SUMMARY

Uranyl thiocyanate complex is extracted from a slightly acid solution, using tributyl phosphate–carbon tetrachloride as solvent. The effect of various factors on the extraction of uranium and the interference of a number of cations and anions was studied. After extraction, uranium is determined spectrophotometrically in the organic solvent.

RÉSUMÉ

On propose une méthode de dosage spectrophotométrique de l'uranium. Elle est basée sur l'extraction du thiocyanate complexe au moyen du mélange phosphate de tributyle–tétrachlorure de carbone. L'influence d'un certain nombre de cations et d'anions a été examinée.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Uran beschrieben. Sie beruht auf der Extraktion des Uranyl-thiocyanat Komplexes mit einem Gemisch von Tributylphosphat und Tetrachlorkohlenstoff. Der Einfluss einer Anzahl Kationen und Anionen wird untersucht.

REFERENCES

1 J. E. CURRAH AND F. E. BEAMISH, *Ind. Eng. Chem., Anal. Ed.*, 19 (1947) 609.
2 O. A. NIETZEL AND M. A. DE SESA, *Anal. Chem.*, 29 (1957) 756.
3 M. GERHOLD AND F. HECHT, *Mikrochemie ver. Mikrochim. Acta*, 37 (1951) 1100.
4 L. SILVERMAN AND L. MOUDY, *Nucleonics*, 12 (1954) 60.
5 J. CLINCH AND M. J. GUY, *Analyst*, 82 (1957) 802.
6 A. RINGBOM, *Z. anal. Chem.*, 115 (1939) 332.
7 F. W. BURSTALL AND R. A. WELLS, *Analyst*, 76 (1951) 396.

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OXIDATION OF HYDROXYLAMINE BY FERRICYANIDE IN PRESENCE OF ZINC SULFATE

A RAPID METHOD FOR ESTIMATING HYDROXYLAMINE AND HYDRAZINE IN A MIXTURE

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Both hydrazine and hydroxylamine are powerful reducing agents and their determination in presence of each other is usually a difficult problem. While hydrazine is almost always oxidized exclusively to nitrogen by various reagents, hydroxylamine tends to be converted non-stoichiometrically to several products such as N_2, N_2O, HNO_2, HNO_3 and other related compounds[1]. Nonetheless, under prescribed conditions, hydroxylamine is oxidized to nitrous oxide by cerium(IV)[2] and iron(III)[3], to nitric acid by bromate[4], and to nitrogen by ferricyanide[5]. The standard method of determining hydroxylamine is based on its conversion to nitric acid by an excess of potassium bromate in hydrochloric acid solution followed by an iodometric titration of the excess against thiosulfate[4]. Experience has shown that the bromate method requires considerable skill and rigid adherence to the prescribed conditions, especially in preventing the loss of free bromine which is formed during the reaction. FURMAN AND

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FLAGG[6] have suggested a useful modification of this procedure by adding an excess of standard arsenite solution to the unreacted bromate, and backtitrating with 0.1 N bromate using methyl orange indicator. The results by this modification were found to be much better than by direct iodometry of the excess of bromate, but the method is still involved. Perhaps it might be preferable to use a bromate–bromide mixture in strongly hydrochloric acid or glacial acetic acid medium.

In the literature, two methods are described for the determination of hydrazine and hydroxylamine when present together. Potassium bromate in hydrochloric acid solution oxidizes hydrazine and hydroxylamine respectively to nitrogen and nitric acid. The excess of bromate is determined in one sample whereas in the second sample the volume of nitrogen evolved is measured[7]. According to LANG[8], hydrazine can be titrated in sulfuric acid solution with potassium iodate by the iodine cyanide procedure without oxidation of hydroxylamine, provided that not more than the equivalent of 0.07 g of $NH_2OH \cdot HCl$ are present. After the ICN is destroyed by just a sufficient quantity of sodium sulfite, the iodide ion is precipitated with silver nitrate. The hydroxylamine is then oxidized to nitrous oxide and water by boiling with an excess of ferric ammonium sulfate, and the iron(II) formed is titrated in presence of manganous sulfate catalyst with standard permanganate. While the former method necessitates a gasometric measurement, the latter is a lengthy procedure and is dangerous owing to the use of potassium cyanide.

SANT[5,9] developed a method of determining hydroxylamine, based on its conversion to nitrogen by an excess of ferricyanide in a weakly alkaline solution (pH 8–9). The analysis was completed by titrating the ferrocyanide formed with ceric sulfate or the unused ferricyanide iodometrically. In strongly alkaline medium the reaction is non-stoichiometric. Recently it has been shown that hot standard solutions of ferricyanide can be titrated directly with hydrazine sulfate[10] or sodium nitrite[11] in presence of zinc sulfate. Zinc sulfate raises the oxidation potential of the ferricyanide ion through the removal of ferrocyanide ion as sparingly soluble zinc potassium ferrocyanide. The complete decolorization of the solution indicates the end-point.

