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X-426 (Revised 1-52)

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CENTRAL FILES NUMBER
55-7-103

DATE: July 22, 1955

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SUBJECT: Determination of Iron(III) in Mixtures of Alkali Metal Fluoride Salts

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JWM-1

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ABSTRACT

DETERMINATION OF IRON(III) IN MIXTURES OF ALKALI METAL FLUORIDE SALTS, JWM-1

An Ultraviolet Spectrophotometric Method for Iron(III) Complexed With Phosphoric Acid

A method which is based on the absorption of the ferric phosphate complex in the ultraviolet has been developed for the determination of iron(III) in the presence of iron(II) in mixtures of alkali metal fluoride salts. Iron(III) in concentrations of 1 to 5 μg/ml in 0.5 M H_2SO_4 and 1 M H_3PO_4 solution may be determined accurately by observing the absorbance at 260 mμ. Alkali metals, Ni(II), Cr(III), Fe(II) and fluorides do not interfere, however zirconium and uranium interfere seriously.

DETERMINATION OF IRON(III) IN MIXTURES OF ALKALI METAL FLUORIDE SALTS

An Ultraviolet Spectrophotometric Method for Iron(III) by Complexation With Phosphoric Acid

Purpose

To find a sensitive method for the determination of iron(III) in the presence of a large excess of iron(II) in mixtures of alkali metal salts.

Introduction

The concentration of iron(III) may be obtained indirectly in a given sample after the determination of iron(II) and total iron. This method is unsatisfactory when the ratio of iron(III) to iron (II) is small. A more desirable approach to the problem would be the development of a direct method for iron(III). A number of sensitive colorimetric methods for the determination of iron(III) are available, but all have the disadvantage that iron(II) is readily oxidized to iron(III) by air in the pH range required for color development of the complex.

Iron(III) and phosphoric acid form a stable complex which exhibits an absorption peak at 260 mμ. In 1 M H_3PO_4 the molecular absorbancy index of this complex is 5.0×10^3 (1) which compares favorably with that of the ferrous-1,10-phenanthroline complex, which is reported to be 11.1×10^3 at 510 mμ (2). The work described herein was designed to develop a method for iron(III) based on the ultraviolet absorption of the phosphate complex at 260 mμ and to determine the effect of other ions which are normally present in these fluoride salt mixtures, such as nickel, chromium, and possibly zirconium and uranium in rather large concentrations.

It was anticipated that the fluoride salts would be dissolved in cold dilute sulfuric acid. Under these conditions any chromium present would be in the form of Cr(III) which is known to give no interference (1). Nickel would appear as Ni(II), and, if present, zirconium would be in the form of zirconyl ions and uranium as U(VI). High concentrations of alkali metal and fluoride ions would also be present.

Experimental

1. Spectra of Possible Interfering Ions. The ultraviolet spectra of the following solutions were determined.

a. Nickel, 100 μg per ml. Prepared by dissolving $NiSO_4(NH_4)_2SO_4.6H_2O$ in 0.5 M H_2SO_4.

b. Iron, 11.2 μg per ml. Prepared by dissolving Fe $NH_4(SO_4)_2.12\ H_2O$ in 0.5 M H_2SO_4 and 1 M H_3PO_4.

c. Chromium 17.2 μg per ml. Prepared by dissolving $CrCl_3.6\ H_2O$ in 0.5 M H_2SO_4 and 1 M H_3PO_4.

d. Zirconium, 5.92 mg per ml. Prepared by dissolving $ZrOCl_2.8\ H_2O$ in 0.5 M H_2SO_4.

e. Uranium, 1.36 mg per ml. Prepared by dissolving UO_2Cl_2 in 0.5 M H_2SO_4 and 1 M H_3PO_4.

The spectra of the above solutions, with the exception of nickel, which showed no absorption in the region from 255 to 280 mμ, are shown in Figure 1.

2. Preparation of Calibration Curve. Pure glassy crystals of $FeNH_4(SO_4)_2.12\ H_2O$ were dissolved in water and diluted to 100 ml so as to contain 0.1 mg Fe per ml in 1 N H_2SO_4. Aliquots of this solution were transferred to 100-ml flasks and 50 ml of 2 N H_2SO_4 and 7 ml of 85 per cent H_3PO_4 added to each flask. These solutions were made to volume with water and the absorbance read against a reference solution, containing no iron, at 260 mμ with a Beckman spectrophotometer, Model DU, equipped with a photomultiplier attachment. A hydrogen discharge tube was used as a light source. A plot of absorbance versus iron(III) concentration (μg per ml) gave a straight line passing through the origin. See Figure 2.

