

DETERMINATION OF URANIUM IN A PHOSPHATE ROCK SAMPLE

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الخلاصة :

يتم فصل عنصر اليورانيوم من الصخور الفوسفاتية بإدمصاصه على مُبادل أيوني ذي قلووية قوية ، أو باستخلاصه بواسطة أكسيد الفوسفين ثلاثي الأوكسيل . وتتميز عملية الاستخلاص هذه ببسرها وأفضليتها في التطبيق على عملية التبادل الأيوني . وتمّ تعيين اليورانيوم المفصول بالطريقة الطيفية وذلك باستخدام [٢ - (٥ - برومو - بيريدايلازو) - ٥ - فينول أمين ثنائي الاثيل] . وقد أُجريت الدراسة على عينات تحتوي على الصخور الفوسفاتية الموجودة في مكانين مختلفين . وتمّ تحديد كميات اليورانيوم بنجاح في هذه العينات ، ووجد بأنها ذات علاقة مع المكونات الكيميائية الأخرى لتلك الصخور .

ABSTRACT

Uranium in phosphatic rocks is separated by adsorption on a strongly basic anion-exchange resin or extracted by tri-*n*-octylphosphine oxide. The extraction method is simpler and more applicable than the anion-exchange method. The separated uranium is determined spectrophotometrically by means of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol. Samples from two different places which have phosphatic beds were investigated. The uranium contents of those samples have been successfully determined and found to correlate with other chemical constituents.

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INTRODUCTION

Spectrophotometry is one of the most suitable methods for the determination of uranium in a variety of geological samples. This method requires a special reagent which reacts with uranium to form a colored complex. Arsenazo-III has been used for the determination of uranium, zirconium, and thorium in silicate rocks [1]. Uranium in minerals and rocks has also been determined by arsenazo-III. A column packed with a strongly basic anion-exchange resin (Dowex 1×8) has been employed to separate uranium from the matrix elements [2]. The reagent 2,4-dinitrosoresorcinol has been applied to determine uranium and iron simultaneously. Complex formation was carried out in the presence of ethyl acetate, which eliminates the interference of certain ions [3]. The schiff base 2,2'-(2,6-Pyridinediyl)-bis-(methylidene nitrilo)phenol has been applied for the determination of uranium(VI) [4]. Certain heterocyclic azo dyestuffs such as 4-(2-pyridylazo)resorcinol (PAR) have been found to be useful for the spectrophotometric determination of uranium [5]. Florence, Johnson, and Farrar have synthesized 2-(2-pyridylazo)-5-diethylaminophenol (PADAP), which is more sensitive than PAR towards uranium [6]. PADAP has been applied to the determination of uranium in ores [7]. The most suitable reagent, which has been found to give accurate results, is 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (bromo-PADAP) [8]. As a result of its sensitivity, this reagent has been successfully applied to the determination of uranium in ores [9]. Bromo-PADAP has also been used for the determination of uranium in the different stages of its extraction from wet phosphoric acid media [10].

It has been reported that the concentration of uranium in phosphate rocks, which ranges from 0.001% to 0.02%, increases with the percentage of P_2O_5 [11]. For the present study, several samples have been collected from phosphatic beds located in two different locations. The aims of this study are: (1) to determine the samples that have high percentages of P_2O_5 ; (2) to determine the uranium contents by applying both ion-exchange spectrophotometry and extraction spectrophotometry; and (3) to investigate the correlation between uranium and other chemical constituents of those samples.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Shimadzu RF-540 recording spectrophotometer using 1 cm cells. A Corning Model 12 pH meter with a combined pH electrode system was used.

Reagents

All reagents were of analytical reagent grade and deionized water was used for preparing the solutions.

Ion-Exchanger

The anion-exchanger DOWEX 1×8 (100-200 mesh) in the chloride form was used. The treatment and the preparation of the column have been previously described [4]. A mixture of methyl isobutyl ketone-tetrahydrofuran and HCl was also prepared according to a literature procedure [5].

Ascorbic Acid Solution 5% W/V

This solution was freshly prepared.

