

Determination of uranium and radium in phosphate rock and technical phosphoric acid

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Bestimmung von Uran und Radium in Phosphatgestein und technischer Phosphorsäure

Zusammenfassung. Uran kann in Phosphatgestein radiometrisch mit γ -Zählung und spektralphotometrisch mit Arsenazo I bestimmt werden. Zur spektralphotometrischen Bestimmung wird die Probe in Salpetersäure gelöst, dann das Uran mit Tributylphosphat extrahiert, in heißes Wasser überführt und bestimmt. Zur Uranbestimmung in technischer Phosphorsäure muß zuerst das als Verunreinigung vorhandene Fluorosilicat gefällt und dann das Uran mit Hilfe von Amberlit IRA-400 in der Sulfatform abgetrennt werden, bevor es im Eluat mit Arsenazo I bestimmt werden kann. Radium kann in Auslaugungslösungen mit Hilfe der Emanationsmethode bestimmt werden.

Summary. Uranium in phosphate rock can be determined radiometrically using gamma-counting and spectrophotometrically using arsenazo I. In the latter case the rock is dissolved in HNO_3 , then uranium is extracted with tributyl phosphate, stripped with hot water and determined. For the determination of uranium in technical phosphoric acid, the fluorosilicate ion present as impurity must first be precipitated, the uranium separated on Amberlite IRA-400 in the sulfate form, then determined in the eluate spectrophotometrically by arsenazo I. Radium can be determined in leach solutions by the emanation method.

Introduction

Phosphate rock of sedimentary origin contains 60 to 300 ppm uranium. When the rock is treated with sulfuric acid to produce phosphoric acid, most of the uranium goes into solution while the radium contaminates the gypsum residue. Uranium in phosphoric acid is recovered on an industrial scale and it is essential to have rapid and precise analytical methods available for plant use [1]. Numerous methods are available for uranium determination, most of these require either ion exchange or solvent extraction separation prior to spectrophotometric, polarographic, X-ray fluorescence, or emission spectrometric determination. Atomic absorption is not suitable because it has a low sensitivity. Of the spectrophotometric methods [2–15], the one using diphenylmethane as chromogene has been re-

commended for phosphoric acid although it has been criticized by previous workers [16]. The arsenazo method is said to be 50% more sensitive than the diphenylmethane method [9], but there is no evidence that it can be applied to technical phosphoric acid [17, 18]. Also, the pollution problems associated with radium-containing phosphogypsum necessitate the availability of rapid methods for radium determination by fertilizer plant chemists. In this communication, methods for uranium and radium determination in phosphate rock and technical phosphoric acid have been especially developed for this purpose.

Experimental

Reagents

- 1) The anionic resin Amberlite IRA-400 in the chloride form (Rohm and Haas) was transformed into the sulfate form using H_2SO_4 .
- 2) Tributyl phosphate, $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$, (Aldrich) was used for extracting uranium.
- 3) Indicator grade o-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo) benzene arsenic acid, tri-sodium salt (formula weight 614,28), known as arsenazo I or neo-thorone was used for spectrophotometric determinations. It develops a blue color with uranium(VI) ion in pH 7–8 and a blue violet color with uranium(IV) ion in pH 1.5–1.8. The color intensities were measured at a wavelength of 595 and 555 nm, respectively.
- 4) Reagent grade uranyl sulfate, ethylene diamine tetraacetic acid disodium salt (EDTA), tartaric acid, ascorbic acid, ammonium hydroxide, nitric and hydrochloric acids were used.

Equipment

- 1) Ion-exchange column 5 mm diameter containing 1 g resin. The sample solution was put in a 250 ml reservoir connected to the column.
- 2) Electrode potential in solution was measured by a platinum electrode connected to a calomel reference electrode.
- 3) X-ray diffraction equipment was used to identify any precipitates formed.

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4) Atomic absorption spectroscopy was used to determine traces of iron, silicon, aluminum, magnesium, vanadium, and molybdenum in solution.

5) Beckman DK-2A Ratio Recording Spectrophotometer was used together with 1-cm absorption cells, to measure the intensity of the color developed.

6) For the radiometric analysis the following apparatus were used:

a) Nuclear Chicago Scintillation Detector Model 403 connected to Model 8770 Scaler for gamma-counting of phosphate rock samples.

b) RD/RDU-200 Radon detector for alpha-counting of solutions.