3. Check of Calibration Curve With Standardized Ferric Sulfate Solution. A solution of ferric ammonium sulfate was prepared and standardized against standard ceric sulfate solution; it contained 3.069 mg Fe/ml. After diluting this solution ten-fold, 1 and 2 ml aliquots were transferred to 100 ml flasks and H_2SO_4 and H_3PO_4 were added in the same manner as described previously. The final concentrations of iron in the two solutions were 3.069 and 6.138 μg/ml. The absorbance of these solutions was measured at 260 mμ against a reference solution containing the acids. The average of three observed absorbance values was 0.240 and 0.492 which compared favorably with values of 0.243 and 0.485 obtained from the calibration curve.

4. Determination of Iron(III) in Alkali Fluoride Salts. A sample of a mixture of alkali metal fluorides weighing 1.0184 g was dissolved in 100 ml of 1 N H_2SO_4. Five 10-ml aliquots of this solution were transferred to five 100-ml flasks. Fifty ml of 2 N H_2SO_4 and 7 ml of 85 per cent H_3PO_4 were added to each flask. One,-2,-3,-4,-and-5 ml aliquots of the standard solution containing 0.1 mg of iron(III) per ml were transferred to the flasks. (This corresponded to an iron(III) content of about 0.1 to 0.5 per cent in the original 1.0 g sample.) The absorbance of the resulting solutions was measured against a reference solution of the acids at 260 mμ. Measurements were repeated on the same samples using a reference solution containing the acids plus an appropriate amount of the alkali fluoride mixture. Results are given in Table I.

5. Determination of Iron(III) in $NaF-ZrF_4$. When phosphoric acid is added to samples containing zirconium, the flocculent precipitate of zirconium phosphate which forms may be removed by centrifugation. It was feared, however, that

iron would be lost by adsorption on the precipitate. Four solutions were prepared containing 4 μg/ml of iron(III). Varying amounts of zirconium were added and the ferric iron determined by the method outlined above with the exception that the solutions were centrifuged to remove the zirconium phosphate prior to taking absorbance readings. Results are given in Table II.

Data

Table I

Determination of Iron(III) Added to Mixtures of Alkali Fluoride Salts

Composition of Ref. Solution	Absorbance	Iron Added (A)	Iron Found (B)	Iron Difference, B-A
		milligrams		
0.5 M H_2SO_4 and 1 M H_3PO_4	0.076	1.0	0.98	-0.02
	0.073		0.94	-0.06
	0.155	2.0	1.96	-0.04
	0.153		1.94	-0.06
	0.232	3.0	2.92	-0.08
	0.233		2.94	-0.06
	0.310	4.0	3.90	-0.10
	0.308		3.88	-0.12
	0.388	5.0	4.87	-0.13
	0.384		4.82	-0.18
0.5 M H_2SO_4, 1 M H_3PO_4 and 1 mg/ml NaF-KF-LiF	0.082	1.0	1.05	+0.05
	0.160	2.0	2.03	+0.03
	0.237	3.0	2.99	-0.01
	0.314	4.0	3.95	-0.05
	0.390	5.0	4.90	-0.10

Table II

Determination of Iron(III) in the Presence of Zirconium

Zr	Iron(III) Taken	Iron(III) Found	Loss
mg	mg		Per Cent
0.0	0.4	0.400	0.0
23.7		0.359	10.3
35.6		0.248	38.1
47.5		0.240	40.0

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Discussion

The determination of iron(III) based on the ultraviolet absorption of the phosphate complex is simple and rapid. The method is sensitive and has the advantage that it may be carried out at extremely low pH ranges. Color formation is immediate and permanent. Alkali metals, fluorides, nickel, chromium, and divalent iron do not interfere.

No attempt was made to analyze samples containing uranium in view of the high absorption exhibited by the uranyl ion at wavelengths below 350 mμ.

It was found that zirconium could be removed by precipitation as the phosphate; however, this resulted in a serious loss of iron. It was assumed that the loss was due to the coprecipitation of the iron on the flocculent zirconium phosphate precipitate.

