Turkish Journal of Nuclear Sciences, 10 (1983) 140-145

DETERMINATION OF URANIUM IN WET-PROCESS PHOSPHORIC ACID

C. KALDIRIMCI - Z. YÖNTEM - H. KUMBUR

Ankara Nuclear Research and Training Center,
Beşevler - Ankara,

ABSTRACT

Colorimetric (Dibenzoylmethane, Arsenazo III) and fluorimetric methods were applied in rutine for the determination of uranium in phosphoric acid. Although the uranium values obtained from the three methods were in agreement; our laboratory practice revealed that the Arsenazo III method to be the most favourable one.

ÖZET

Fosforik asit içinde bulunan uranyumun tayin edilmesinde Kolorimetrik (Dibenzoilmetan, Arsenazo III) ve fluorometrik yöntemler uygulanmış ve yöntemler rutin hale getirilmiştir. Her üç yöntem ile saptanan uranyum değerleri arasında uyum bulunmaktadır. Ancak kendi çalışma pratiğimiz ve çalışma koşullarımız açısından Arsenazo III yöntemi tercih edilecek bir yöntem olarak ortaya çıkmıştır.

INTRODUCTION

In general, for the determination of uranium in various solutions, methods such as Radiometry, Chromatography, Atomic Absorption Spectroscopy, Emission Spectroscopy, Volumetry, Potentiometry, Fluorometry, Colorimetry, Gravimetry, Neutron Activation Analysis etc.., can be used.

The concentration of uranium in phosphoric acid is low and it is strongly complexed by phosphate ions. Besides that, the acid contains various amounts of interfering ions and organic components. So, only a few of the numerous methods can be used for the determination of uranium in phosphoric acid. In this study, the Colorimetric (Dibenzoylmethane, Arsenazo III) and the Fluorometric methods were used.

EXPERIMENTAL

I. TOPO-Dibenzoylmethane Method /2-5/

This method is suitable for the determination of 20-2700 µg of uranium (VI) in solutions of nitrate, sulfate or perchlorate which also contain other metals as impurities. The concentration of uranium (VI) in the final volume in which the spectrophotometric measurement will be made, should be 1-11 ppm. In this range the standart deviation is 2%.

This method is based on the extraction of U (VI) from a nitric acid medium into the Tri-n-octyl-phosphine oxide (TOPO) solution and complexing the uranium in the organic phase with dibenzoylmethane. An aliquot taken from the organic phase is diluted with butanol and buffered with pyridine. The absorbance measurement is made after 10 minutes at 405 nm. against the blank.

The TOPO-DBM method is applied in two ways: DBM(I)-First application is based on the additions of only one standard /2/. The phosphoric acid sample was taken according to Table-1.

TABLE-1. Sampling of the phosphoric acid.

Estimated U (g/l)	Volume required for the analysis (ml)	Added $Al(NO_3)_3$* (ml)	Added HNO_3** (ml)	Added H_2O (ml)	Volume taken for extraction	Dilution factor
0.00-0.05	20	25	0	55	20	0.25
0.05-0.20	5	25	5	65	20	1.00

* 1000 g of $Al(NO_3)_3 \cdot 2H_2O$/450 ml H_2O
** Concentrated

Interference that is due to excessive amounts of phosphate is eliminated by addition of aluminum nitrate.

Their absorbances are measured at 405 nm. The Uranium concentration in phosphoric acid is calculated according to the following formula:

$$U(g/l) = \frac{X.B.K}{(A-B)1000}$$

where, A: Absorbance of the uranium added sample
B: Absorbance of the sample
X: Weight of additional uranium (µg)
K: Dilution factor

DBM (II)-In the second application of DBM-TOPO method, the effects of interfering ions are minimized or eliminated. Interferences by chromium (VI), vanadium (V) and iron (III) are decreased by selective reduction with hydroxylammonium sulphate. Interferences that are due to titanium (IV), thorium (IV) and zirconium (IV) can be minimized by complexation of these ions with fluoride. Excess of fluoride and phosphate can be decreased by the addition of aluminum nitrate. Concentrated nitric acid is added to make the final solution 2-3M in both nitrate and hydrogen ion concentration.

The absorbances of the solutions are measured at both 405 and 416 nm. The uranium concentration is calculated from the data of 405 and 416 nm measurements must be in agreement. If not, the amount of reagents used for the elimination of the effects of the interfering ions must be readjusted again and the analysis should be repeated until the agreement is achieved.

II. Arsenazo III Method /6/.

Arsenazo III is one of the most sensitive reagents used for colorimetric uranium determination. In the mineral acid medium a blue color is produced by the reaction of uranyl ions with Arsenazo III /3-(2-arsenophenyl-azo)-4,5-dihydroxy-2,7- naphthalenedisulfanic acid/. In the determination of uranium, interferences by Al(III), Ba(II), Bi(III), Ca(II), Cd(II), Cu(II), Dy(III), Fe(III), Hg(II), Mn(II), Ni(II), Pb(II), Sc(III), Sr(II), Ti(IV), VO(II), VO_3^-, Y(III), Zn(II), Zr(IV) can be minimized by complexation of these ions with EDTA, titriplex (IV) and NaF. Interferences that are due to Mo(VI), W(VI) or Ti(IV) can be eliminated with tartaric acid. Excess of these masking agents do not affect the uranium results. Phosphate interferes seriously, but nitrate, chloride, perchloride do not interfere. For the elimination of other interferences, uranium must be extracted from aqua phase into organic phase.

