

Direct Spectrophotometric Determination of Uranium in Industrial Grade Phosphoric Acid and Phosphorites without its Prior Separation using Arsenazo III Dye

***Hisham kadry Fouad, Randa Maged El-Rakaiby and Abdo Ali Abdo**

Analytical Chemistry Department, Nuclear Materials Authority, P.O box 530 Maadi, Cairo, Egypt

Corresponding author; Tel.; +201223320504; Fax; 202-27585831

E-mail address: hishamfouad66@hotmail.com

Summary: A developed, direct, rapid and sensitive spectrophotometric determination of uranium in Egyptian industrial grade phosphoric acid and phosphorites using arsenazo III as a chromogenic dye was proposed in the present article. The determination was performed without prior separation either by solvent extraction or ion exchange of uranium from its matrix. The basis of the developed method was to overcome the interference effect using masking agents without prior separation of uranium by either technique during the direct determination of uranium using arsenazo III dye. The formed 1:1 U - Arsenazo III complex was stable for 20 minutes. The severe interference due to phosphate anion (39.5 % in H₃PO₄ and about 25 % in phosphorites) was treated by using 10 % ammonium molybdate, where calcium (47 % in phosphorites and 4 % in H₃PO₄) and iron (about 1.5 % in phosphorites and H₃PO₄) were masked using 10 % EDTA - 2Na. The other accompanying elements show no interference effect. Beer's law was obeyed in the range from 0.2 to 3 µg/mL with molar absorptivity $\epsilon = 0.56 \times 10^3 \text{ L. mol}^{-1} \text{ cm}^{-1}$ and an average standard deviation of 0.36. The R.S.D for 10 replicate measurements of 50 µg/mL was 0.51 %.

Introduction

Phosphoric acid (PA) is an important alternative source of uranium. Its concentration in phosphate rock ranges from 0.01 to 0.02 %. Although this concentration is relatively small, yet phosphate deposits represent a large uranium source when one considers the total production of phosphate rock. Approximately 13,000 metric tons of U₃O₈ could be recovered each year and there are many reasons that make the recovery of uranium from PA attractive, especially in countries without conventional uranium ore bodies ⁽¹⁾.

The reagent, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (bromo-PADAP), is described for the spectrophotometric determination of uranium(VI) in waters, ores, phosphoric acid, phosphate rocks, thorium oxide, and zirconium oxide. Extraction of uranium into tri-n-octylphosphine oxide is performed first then measuring the colored uranium complex in the organic phase ⁽²⁾.

The determination of uranium (VI) has been carried out by extraction-spectrophotometric methods based on the use of tributyl phosphate dissolved in isobutyl methyl ketone and trioctylphosphine oxide in benzene. Arsenazo III was used as the metallochromic reagent for the determination of uranium in phosphoric acid solutions of the type used for the leaching of low grade uranium ores ⁽³⁾.

Uranium in a phosphoric acid solution is quantitatively extracted from 2 mol dm⁻³ nitric acid into molten TOPO - biphenyl at about 70°C. It was then determined spectrophotometrically with 1-(2-pyridylazo) naphth-2-ol ⁽⁴⁾.

Uranium in phosphate rock was determined spectrophotometrically using arsenazo I. It was separated on Amberlite IRA - 400 in the sulfate form, and then determined in the eluate by arsenazo I ⁽⁵⁾.

A selective anion-exchange separation and spectrophotometric method has been developed for the determination of uranium and thorium in phosphate rocks using Amberlite CG 400 (NO₃⁻) column then eluted consecutively and determined spectrophotometrically with arsenazo III ⁽⁶⁾.

An extraction of trace amounts of uranium in phosphate fertilizers with trioctylphosphine oxide in benzene and its spectrophotometric determination with arsenazo III was described ⁽⁷⁾.

A method for quantitative determination of uranium in wet phosphoric acid depends on the extraction with di-nonylphenyl phosphoric acid. The uranium was stripped and determined spectrophotometrically with arsenazo III ⁽⁸⁾.

The uranium present in phosphoric acid was extracted with di(2-ethylhexyl)phosphoric acid and TBP then stripped with iron (II). The uranium was finally determined with arsenazo III ⁽⁹⁾.

An analytical procedure was developed for the determination of small amounts of uranium in presence of excess phosphoric acid using the anion exchanger Amberlite IRA - 400 in a micro column. After elution with 1N HCl, uranium concentration as low as 0.01 µg/mL can be readily polarographed by the use of nitrate reduction wave catalyzed by uranium ⁽¹⁰⁾.