7) Radium disc standard 0.9 μCi , Amersham Searle model 184100

8) Uranium ore sample of known uranium content and in which uranium is present in radioactive equilibrium with its decay products procured from the International Atomic Energy Agency in Vienna.

Results and discussion

Phosphate rock

Determination of uranium

1) *Spectrophotometric method.* A 5 g phosphate rock sample was solubilized in 15 ml 60% HNO_3 and the insoluble minerals (mainly siliceous gangue) were filtered off and washed. Uranium was extracted from the solution by tributyl phosphate at an organic/aqueous ratio 1/1; it was found that one stage extraction was enough. The organic phase was scrubbed by hot water to remove the co-extracted impurities; it was found that one stage scrubbing at organic/aqueous phase ratio 1/1 was enough to remove all the impurities; no uranium was detected in this solution. These impurities when precipitated by ammonia and analyzed by X-ray diffraction were identified as $\text{Ca}_2\text{Fe}(\text{PO}_4)_2(\text{OH}) \cdot 1.5 \text{H}_2\text{O}$ (ASTM card no. 5-0571) and $\text{Ca}_2\text{Mg}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (ASTM card no. 26-1063). Uranium is then stripped from the organic phase by hot water at organic/aqueous ratio 1/1; six extraction stages were necessary as shown in Fig. 1. On analyzing the strip solution it was found that it contained beside uranium only traces of iron, calcium, and phosphates.

Arsenazo I develops an intense bluish-violet color at 555 nm with uranium(IV) at pH 1.5–1.8 and a blue color at 595 nm with uranium(VI) at pH 7–8. The first reaction is more advantageous than the second because of its greater sensitivity and due to the lower pH many impurities that would otherwise precipitate at high pH need not be separated. However, it was found that the determination of uranium(IV) by this method was not practical because of the elaborate measures that should be taken to prevent its oxidation. Therefore the determination was made on uranium(VI).

To mask the iron present, 0.5 ml of 0.1 M EDTA sodium salt was added; this was followed by 4 ml of 0.001 M arsenazo I. The natural pH of solution was 1–2 and it should be raised to 7–8 by adding sodium or ammonium hydroxide, then the volume adjusted to 100 ml in a measur-

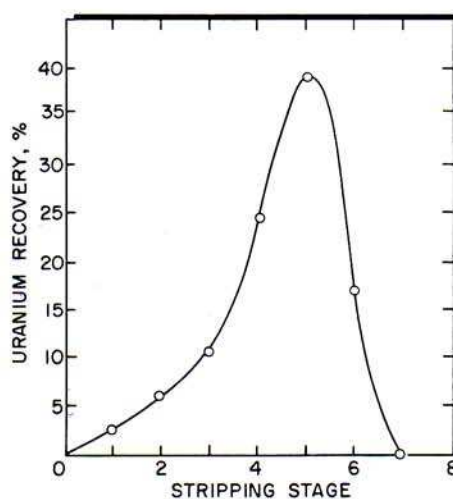


Fig. 1. Stripping of uranium from tributyl phosphate by hot water

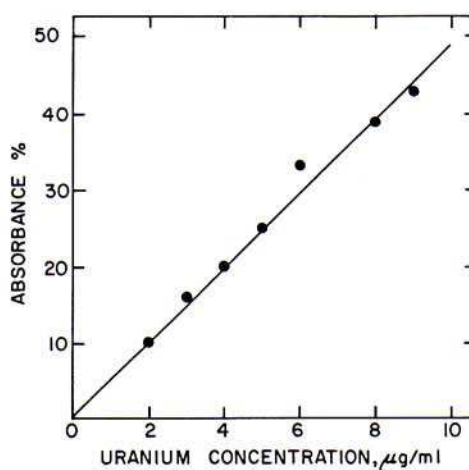


Fig. 2. Standard curve for the spectrophotometric determination of uranium(VI) by arsenazo I

ing flask. The blue color developed was measured in a spectrophotometer at 595 nm against blank and the absorbance was compared with a standard curve in the range 1–10 ppm as shown in Fig. 2. The method was tested by spiking with a known amount of uranium in the leach solution; all the uranium was accounted for.