Results were consistently low when readings were made against blanks containing only 0.5 M H_2SO_4 and 1 M H_3PO_4. When mixtures of alkali fluoride salts were added to the blanks in concentrations approximating those in the sample solutions, more nearly theoretical results were observed.

Future Work

Other complexing agents for ferric iron will be tested in an effort to find a method which can be used in the presence of zirconium and uranium.

References

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2. G. F. Smith, and F. P. Richter, Phenanthroline and Substituted Phenanthroline Indicators, p. 78, G. Fredrick Smith Publishing Co., Columbus, Ohio, 1944.

3. Notebook 4647, pp. 1 through 17.

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Figure 1. Absorption Spectra of Iron, Chromium, Zirconium and Uranium Ions in 1 N H_2SO_4, 1 M H_3PO_4

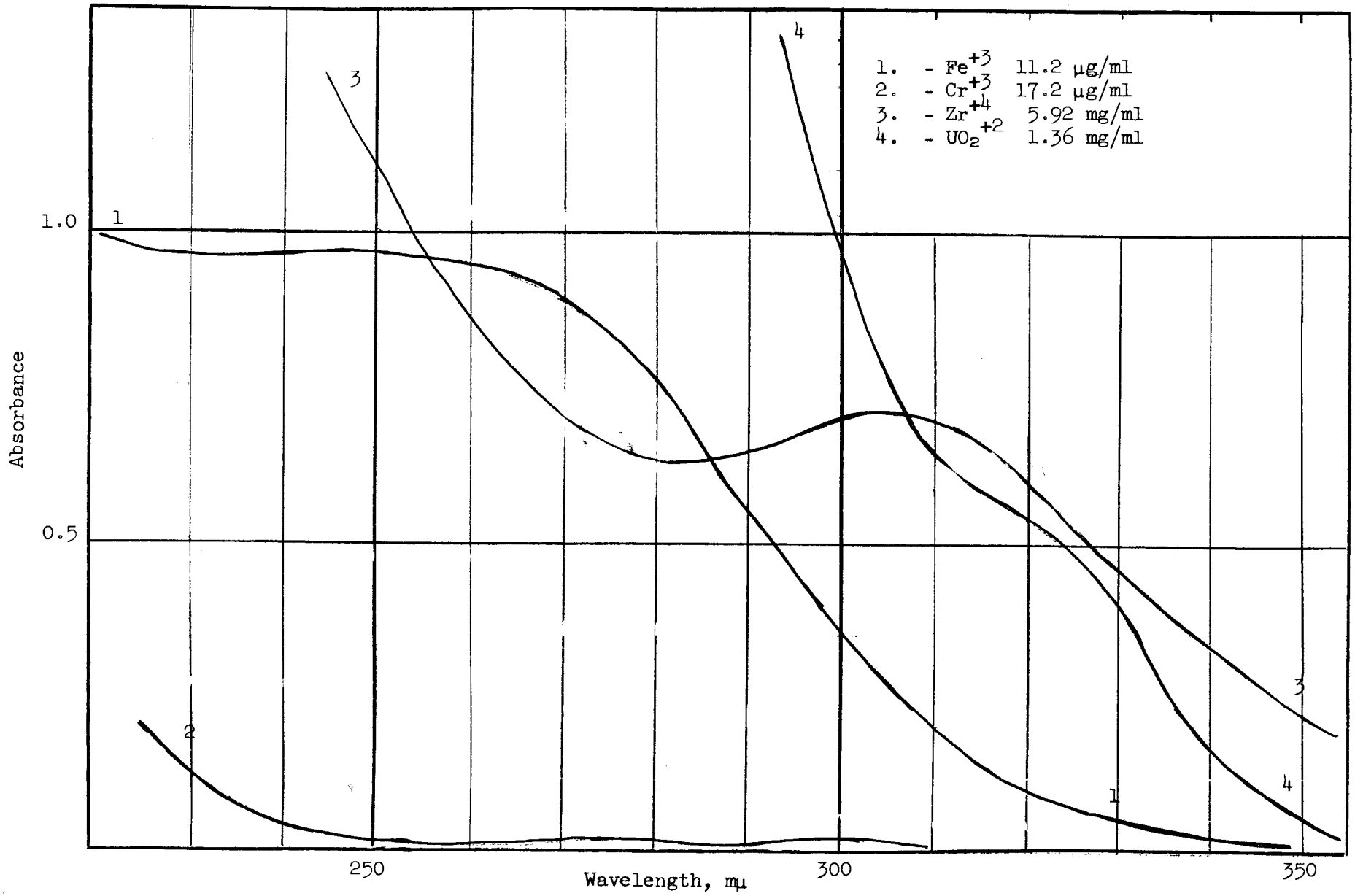

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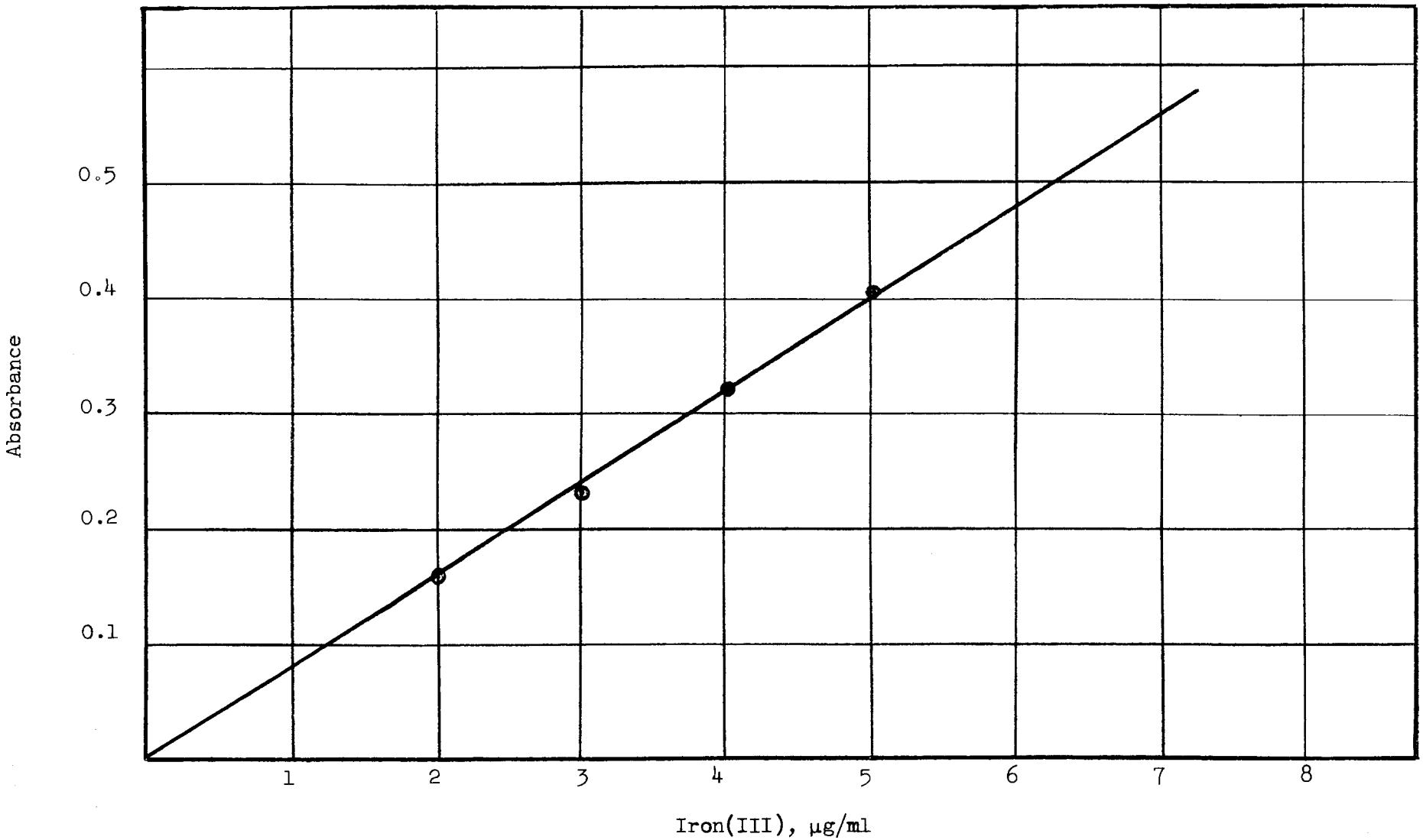
Figure 2. Calibration Curve for the Determination of Iron(III) in 0.5 M H_2SO_4, 1 M H_3PO_4

Wavelength - 260 mμ
Cell path - 1 cm



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