III. Fluorometric Method /4,9/

The fluorometric method for the determination of uranium is one of the most sensitive methods because

even less than 10^{-16} g of U can be determined.

A number of ions such as Fe, Cr, Cu, Si, Ca, Mo, Ce, Ni, V, Zn, Sn, Al, Pb, Mg, Ti, SO_4^{-2}, Cl^-, PO_4^{-3} quench uranium fluorescence. The tolerances and effects of addition of ions above were given in the literature /4,9/. The quenching of the emitted fluorescent light by interfering ions are eliminated by dilution, internal-standard addition and extraction techniques. An aliquot of the liquid sample is diluted and acidified so that the diluted sample contains approximately $1x10^{-2}$ g of U_3O_8 per ml in a 5% nitric acid solution. 30% hyrogen peroxide is added dropwise until the characteristic permanant light yellow color of uranium (VI) is obtained. One milliliter of the diluted sample is salted with saturated aluminum nitrate solution and the uranium is extracted into 10 ml ethyl acetate. Aliquots of 0,1 ml are removed and transfered onto the flux in platinum dishes. The composition of this flux is 9 parts of sodium fluoride, 45,5 parts of sodium carbonate and 45,5 parts of potassium carbonate by weight. Fluxes are dried, fused at 650°C and allowed to cool. The fluorescence intensities of the melts are measured by a fluorimeter in 1 hour.

RESULTS AND DISCUSSION

Results of the analysis of uranium in phosphoric acid are given in Table-2. Phosphoric acid samples were obtained from Samsun Fertilizer Plant of Turkish Nitrogen Industries Corporation.

Three different methods were applied for the analysis of uranium. As it is obtained from the results in Table-2, the uranium concentration of H_3PO_4 comes out to be 37.2±4.7 ppm as the overall average of last four values. However, in the application of DBM (1) method a very high standard deviation is obtained. This method was studied for only once and 0.190 and 0.210 absorbance units were obtained for the simultaneously studied aliquots of the same sample. On the other hand, the concentrations calculated by the formula using these absorbance values above were 64.8 and 39.1 ppm. Since the standard deviation is comparatively higher than that of the others, this method was not further used.

In the application of DBM (2) method the required amounts of the reagents to eliminate the interferences were searched and estimated. The absorbance measurements were made at both 405 and 416 nm and concentration of

uranium for both wavelengths were found to be similar to each other. This similarity shows that elimination of the interferences was achieved.

The analysis of the same sample was repeated by all of the DBM (2), Arsenazo III and Fluorimetric methods. The results of the DBM (2) and Arsenazo III methods were similar. Results of the Fluorometric method were found to be relatively smaller than those of the others. This shows that the effects of the interfering ions were not eliminated completely.

TABLE-2. Results of the Analysis of uranium in commercial phosphoric acid samples (ppm) with their average values.

DBM (I)	DBM(II) 405nm	DBM(II) 416nm	Arsenazo III	Fluorimetric
64.8	41.1	37.8	41.4	30.4
39.1	40.8	34.2	41.2	32.8
	43.9	36.3	37.3	31.7
	42.0	36.5		30.2
				30.0
52±18.2	41.9±1.4	36.2±1.5	39.9±2.3	31.0±1.2

CONCLUSION

It is concluded that although all of the methods can be used for the determination of uranium in H_3PO_4, the Arsenazo (III) method seems to be the most practical and favourable one regarding our relevant facilities. Unfortunately, including the latter, all of the methods are time consuming.

REFERENCES

/1/ Uzmen, R., CNAEM Report No. 185 (1979) (In Turkish)
/2/ Cogema S.E.C. Determination de l'uranium dans les phosphates et l'acide phosphorique Nov (1978).100
/3/ ORNL Master Analytical Manual TID-7015 (1953).
/4/ Analysis of Essential Nuclear Reactor Materials, New Brunswich Laboratory, USAEC, Division of Technical Information, Library of Congress Catalog Card Number: 64-60035 (1964)
/5/ Jones, M.M., Mac Duff J.S.,White Head A.B., Department of the Interior, Bureau of Mines Report

of Investigations, RI 8433 (1980)
/6/ Rodriquez, B., Junta De Energia Nuclear Division De Material, R. 5. 78 (Rev I) Octobre (1981).
/7/ Rodden, J.C., Analytical Chemistry of Manhattan Project, Division VIII, Volume I, Mc Graw-Hill Book Company Inc. (1950)
/8/ Collected Papers on Methods of Analysis for U and Th, Geological Surrey Bulletin 1006 U.S Government Printing Office (1954).
/9/ Centanni, F.A., Ross, A.M., Desesa, M.A., Analytical Chemistry 28 (1956) 11.
/10/ ORNL Master Analytical Manual TID-7015 Supplement (1953).