In the present work, a developed, direct, rapid and sensitive spectrophotometric determination of uranium in phosphorites and phosphoric acid using arsenazo III ⁽¹¹⁾ as a chromogenic dye was proposed but without prior separation of uranium from its matrix using either solvent extraction or ion exchange techniques. Masking agents were used to overcome the interference effect of the accompanying elements, mainly phosphate, iron and calcium ions which were masked with 10% ammonium molybdate and 10% EDTA – 2Na solutions respectively.

Experimental

Chemicals and Reagents

- All the chemicals used in this work were analytical grade quality. Double distilled water was used in all preparations. Arsenazo III chromogenic dye, purchased from Merck. The EDTA – 2Na salt, from Riedel De Haen, Netherlands, oxalic acid (Adwic, Egypt), ammonium fluoride (Adwic, Egypt), ammonium molybdate (Merck, Germany) and tartaric acid (BDH).

Stock solutions of different reagents

- Arsenazo III dye (0.25%, w/v) was prepared by dissolving 0.25 g of the dye in double distilled water containing 0.5g sodium acetate, diluted to 100 mL volumetric flask and stored in a dark bottle.

- Stock solutions of 1, 5, 10 % (w/v) of each of ammonium molybdate, ammonium fluoride, oxalic acid, tartaric acid and EDTA – 2Na were prepared by weighing 1, 5, 10 g of each and dissolved in 100 mL double distilled water.
- A synthetic uranium solution (100 µg/mL) was prepared by dissolving 0.0211g uranyl nitrate hexahydrate in 100 mL double distilled water.

Instrumentations

A double beam UV-Visible spectrophotometer of high resolution power model Unicam with a wavelength ranging from 190 to 1100 nm, computer controlled data and reporting software was used in systematic study for the determination of phosphate, uranium, and various cations and anions⁽¹¹⁾. An atomic absorption spectrometer model Unicam 969 supplied with acetylene and nitrous oxide burner heads, regulators and integrated reading in absorbance, was used for the determination of trace impurities in phosphoric acid and phosphatic samples. A flame photometer model Sherwood 410 was used for sodium and potassium determination. A pH meter model Jenway was applied satisfactorily in the present work and calibrated daily by using two successive buffer solutions (pH 4 and 7 or 7 and 10).

Recommended method for decomposition and analysis of uranium in three phosphate samples

- 1) A weight of 0.5g of each quartered phosphate sample was placed in a glass beaker.
- 2) A 20 mL of 4 M HNO₃ were added and the beaker was covered with watch glass.
- 3) The whole content was heated for 2 hours on a water bath at 70°C.
- 4) After filtration the filtrate was completed to a proper volume in a volumetric flask.
- 5) An aliquot of 1mL was taken and the recommended masking agents were added; about 2 mL of 10 % (w/v) ammonium molybdate and 0.6 mL of 10 % (w/v) EDTA - 2Na solution.
- 6) Uranium concentration was then determined by the arsenazo III method.

Results and Discussion

The efficiency of different masking agents with different concentrations used to mask several accompanying elements mainly phosphate, iron and calcium during direct uranium determination using arsenazo III chromogenic dye were studied.

Effect of P₂O₅ concentration

Synthetic solutions containing pure phosphoric acid (30% P₂O₅) and different concentrations of uranium (40, 50, 100 and 150 µg/mL) were prepared, and uranium was directly determined spectrophotometrically using arsenazo III dye. From the data obtained in Table (1), severe interference for uranium concentration was due to high concentration of phosphate anion present in phosphoric acid and phosphorites.

Table(1): Spectrophotometric determination of uranium in presence of constant concentration from phosphate anion

Uranium concentration added (µg/mL)	Uranium concentration determined without masking, (µg/mL)
40	5.6
50	8.7
100	20.3
150	58.8

Several masking agents such as ammonium molybdate, tartaric acid and oxalic acid⁽¹²⁾ with different concentrations (1, 5 and 10 %, w/v) were used for masking phosphate anion during determination of uranium [30 % P₂O₅ and 50 µg/mL U].