Preliminary experiments in these Laboratories revealed that the above ferricyanide procedures for hydrazine and nitrite could be extended to determine hydroxylamine. However, in presence of zinc sulfate, hydroxylamine is oxidized to nitric acid instead of to nitrogen as when ferricyanide is used in a weakly alkaline medium. Ferricyanide in strongly alkaline solutions or in presence of zinc sulfate always converts hydrazine to nitrogen so that oxidation of a sample containing both hydrazine and hydroxylamine by ferricyanide under different conditions should give a measure of the quantity of each reductant present. Ferricyanide in strongly alkaline medium does not convert hydroxylamine quantitatively to nitrogen but no data exist on the reaction between hydrazine and ferricyanide in weakly alkaline medium. A series of experiments showed that hydrazine is oxidized quantitatively to nitrogen by excess of ferricyanide in borax–boric acid buffer solution (pH 8–9). The analysis was completed by titrating both the ferrocyanide formed against standard ceric sulfate[12] and the unused ferricyanide iodometrically against standard thiosulfate[13]. These observations were used in the present work.

The present paper reports a simple method of determining milligram amounts of hydroxylamine by direct titration of alkaline ferricyanide in presence of zinc sulfate

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and a rapid procedure for the analysis of hydroxylamine and hydrazine when present together.

EXPERIMENTAL

An aqueous solution of hydroxylamine sulfate was prepared from a pure sample supplied by the Commercial Solvents Corporation. Its hydroxylamine content was checked by titrating the acid part and also by the ferricyanide method[5,9]. All other chemicals used were of reagent grade.

Procedure

Determination of hydroxylamine. To a measured volume of standard potassium ferricyanide solution, 2–3 g of crystalline zinc sulfate and a sufficient quantity of sodium or potassium hydroxide to maintain the total alkalinity at 0.5–1.0*N* were added and the mixture was heated to boiling. The hydroxylamine sulfate solution was added from a buret gradually till the precipitate was clear white and the supernatant liquid colorless. The reaction corresponds to the oxidation of hydroxylamine to nitric acid and water:

$$2K_3Fe(CN)_6 + 2KOH \rightarrow 2K_4Fe(CN)_6 + H_2O + [O]$$
$$2K_4Fe(CN)_6 + 3ZnSO_4 \rightarrow Zn_3K_2[Fe(CN)_6]_2 + 3K_2SO_4$$
$$NH_2OH + 3[O] \rightarrow HNO_3 + H_2O$$

Thus 1 ml of 1*N* $K_3Fe(CN)_6$ is equivalent to 5.505 mg NH_2OH. A typical set of results is given in Table I.

TABLE I

ESTIMATION OF HYDROXYLAMINE

NH_2OH (mg)		*Difference (mg)*
Calculated	*Found*	
1.114	1.101	0.013
2.228	2.203	0.025
4.450	4.407	0.049
8.912	8.818	0.094
13.368	13.224	0.144

Determination of hydroxylamine in presence of hydrazine. Measured quantities of hydroxylamine and hydrazine sulfates were mixed and the solution diluted to 250 ml. Oxidation was effected by ferricyanide as follows:

(*a*) An aliquot portion of the mixture was treated with a known excess of ferricyanide solution followed by 25–30 ml of borax–boric acid buffer solution (pH 8–9). After 15–30 min, the solution was diluted to a suitable volume. In aliquots of this solution either the unused ferricyanide was titrated iodometrically or the ferrocyanide formed was titrated with standard ceric sulfate.

(*b*) A known volume of ferricyanide was titrated hot in presence of zinc sulfate and at a total alkalinity of 0.5–0.8*N* with the mixed solution of hydrazine and hydroxylamine sulfates. The end-point was shown by the appearance of a clear white precipitate.

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In the two methods (*a*) and (*b*), the reactions taking place are:

(*a*) $N_2H_4 + 4K_3Fe(CN)_6 + 4KOH \rightarrow N_2 + 4K_4Fe(CN)_6 + 4H_2O$ . . . . (1)

$2NH_2OH + 2K_3Fe(CN)_6 + 2KOH \rightarrow N_2 + 2K_4Fe(CN)_6 + 4H_2O$ . . . (2)

(*b*) $N_2H_4 + 4K_3Fe(CN)_6 + 4KOH + 6ZnSO_4 \rightarrow N_2 + 2Zn_3K_2[Fe(CN)_6]_2 + 6K_2SO_4 + 4H_2O$ . . . . . (3)

$NH_2OH + 6K_3Fe(CN)_6 + 6KOH + 9ZnSO_4 \rightarrow HNO_3 + 3Zn_3K_2[Fe(CN)_6]_2 + 9K_2SO_4 + 4H_2O$ . . . . . (4)

Let V_1 and V_2 be the volumes of ferricyanide consumed by the same quantity of the mixture in methods (*a*) and (*b*) respectively. If x ml of ferricyanide are consumed by hydrazine, then $(V_1 - x)$ ml will have been consumed by hydroxylamine in (*a*) and $(V_2 - x)$ ml in (*b*). Whereas the equivalent weight of hydroxylamine in (*a*) is the same as the molecular weight, it is one-sixth in (*b*). Therefore

$$(V_1 - x) = \frac{(V_2 - x)}{6}$$

From this the values of x, $(V_1 - x)$, and $(V_2 - x)$ can be obtained. The quantity of hydrazine equivalent to x ml of ferricyanide can be calculated from the relation 1 ml of 1*N* $K_3Fe(CN)_6$ = 8.012 mg hydrazine and the hydroxylamine equivalent of $(V_2 - x)$ ml of ferricyanide from the relation 1 ml of 1*N* $K_3Fe(CN)_6$ = 5.505 mg hydroxylamine.

