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Determination of Uranium by Spectrophotometric Method with Arsenazo III

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Uranium is separated and preconcentrated from interfering elements by liquid extraction with 20% tributylphosphate (TBP) in benzene solution, prior to spectrophotometric determination with Arsenazo III in HCl medium (pH = 2.5), stabilized by buffer solution. Sodium fluoride and EDTA are used to complex calcium, rare earth elements (RE) and iron because they interfere in uranium determination. The method is applicable in sediments and soil samples in the range of 0.25–10.0 μg of U/L. It should be used in water samples, too, in the range up to 0.25 μg of U/L for 20 to 50 mL of water sample.

INTRODUCTION

Extensive uranium prospecting activities in Albania were carried out from 1961 to 1991. Significant uranium sources were discovered at six sites, but no commercial mining of uranium has been performed. The method has widely been used on verification of radiometric anomalies, identified by radiometric investigations. As the asessment of health and environment has had increasing interest in recent years, the method we propose has to be useful, being, specifically tailored to the smaller liabilities of Albania.

Some powerful techniques for instrumental analysis are used[1,2] for the determination of uranium in natural water samples by α-spectroscopy, after the preconcentration and separation of uranium by ion chromatography. Civici[3] has used energy-dispersive X-ray fluorescence analysis after the preconcentration of uranium in water samples, with APDC. The sensitivity achieved is 1 μg of U/L. Other authors[4, 5] have used electrochemical methods for the analysis of uranium in water and seawater samples. The RSD and the detection limit achieved are respectively 11% and 67 ng U/L. Toole *et al.*[6], have used ICP-Mass Spectroscopy method to determine uranium in water samples. Only 0.25 mL sample was used and the detection limit was 2 ng of U/L.

The application of spectrophotometric methods with arsenazo III for the determination of uranium in water, soil or sediment samples after preconcentration and separation by ion exchange method have been considered important in recent years[7–9] The detection limit achieved is in the range of 0.05 μg of U/L. A simple

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extraction method with TBP is proposed in this paper, to separate and preconcentrate the uranium in sediments and soil samples. The method can be used in water samples, too. Wu[10] has used TBP, too, to extract uranium in SCN state, TBP-xylene solution was used and the detection limit was 0.5 ng of U/bead.

EXPERIMENTAL

Preparation of uranium standard solution: Stock uranium standard solution is prepared from high purity UO_3 (Koch Light, 99.99%). It is digested with HNO_3-$HClO_4$-HF in water bath till dryness. The dry residue is dissolved with hot 4 N HNO_3. A solution containing 1 mg of U/L is obtained. All acids used are from Merck (p.a.).

A Pye Unicam SP6–550 UV/Vis spectrophotometer is used for the absorbance measurements in $\lambda = 665$ nm with 1 cm cell. The instrumental parameters are optimized to achieve good analytical performance, aiming mainly to increase the sensitivity of the method.

Sampling and treatment of samples for chemical analysis

The method was used to perform the analysis for more than two thousand samples, in different years, from six sites well known as uranium sources in Albania. All the samples are collected by Tirana Geochemical and Geophysical Survey Center, Albania. Three natural samples, monzonite from Nimce region, near Kukes (Northeast of Albania), are used for quality control analysis of uranium with arsenazo III. The samples are analyzed for uranium from two other laboratories too, the Laboratory of Tirana Geochemical and Geophysical Exploration Centre, Albania and the Laboratory of Nuclear Physics Institute of Albania. The results of the analysis are listed in Table-1. After grinding and homogenizing (sieving to 200 mesh), the samples are wet digested with an acid mixture of HNO_3-$HClO_4$-HF, following the procedure described above for uranium standard solution. The dry residue is dissolved with 4 N HNO_3 and then it is extracted with 20% solution of TBP in benzene. The organic phase is washed three times with 4 N HNO_3 solution and is back-extracted by 0.01 N HNO_3. The pH of the solution is adjusted to 2.2 (HNO_3 solution and stabilized with buffer solution). Adding NaF and EDTA are used to complex Ca, rare earths and Fe which interfere in the determination of U with arsenazo III. Blank solution is prepared following all the steps of this procedure.