Table (2): Masking of phosphate anion using different concentrations of ammonium molybdate, tartaric and oxalic acid

Volume (mL)	Ammonium molybdate Concentration (w/v)			Tartaric acid concentration (w/v)			Oxalic acid concentration (w/v)		
	1%	5%	10%	1%	5%	10%	1%	5%	10%
	Uranium Concentration (µg/mL)								
0.2	9.7	14.8	16.5	6.4	9.4	30.5	5.2	5.8	14.1
0.5	10.6	16.1	27.5	8.6	13.6	36.4	5.3	6.1	14.4
1.0	8.9	15.7	41.5	7.2	14.1	35.8	5.7	13.7	14.2
1.5	11.8	15.6	46.5	7.9	18.5	36.8	5.9	13.6	14.5
1.6	11.7	16.5	47.2	7.8	18.6	40.2	5.8	13.5	14.3
1.7	11.9	16.8	48.3	7.9	18.9	42.3	6.1	13.8	14.8
1.8	12.1	17.2	48.5	8.5	19.2	44.5	5.9	13.9	14.6
1.9	12.5	18.6	50.6	8.9	19.5	45.2	6.2	14.2	14.7
2.0	13.5	20.3	51.2	10.2	19.6	45.3	6.3	14.3	14.6

From the data gathered in Table (2), it was clear that ammonium molybdate (1.8 - 2 mL from 10% w/v) was the most efficient masking agent for phosphate anion during the direct spectrophotometric determination of uranium with a standard deviation of 0.081 and a standard error of 0.033, where phosphate anion reacts with ammonium molybdate to form soluble molybdophosphate complex, hence masking phosphate completely⁽¹²⁾. On the other hand, tartaric acid showed lesser efficiency and oxalic acid was the least efficient masking

agent. The determination of constant concentration of uranium in presence of different phosphoric acid concentrations (30, 40 and 50% P_2O_5) were studied using ammonium molybdate as masking agent. From the results obtained in Table (3), it was found that good results were obtained for uranium in presence of different phosphate concentrations.

Table(3): Spectrophotometric determination of uranium ($40 \mu\text{g/mL}$) in presence of different phosphate concentrations (30 , 40 and 50 % P_2O_5) using 1.8 mL from 10 % ammonium molybdate as masking agent

P_2O_5 concentration added (%)	Uranium concentration determined without masking, $\mu\text{g/mL}$	Uranium concentration determined with masking, $\mu\text{g/mL}$
30	6.1	39.5
40	5.5	39.0
50	4.5	39.0

Effect of iron concentration

A synthetic solution containing pure phosphoric acid (30% P_2O_5), $40 \mu\text{g/mL}$ uranium and an equivalent amount to 1.5 % ferric ions (average concentration found in phosphorites and phosphoric acid) was prepared. Uranium was directly determined spectrophotometrically using arsenazo III dye. From the data gathered in Table (4) it was found that severe interference for uranium concentration caused by iron has occurred.

Table(4): Spectrophotometric determination of constant concentration for uranium ($40 \mu\text{g/mL}$) in presence of different concentrations from iron without using masking agent

Fe_2O_3 concentration added, %	Uranium concentration determined without masking, $\mu\text{g/mL}$
1.0	3.1
1.5	2.8
2.0	2.5

Different masking agents were used such as ammonium fluoride⁽¹³⁾ and EDTA - 2Na⁽¹⁴⁾ in different concentrations (1, 5 and 10 % w/v) to mask iron during the direct spectrophotometric determination of uranium ($50 \mu\text{g/mL}$). Data obtained were gathered in Table (5).

Table (5): Masking of iron using different concentrations of ammonium fluoride and EDTA - 2Na

Volume (mL)	Ammonium Fluoride Concentration (w/v)			EDTA - 2Na concentration (w/v)		
	1 %	5 %	10 %	1 %	5 %	10 %
	Uranium Concentration ($\mu\text{g/mL}$)					
0.2	6.3	14.4	38.4	8.6	15.2	40.8
0.5	4.7	18.6	39.5	8.5	14.6	48.9
0.6	4.6	18.5	45.2	8.1	15.6	49.5
0.7	5.2	18.6	48.6	9.2	18.6	48.8
0.8	5.9	18.9	49.2	9.4	19.8	48.9
0.9	6.5	18.7	48.9	10.3	19.6	49.2
1.0	10.6	19.6	48.8	10.5	20.5	49.3
1.5	10.2	20.4	48.5	10.4	21.6	48.9
2.0	10.5	20.8	48.7	10.6	21.5	49.3

From the results obtained in Table (5) it was obviously found that 0.8 – 1 mL of 10 % ammonium fluoride and 0.5 – 2.0 mL of 10 % EDTA - 2Na were quite sufficient to mask nearly the interfering iron found, where they gave concentration values from 48.9 $\mu\text{g/mL}$ to 49.5 $\mu\text{g/mL}$ for uranium with average standard deviation of 0.092 and 0.187 and standard errors of 0.04 and 0.08 for ammonium fluoride and EDTA – 2Na respectively. The concentrations obtained were the closest to the concentration of uranium (50 $\mu\text{g/mL}$) found in the prepared synthetic solution.

