recalibration of standard curves.

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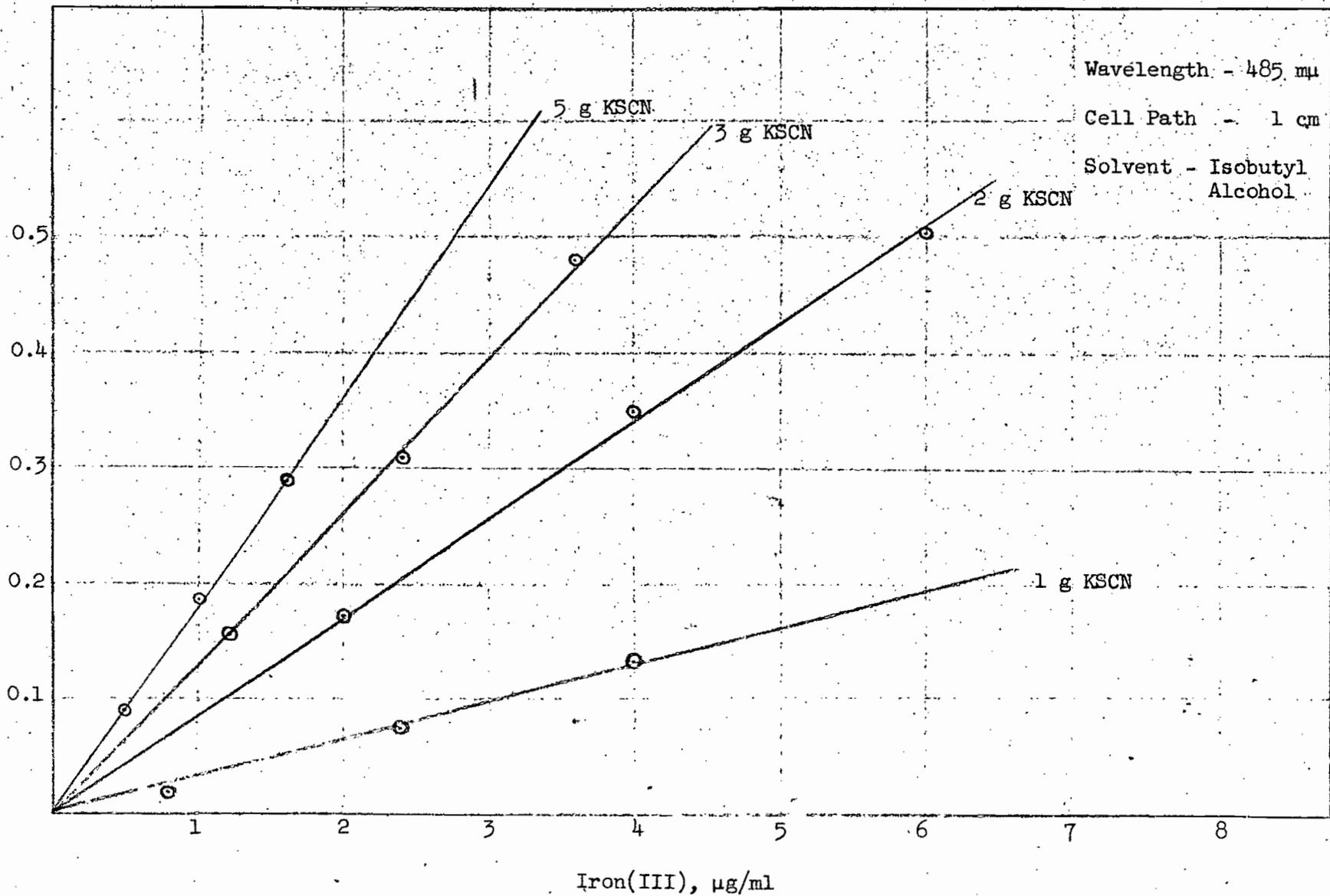
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September 13, 1955

Figure 1. Calibration Curve for Determination of Iron(III) in Alkali Metal Fluoride Samples by Thiocyanate Method



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