Sodium Fluoride Solution 2% W/V

Sodium Hydroxide Solution 40% W/V

Bromo-PADAP Solution, 0.05% W/V

Dissolve 0.05 g of bromo PADAP in 100 ml of absolute ethanol. Prepare sufficient amount to last for one week.

Buffer Solution pH 8.35

Dissolve 149 g of triethanolamine in 800 ml of water, neutralize to pH 8.35 with perchloric acid, allow to stand overnight. Readjust the pH to 8.35 with perchloric acid and dilute to 1 litre.

Complexing Solution

Suspend 25 g of 1,2-diaminocyclohexane tetraacetic acid (CYDTA, available from Aldrich as TITRIPLEX IV), 5 g of sodium fluoride, and 65 g of sulfosalicylic acid in 800 ml water. Neutralize to pH 7.85 with 40% sodium hydroxide and dilute to 1 litre.

Dilute Complexing Solution

Dilute one part of the complexing solution with an equal part of water and adjust the pH to 8.35 with 40% sodium hydroxide solution.

TOPO Solution, 0.1 M

Dissolve 19.3 g of tri-*n*-octylphosphine oxide in cyclohexane and dilute to 500 ml with cyclohexane.

Nitric Acid Solution 2 M

Standard Uranium Solution 1 mg ml⁻¹

Reagent grade uranyl acetate or uranyl nitrate are often adequate reference materials. The 1 mg ml⁻¹ standard solution of uranyl nitrate was made up in 0.1 M HNO₃ in order to prevent hydrolysis. More dilute standard solutions of lower concentrations can be prepared from the stock solution by dilution with 0.1 M HNO₃.

Procedures

1. Sample Preparation for Phosphorus Determination

Weigh accurately about 1 g of the sample in a 125 ml beaker and moisten with distilled water. Add 25 ml of a 1:1 HNO₃/HCl solution and heat gently, then evaporate. Repeat this process twice and take the remaining residue up in dilute HNO₃ solution and filter. Collect the filtrate in a 100 ml volumetric flask and dilute to the mark. Place 25.00 ml of ammonium molybdate solution into a 50 ml volumetric flask. Pipette 25 ml of the phosphate solution into this flask and mix well. Measure the absorbance of the resulting yellow complex at 430 nm. The concentration of phosphorus can be determined by means of a calibration curve.

2. Procedures for the Determination of Calcium Oxide and Fluorine

(a) *Calcium oxide*: the phosphate sample was digested with a mixture of 1:1 HCl/HNO₃. Silica was removed by filtration and the filtrate containing calcium was collected in a 100 ml volumetric flask and diluted to the mark with deionized water. The calcium content was determined by atomic absorption.

(b) *Fluorine*: a fixed weight of phosphate sample was fused in a platinum dish with sodium carbonate. The melt was leached out with 1:1 HCl and the resulting solution was made up to 100 ml in a volumetric flask. Various aliquots were placed in 50 ml

volumetric flasks which contained 25 ml TISAB buffer. The fluoride contents were determined by means of a fluoride-ion selective electrode.

3. Separation of Uranium by the Ion-Exchange Method

A sample of 4.50 g of phosphate rock powder was taken in a platinum dish and treated with 25 ml (1:1) HNO₃, 10 ml HClO₄ and 25 ml HF. This mixture was heated gently on a sand bath to dryness. The resulting cake was dissolved in 40 ml concentrated HCl, then diluted with distilled water and filtered. The volume of the filtrate was made up to 500 ml to give a solution whose final concentration did not exceed 1 M HCl. This solution was passed through the ion-exchange column and then was washed with 2.0 l of 1 M HCl. The eluate was collected into four portions and each portion was diluted into a separate volumetric flask. The final volumes of the first, second, third, and fourth portions were 250, 500, 500, and 1000 ml respectively. Finally the column was eluted with 1.0 l of 12 M HCl. The eluent was collected in a 1.0 l volumetric flask to give the fifth portion. From each of the five solutions, a volume of 10 ml was separately taken into a separatory funnel and to each funnel, a volume of 5.0 ml of 2% NaF was added, and the mixture was subsequently shaken and 2 ml of 5% freshly prepared ascorbic acid were added. After mixing, a volume of 5.0 ml of 0.1 M tri-*n*-octylphosphine oxide (TOPO) was pipetted into the mixture, which was then shaken for 1 minute. Two phases were formed and allowed to separate and the aqueous phase was discarded.