Effect of Calcium concentration

Calcium in phosphorites and industrial grade phosphoric acid was found in high concentrations (maximum concentration in phosphorites is 47 % and in industrial grade H_3PO_4 was about 4 %) while uranium concentration was in microgram per milliliter ($\mu\text{g/mL}$) concentrations, hence interference of calcium was expected. A synthetic solution containing pure phosphoric acid (30 % P_2O_5), 50 $\mu\text{g/mL}$ uranium and an equivalent amount to 40 % CaO was prepared. Uranium was directly determined spectrophotometrically using arsenazo III dye, where a concentration of 37.2 $\mu\text{g/mL}$ instead of 50 $\mu\text{g/mL}$ was obtained indicating that calcium interferes during direct determination of uranium. One of the most important and efficient masking agent for both calcium and magnesium was EDTA - 2Na, where several concentrations (1, 5, 10%, w/v) were added in different volumes to the synthetic solution, and uranium was determined.

Table (7): Masking for calcium using different concentrations from EDTA - 2Na [40 % CaO and 50 µg/mL U]

Volume (mL)	EDTA – 2Na Concentration (w/v)		
	1 % EDTA – 2Na	5 % EDTA – 2Na	10 % EDTA – 2Na
	Uranium Concentration (µg/mL)		
0.2	45.2	45.6	49.1
0.4	45.1	45.8	49.3
0.6	45.5	46.9	49.1
0.8	45.8	48.2	49.2
1.0	45.9	48.6	49.3

From the gathered results obtained in Table (7), it was found that an aliquot of 0.2 - 1.0 mL of 10 % EDTA - 2Na were quite efficient for total masking of interfering calcium ion.

Application

After optimizing the concentrations of masking agents for the major interfering elements (phosphate, iron and calcium) found in phosphoric acid and phosphorites during direct determination of uranium using arsenazo III chromogenic dye, an Egyptian industrial grade phosphoric acid and three phosphate samples, two standards [phosphate (1) and phosphate (2)]⁽¹⁵⁾ and the third phosphate sample was analyzed in ACME laboratories in Canada using ICP-MS⁽¹⁶⁾, were used for application for direct determination of uranium in phosphoric acid and phosphorites. Complete analyses of the industrial grade phosphoric acid was obtained by a number of chemical and instrumental methods of analysis for the quantitative determination of major, minor and trace elements. An ion exchange method was used for the present study for the analysis of phosphoric acid. This method was applied where it separates the phosphate radical together with the other anions from the metal cations using the strongly cationic resin Dowex 50X⁽¹⁷⁾. The obtained complete chemical analysis of the locally industrially produced phosphoric acid was shown in Table (8) and three phosphate samples were shown in Table (9).

Table (8): Complete chemical analysis of industrial grade phosphoric acid

Major and Minor elements		Trace elements (mg/L)	
Component	Assay (%)	Component	Assay (mg/L)
P ₂ O ₅	39.5	U	73.5
Fe ₂ O ₃	1.5	Cr	125
TiO ₂	0.015	V	90
Al ₂ O ₃	1.03	Ni	55
CaO	3.9	Cu	9
MgO	1.2	Zn	240
SiO ₂	0.02	Mo	340
MnO	0.106	Cd	U.D.L

SO ₄ ²⁻	6.1	Pb	U.D.L
Cl ⁻	0.00045	Co	U.D.L
Combined water	48.09		
Total	102.05		

U.D.L stands for under detection limit

Table (9): Complete Chemical Analysis of Phosphate (1) and (2) and a Third phosphate Sample Analyzed Using ICP-MS of ACHME Laboratories in Canada

Oxides / Elements	Phosphate (ACME) ICP-MS	Phosphate (1)	Phosphate (2)
SiO ₂ %	4.75	11.46	8.74
TiO ₂ %	< 0.01	0.04	0.07
Al ₂ O ₃ %	0.1	0.86	1.62
Fe ₂ O ₃ %	1.55	1.56	1.34
MgO %	0.22	2.83	5.51
CaO %	47.92	40.16	33.99
Na ₂ O %	0.54	0.99	0.63
K ₂ O %	0.04	0.16	0.17
P ₂ O ₅ %	27.67	23.17	20.58
MnO %	0.02	0.08	0.057
Total C %	3.69	8.72	14.74
Th (ppm)	1.3	42.1	2.09
U (ppm)	125.9	49.7	87.7