2) *Radiometric method.* For this purpose a uranium ore sample of known uranium content and known to be in radioactive equilibrium (procured from the International Atomic Energy Agency in Vienna) was diluted with silica sand to obtain mixtures containing uranium concentrations in the range of that found in phosphate rock, namely 0 to 0.02% U. The specific activity of these samples were measured in gamma counter and a standard curve was obtained as shown in Fig. 3. Uranium content of phosphate rock samples from different localities were measured by this method and compared with measurements made polarographically on the same samples. Good agreement was obtained as shown in Table 1.

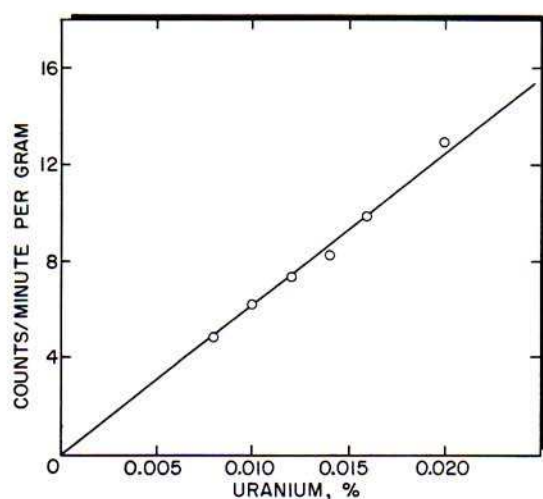


Fig. 3. Standard curve for the radiometric determination of uranium in phosphate rock by gamma counting

Table 1. Uranium content in different phosphate samples

	Phosphate	P ₂ O ₅	Uranium content, ppm	
			Radio-metrically (This work)	Polaro-graphically [19]
Sedimentary	Florida	33.42	190	180
	Jordan	33.37	176	170
	Safi	33.47	(237)	155
	Israel	30.37	154	140
	Kosseir	30.31	115	90
	Gafsa	30.83	74	80
	Marocco	28.90	52	40
Igneous	Kola	38.22	18	12

Determination of radium

Radium was determined in phosphate rock by the emanation method. A 25 g phosphate sample was dissolved in nitric acid, filtered to remove the gangue minerals then neutralized by ammonium hydroxide and kept in tightly closed bottles for 6 days for the establishment of radioactive equilibrium. Radon was then collected in an evacuated counting chamber and the alpha activity was counted after 5 h to get a broad maximum in the RD-200 detector. By comparing with a standard curve constructed from samples of known radium contents, radium was determined (Fig. 4).

Technical phosphoric acid

Determination of uranium

Uranium in technical phosphoric acid can be determined spectrophotometrically using arsenazo I. It is necessary first to oxidize uranium(IV) to uranium(VI) using 0.5 M KClO₃. This can be followed by measuring the oxidation potential of the solution using a platinum electrode vs. standard calomel electrode as reference electrode. In a typical test the potential increased from about 375–900 mV as indicated by Fig. 5. Manganese dioxide and sodium persulfate, known to be

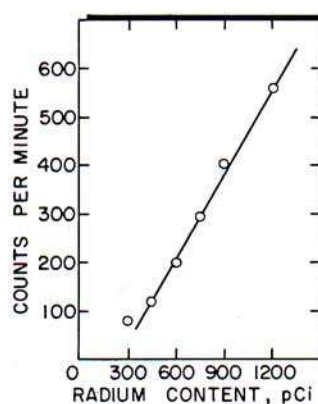


Fig. 4. Standard curve for the radiometric determination of radium by alpha counting

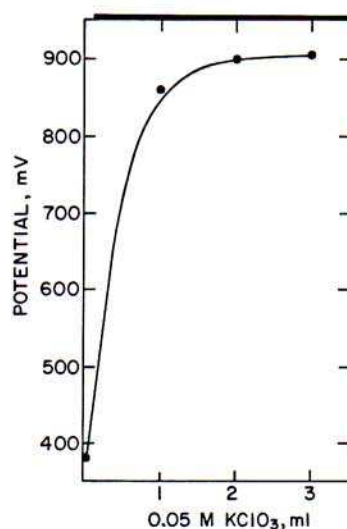


Fig. 5. Oxidation potential of 50 ml technical phosphoric acid (45% P₂O₅) by potassium chlorate measured by Pt-electrode vs. calomel electrode