RESULTS

A representative set of data is shown in Table II. The results are the average values of duplicate experiments.

TABLE II

ESTIMATION OF HYDRAZINE AND HYDROXYLAMINE IN A MIXTURE

Expt. No.	N_2H_4 (mg)			NH_2OH (mg)		
	Calcd.	Found	Diff.	Calcd.	Found	Diff.
1.	3.174	3.186	0.012	0.9635	0.9545	0.009
2.	1.440	1.450	0.010	1.927	1.909	0.018
3.	6.348	6.362	0.014	1.927	1.909	0.018
4.	1.440	1.450	0.010	3.854	3.820	0.034
5.	2.880	2.900	0.020	3.854	3.818	0.036
6.	2.880	2.900	0.020	7.708	7.640	0.068

DISCUSSION

The reaction between ferricyanide and hydroxylamine in presence of zinc sulfate was shown to be quantitative at an alkalinity of 0.5–1.0*N*. At lower alkalinity the reaction is slow, whereas in too alkaline a solution zinc ions tend to go into solution and interfere with reaction(4). This difficulty can be obviated by using larger quantities

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of zinc sulfate. The amount of zinc sulfate is not critical provided that more than 2 g are present during each titration.

When hydroxylamine is oxidized to nitric acid, a good conversion factor is obtained so that the method is suitable for the determination of small amounts of hydroxylamine. Potassium bromate also effects this oxidation completely, but the present ferricyanide method is simpler and much less time-consuming. The availability of very pure potassium ferricyanide and its large equivalent weight (about 12 times that of potassium bromate) are also important.

In contrast to the bromate and the iodine cyanide methods for analyzing a mixture of hydrazine and hydroxylamine, the ferricyanide procedure described is not exacting and it can be completed within 45 minutes. The error rarely exceeds 2% which may be acceptable considering the difficulties involved in such an analysis.

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SUMMARY

The direct titration of alkaline ferricyanide in presence of zinc sulfate with hydroxylamine sulfate has been studied. A clear white precipitate of zinc potassium ferrocyanide indicates the end-point. Hydroxylamine is oxidized to nitric acid and water, and milligram quantities of hydroxylamine can be determined. In the absence of zinc sulfate and in weakly alkaline medium, hydrazine and hydroxylamine are converted to nitrogen, while in presence of zinc sulfate hydrazine is oxidized to nitrogen. By ferricyanide oxidation of a mixed sample under different conditions, hydrazine and hydroxylamine when present together can be determined rapidly.

RÉSUMÉ

L'auteur décrit une méthode simple pour le microdosage de l'hydroxylamine, au moyen de ferricyanure, en présence de sulfate de zinc. Il propose également une méthode rapide pour le dosage de l'hydrazine et de l'hydroxylamine, en présence l'une de l'autre, par le ferricyanure de potassium, avec et sans sulfate de zinc.

ZUSAMMENFASSUNG

Es wird eine einfache Mikromethode beschrieben zur Bestimmung von Hydroxylamin mit Alkaliferricyanid in Gegenwart von Zinksulfat. Unter Einhaltung bestimmter Bedingungen können auch Hydroxylamin und Hydrazin nebeneinander mit Alkaliferricyanid bestimmt werden.

REFERENCES

1 L. F. AUDRIETH, *The Chemistry of Hydrazine*, J. Wiley & Sons, New York, 1951.
2 S. R. COOPER AND J. B. MORRIS, *Anal. Chem.*, 24 (1952) 1360.
3 F. RASCHIG, *Ann.*, 241 (1887) 161.
4 A. KURTENACKER AND J. WAGNER, *Z. anorg. Chem.*, 120 (1921) 261.
5 B. R. SANT, *Z. anal. Chem.*, 145 (1955) 257.
6 N. H. FURMAN AND J. H. FLAGG, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 738.
7 W. BÖTTGER, *Newer Methods of Volumetric Chemical Analysis*, D. Van Nostrand Co., New York, 1938, pp. 89, 107.
8 R. LANG, *Z. anorg. Chem.*, 142 (1925) 280.
9 B. R. SANT, *Z. anal. Chem.*, 158 (1957) 116.
10 B. R. SANT, *Anal. Chim. Acta*, 19 (1958) 205.
11 B. R. SANT, *Anal. Chim. Acta*, 19 (1958) 523.
12 C. J. DERNBACH AND J. P. MEHLIG, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 58.
13 E. J. CUY AND W. C. BRAY, *J. Am. Chem. Soc.*, 46 (1924) 1786.

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