Table (10): Spectrophotometric determination of uranium in industrial grade phosphoric acid and three phosphate samples after using masking agents

Sample	Uranium concentration (µg/mL) (Published data)	Uranium concentration determined without masking agents (µg/mL)	Uranium concentration determined using masking agents (µg/mL)	Standard Deviation	Standard Error
Industrial H ₃ PO ₄	70	8.9	70.6	0.260	0.110
Standard Phosphate (1)	49.7	15.6	49.3	0.415	0.170
Standard Phosphate (2)	195.7	50.8	195.2	0.423	0.173
Phosphate Sample (ICP-MS)	125.9	31.5	126.5	0.34	0.140

From the data gathered in Table (10), it was concluded that masking agents added to the phosphoric acid and phosphate samples for the direct determination of uranium without its prior separation were efficient with good values of standard deviation and standard error for a spectrophotometric analysis procedure.

Conclusion

- 1) Uranium was directly determined spectrophotometrically in industrial grade phosphoric acid and phosphorites using arsenazo III as a chromogenic reagent without separation from its matrix using either solvent extraction or ion exchange techniques.
- 2) This was performed using masking agents during determination to overcome the effect of interfering accompanying elements.
- 3) The main interfering elements were phosphate, iron and calcium ions which were present in high concentration values (%) relative to uranium which is present in microgram per milliliter ($\mu\text{g/mL}$).
- 4) Those interfering elements were masked using different volumes of 10% ammonium molybdate (w/v) for phosphate and 10% EDTA for iron, calcium and magnesium.
- 5) On applying the developed method for direct determination of uranium in Egyptian industrial grade phosphoric acid and three phosphate samples, two standards and a third was analyzed using ICP-MS as an analytical tool, it was found that good, accurate and precise uranium concentration values using the present method compared with that obtained using advanced analytical techniques as ICP-MS or separation techniques as solvent extraction and ion exchange.

References

- 1) Recovery of Uranium from phosphoric acid: an overview. IAEA-Tecdoc 533, p. 69-87 (1989).
- 2) D. A. Johnson and T.M. Florence, *Anal. Chim. Acta*, 53 (1), 73-79 (1971).
- 3) J. A. Perez-Bustamante and F. Palomares Delgado, *Analyst*, 96, 407-422 (1971).
- 4) T. Kojima, Y. Shigetomi, H. Kamba, H. Iwashiro, T. Sakamoto, *Analyst*, 107, 519-524 (1982).

- 5) F. T. Awadalla and F. Habashi, *Fres. J. Anal. Chem.*, 324 (1), 33-36, (1986).
- 6) T. Kiriyaama, R. Kuroda, *Microchim. Acta*, 87 (5-6), 369-375 (1985).
- 7) N. Vucic and Z. Ilic, *JRNC*, 129 (1), 113-120 (1989).
- 8) H. Gorecka, H. Gorecki, *Talanta*, 31 (6), 459-462 (1984).
- 9) F. T. Bunus, *Talanta*, 24 (2), 117-120 (1977).
- 10) F. Habashi, *Mikrochim. Acta*, 47 (6), 932-941 (1959).
- 11) Z. Marcezenko, "Spectrophotometric Determination of Elements", John Wiley, London (1976)
- 12) Y. S. Li, Y. Muo, and H.M. Xie, *Anal. Chim. Acta*, 456 (2), 316-325 (2002)
- 13) G. S. R. Krishnamurti and P. M. Huang, *Talanta*, 37 (7), 745-748, (1990)
- 14) A. C. Edwards and M. S. Cresser, *Talanta*, 30 (9), 702-704, (1983)
- 15) M. M. Aly, proceedings of the 2nd conference on Optical Spectroscopy, Laser and their Applications, National Research Center, Cairo, Egypt, 3-6 November (1985)
- 16) H. K. Fouad and R. M. El-Rakaiby, *J. of Appl. Sci. Res.*, 5 (8), 914-921 (2009)
- 17) L. A. Guirguis, H. K. Fouad and R. M. El-Rakaiby, *Mansoura J. of Chem.*, 35 (1), 51-72 (2008)