effective oxidant were tried, but when added in small amounts they interfered with developing the color. Fluorosilicate ion was then separated by precipitation with Na₂SO₄. The precipitate formed was identified by X-ray as Na₂SiF₆ (ASTM card no. 19–1193); it proved to be uranium free. This was essential because it was found that SiF₆²⁻ ion was sorbed on the resin and interfered with the measurement. Also, the addition of sulfate ion is necessary to form the uranyl sulfate complexes which are retained on the resin. Iron(II) oxidises to iron(III) during the addition of KClO₃ solution. Therefore, it is necessary to reduce it by bubbling SO₂ gas, adding ascorbic acid, or iron powder because Fe(II) is not sorbed on the resin but Fe(III) is sorbed and it interferes with the measurements (see Fig. 6). On reducing iron(III) the oxidation potential decreased to 200 mV as measured by the platinum electrode vs. calomel electrode. The solution is now diluted and passed through the resin. The resin is then washed by distilled water till phosphate and sulfate free. The optimum amount of 1 N HCl necessary to elute all the uranium was determined. The eluate contained traces of Fe and Mo; their interference was eliminated by masking with EDTA and tartaric acid,

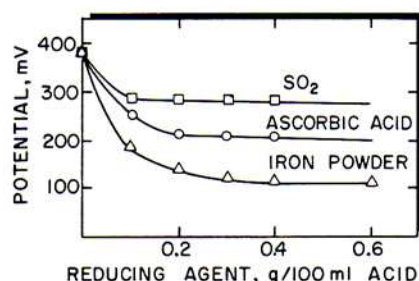


Fig. 6. Electrode potential of technical phosphoric acid (45% P_2O_5) during reduction by SO_2 , ascorbic acid, and metallic iron

respectively. The method was tested by spiking technique and it was found that all the added uranium was accounted for.

The following procedure was found to give accurate and reproducible results:

1) To 5 ml technical phosphoric acid few drops of 0.05 M $KClO_3$ solution are added and the solution heated to $75^\circ C$ for few minutes to oxidize uranium(IV) to uranium(VI).

2) 20 ml of 1 M sodium sulfate solution are added, boil for 2 min then filter and wash the precipitate of Na_2SiF_6 with a small amount of Na_2SO_4 solution.

3) Bubble SO_2 gas for about 2 min or add 0.2 g ascorbic acid to reduce Fe(III) in the solution. The pH of the solution should then be adjusted to 1–1.5 using either NaOH or NH_4OH .

4) Pass the solution through an ion exchange column in the sulfate form, at a rate of about 2 ml/min. Then wash with distilled water until sulfate and phosphate free. Elute the resin with 80 ml 1 N HCl.

5) Add to the eluate 2 ml of 0.1 M tartaric acid to mask any molybdenum present, and 2 ml of 0.1 M EDTA disodium salt solution to mask any iron.

6) Add 4 ml of 0.01 M arsenazo I solution, then adjust to pH 7–8. Complete the volume to 100 ml in a volumetric flask. The blue color developed is measured in a spectrophotometer at 595 nm and the absorbance is compared with standard curve in the range 1–10 ppm.

Determination of radium

Radium content in technical phosphoric acid is low because it precipitates with the gypsum during its manufacture. It can be determined by the emanation method described earlier. One hundred ml sample of 30% P_2O_5 technical acid was analyzed by radon emanation method and it was found to contain typically 30 pCi.

Conclusions

1) Uranium can be determined in phosphate rock either radiometrically or spectrophotometrically. In the first

method the gamma activity of the ground sample is measured in a scintillation counter and compared with standards. The sample, however, must be in radioactive equilibrium with its decay products. In the second method, the rock is dissolved in HNO_3 and uranium extracted by tributyl phosphate. It is then determined in the strip solution by arsenazo I.

2) Uranium can be determined in technical phosphoric acid by first precipitating fluorosilicate ion then separating uranium on Amberlite IRA-400 in the sulfate form. Uranium is determined in the eluate spectrophotometrically using arsenazo I.

3) Radium can be determined in phosphate rock by the emanation method. The rock is solubilized in HNO_3 and stored for 6 days in a closed bottle to achieve radioactive equilibrium with its decay products before the determination. Radium can be determined directly in technical phosphoric acid by the emanation method.

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