TABLE-1
THE DATA OF QUALITY CONTROL OF THE ANALYSIS

No. sample	Content of U (x, μg/kg)			Stand. error	Sum of squares		F-Ratio
	γ-sp*	Neutr. sp.	Chem.		Bet. sampl.	With. sample	
N-1	5.0	5.1	4.87	0.412	0.059	3.501	0.076
N-2	22.0	21.7	20.21	0.827	4.022	40.900	0.443
N-3	86.0	86.8	85.25	0.655	0.387	180.400	0.010

*The results of γ-spectroscopy method are considered as the "true" ones.

Water samples (20–50 mL) are evaporated in the presence of HNO_3 and H_2O_2 to dryness. The dry content is dissolved with 4 N HNO_3 and then the uranium is extracted with 20% TBP in benzene solution. The further procedure is the same as that of soil samples. The method should be even more suitable for water samples, due to the fact of smaller interferences.

RESULTS AND DISCUSSION

Spectral interferences

Arsenazo III is not a specific reagent for the determination of uranium. In pH = 2–4, it forms stable coloured complexes with rare earths, Th, Zr, Nb, Ca, Ni, etc. Most of these elements could be separated from U using the extraction with TBP and their complex formation conditions with arsenazo III differ from those of U (VI). High quantities of Ca and Fe are not separated and interfere in the determination of uranium.

We have studied the effects of the interferences of calcium and iron on U-arsenazo III complex, in two different uranium standard solutions. The results are presented in Figure 1. These show the effects of NaF and EDTA to mask Ca and Fe and to avoid their interference. On the other hand, the presence of EDTA avoids the interference of rare earth elements, too.

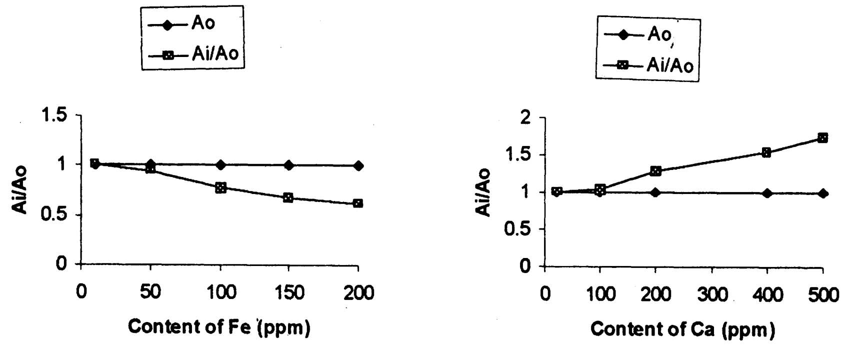

Fig. 1. The interference curves (5 ppb U standard solution is used):
A_0: The absorbance values without interference (after using EDTA and NaF, too)
A_i: The absorbance values under the interference of Fe and Ca.

From Fig. 1 it could be seen that the presence of iron causes a negative effect, and that calcium has a positive effect on the absorbance of U-arsenazo III complexes. On the other hand, it is clear from Fig. 1 that after adding NaF and EDTA, the complex compounds of calcium-EDTA and iron-fluoride are formed and very good results are obtained.

The effect of the concentration of TBP, HNO_3 and the solvent on the extraction process

We have studied the conditions for a good extraction and separation of uranium from the interfering elements. Maximal recovery and preconcentration of uranium during this process is studied, too. Kordfunke[11] has used extraction method as the best one to separate uranium from other elements in the industrial process. Fig. 2 shows the variation of the coefficient of extraction of U(VI) with the concentration of HNO_3, when 20% TBP in benzene solution is used.