A volume of 2.0 ml was pipetted from the organic phase into a dry 25 ml volumetric flask. To this flask, the following volumes were respectively added: 1.0 ml of the complexing solution; 4.0 ml of 0.05% bromo-PADAP; and 1.0 ml of triethanolamine buffer (pH 8.35). The flask was stoppered and allowed to stand for 10 minutes; then 16 ml ethanol were added and the solution was diluted with water. The absorbance was measured at 574 nm against a reagent blank.

4. Separation of Uranium by the Extraction Method

Weigh 0.5–1.0 g sample into a platinum dish then add 5.0 ml of 15 M HNO₃ and 5.0 ml of 40% HF. Evaporate to dryness on a sand bath, then add 5.0 ml of 15 M HNO₃ and 5.0 ml of 40% HF and again evaporate to dryness. Add 2.0 ml of 72% HClO₄

and evaporate on a hot plate until the volume is about 1 ml. Cool, then dissolve the residue in 20 ml of 5 M HNO_3 . Filter the solution through an ashless filter paper (Whatman No. 42 or 44) into a 100 ml volumetric flask, dry the filter paper and ash it in a platinum dish, then add 0.3 g of sodium carbonate and fuse at 1100°C for 5 minutes. Cool, then dissolve the melt into 20 ml of 5 M HNO_3 . Filter through a small filter paper and add the filtrate to the 100 ml volumetric flask containing the previous filtrate, then wash the filter paper and make the solution up to the mark.

Pipette an aliquot of 10.0 ml of the sample into a separatory funnel and add enough HNO_3 to bring the pH to 0.5. Add, in order; 5.0 ml of 2% sodium fluoride solution; 2.0 ml of 5% ascorbic acid solution, and mix well. Pipette in a volume of 5.0 ml of 0.1 M TOPO and shake for 1–2 minutes. Allow the two phases to separate and discard the aqueous phase. Pipette 2-ml of the organic phase into a dry 25 ml volumetric flask and apply the previously described procedure to form the bromo-PADAP complex. Measure the absorbance at 574 nm against a reagent blank. The concentration of uranium can be determined from a calibration curve.

RESULTS AND DISCUSSION

At the beginning of this investigation, it was decided to confirm the presence of uranium in phosphatic samples. For this reason, a sample which was found to contain 23.70% P_2O_5 was selected. The uranium in this sample was separated by a column containing the anion-exchange resin Dowex 1×8 .

The eluate was divided into five portions and each portion was analyzed for uranium using the bromo-PADAP spectrophotometric method. Figure 1 shows the spectra of uranium–bromo-PADAP complex which confirms the presence of uranium in this sample. It is interesting to note that the spectrum of the uranium–bromo-PADAP complex was exhibited in the case of the second and the third portions while the remaining portions did not show any spectra. The concentration of uranium was found to be 78 ppm in the second portion and 84 ppm in the third portion. This shows that the ion-exchange method gave a total concentration of 162 ppm uranium in the sample being studied.

Although the ion-exchange method was successful in confirming the presence of uranium, this procedure was found to be tedious and time consuming and requires large volumes of eluents. Therefore, it was planned to apply the extraction–spectrophotometric method for the determination of uranium in the samples which were found to have high phosphate contents.

The optimum pH-range for the complete extraction of uranium with TOPO was found to be 0.25–0.6. However, vanadium(v) will be reduced in lower acidic solutions and the hydrolyzable metals will be easily kept in such solutions. Therefore, a nitric acid concentration of 2 M was employed.

The validity of the extraction–spectrophotometric method was examined by determining uranium in a reference material which was supplied by Canada Centre for Mineral and Energy Technology. This reference material is a pale yellow arkose sandstone

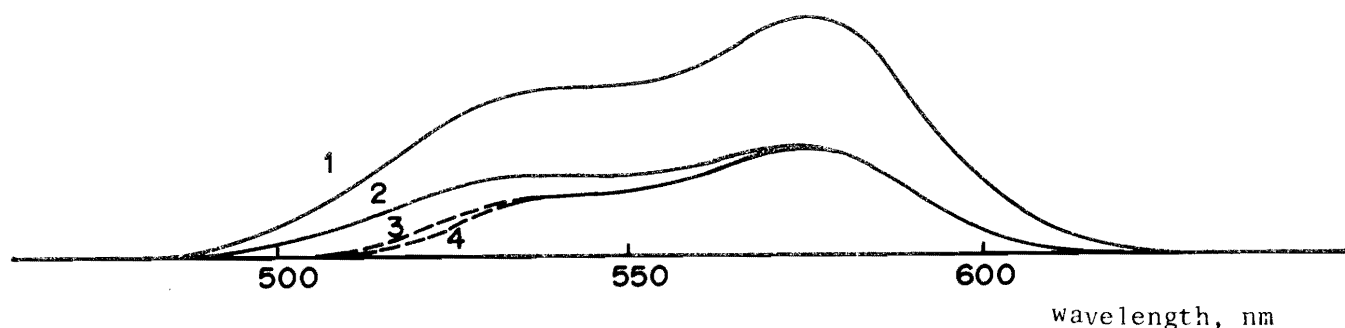


Figure 1. Absorption Spectra of Uranium Bromo-PADAP Complex for:
Curve 1. Standard uranium solution of 50 μg ; curve 2. standard uranium solution of 25 μg ;
curve 3. part of the sample eluted in the second portion; curve 4. part of the sample eluted in the third portion.

containing 116 ppm uranium. The results of four repeated determinations of uranium in this sample were as follows: 113 ppm, 116 ppm, 120 ppm, and 121 ppm. These results gave a relative standard deviation of 2.56%.

The uranium contents of the samples which were found to have high percentages of P_2O_5 were determined by the extraction-spectrophotometric method using bromo-PADAP. Table 1 shows the results of the samples that belong to the area A1. This table also presents the chemical constituents which were found to correlate with uranium. These constituents include CaO, F, and P_2O_5 . The correlation between uranium and the other chemical constituents was investigated by the application of the least squares method. A statistical analysis system package (SAS) supplied by SAS Institute Corporation for Data Analysis was employed. The regression model obtained for the samples from area A1 was:

$$U = -552.7 + 54.52(\%P_2O_5) + 0.1986(\%P_2O_5)(\%CaO) + 242.0(\%F)^2 - 42.86(\%F)(\%P_2O_5)$$

The correlation coefficient was found to be 0.999 which implies that the regression model when applied gives results that do not deviate from the experimental values.

The results obtained for the samples from area A2 are shown in Table 2. This table shows that, on using the extraction method, sample number 7 has a uranium concentration of 228 ppm. However, the same sample, on using the ion-exchange method, gave a uranium concentration of 162 ppm. This indicates that the extraction method is more accurate than the ion-exchange method. The least squares method was also applied to find the correlation

Table 1. Chemical Constituents which Correlate with the Uranium Contents of the Samples From Area A1.

Sample Number	P_2O_5 %	CaO %	F %	U in ppm
1	13.74	52.21	1.87	84
2	15.11	55.55	1.75	46
3	18.32	55.00	1.26	41
4	24.71	53.91	1.48	22
5	21.02	62.00	2.19	40
6	22.32	62.00	1.38	80
7	10.94	72.09	0.23	0.0

Table 2. Chemical Constituents which Correlate with the Uranium Contents of the Samples From Area A2.

Sample Number	P_2O_5 %	CaO %	F %	U in ppm
1	18.16	52.88	1.24	10
2	14.00	52.74	1.45	40
3	16.50	58.76	1.85	60
4	18.33	30.36	1.94	60
5	11.46	26.09	1.71	40
6	19.25	31.78	1.90	108
7	23.70	28.20	1.93	228
8	14.30	25.21	1.27	110

between uranium and other chemical constituents. The following regression model was obtained with a correlation coefficient of 0.990:

$$U = 2484.52 - 241.87(\%P_2O_5) - 26.69(\%CaO) + 1.61(\%P_2O_5)(\%CaO) - 609.76(\%F^2) + 117.4(\%F)(\%P_2O_5)$$

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