It is clear that the recovery of uranium is maximal in 3 N HNO_3, using 20% TBP kerosene solution or 4 N HNO_3, using 20% TBP benzene solution. The coefficient of extraction is about 95% under these extraction conditions. The recovery of uranium is higher than 95%.

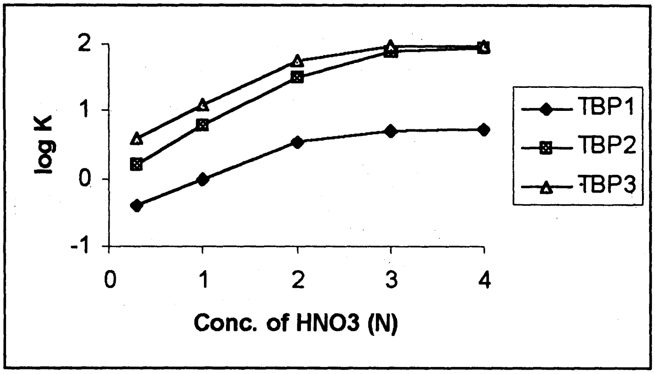

Fig. 2. The effect of [HNO_3] on the extraction of U(VI) using:
TBP 1 5% TBP-kerosene solution (Kordfunke, Ref. 11)
TBP 2 20% TBP-benzene solution
TBP 3 30% TBP-kerosene solution (Kordfunke, Ref. 11)

The effect of the pH on the stability of the complex U-arsenazo III

We have drafted the diagram of the variation of the absorbance of U-arsenazo III complex *via* the pH. The result is given in Fig. 3.

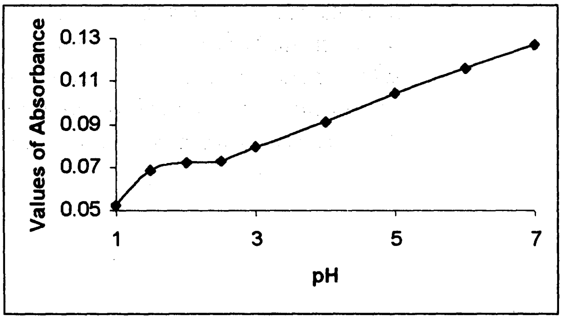

Fig. 3. The effect of pH on the stability of U-arsenazo III complex

From figure 3 it could be seen that U-arsenazo III complex is very stable in pH = 2.8–3.5, where the absorbance of the solution is constant. We have chosen pH = 2.2 to ensure a high stability of U-arsenazo III complex.

Calibration curve and performance parameters

The increase of absorbance values in pH > 2.5, is perhaps due to the association or dissociation effect of U (VI)-Arsenazo III complex or to the stability of U (VI) ions indifferent acidity medium.

The calibration curve is obtained by linear regresssion of the absorbance values vs. concentration of U (VI) standard solution (0 to 10 μg U/L, prepared from 1 mg/L U stock solution). The parameters of the calibration curve, such as the slope, the intercept and correlation coefficient of the fitted values are obtained through the method of linear regression. The results are shown in Fig. 4.

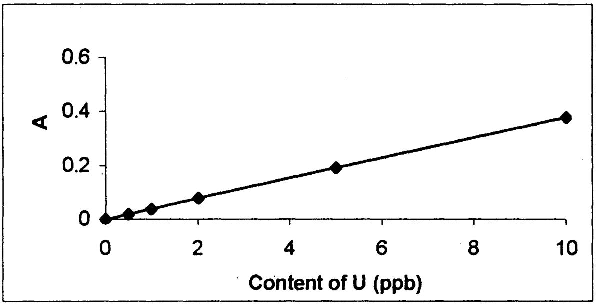

Fig. 4. The calibration curve of U-Arsenazo III (Slope = 0.04, Intercept = 0.0011, Corr. Coeff. = 0.996, St. error = 0.0014)

Fig. 4 shows that there is a very good relationship between the concentration of uranium and the absorbance values of U-arsenazo III system on the range from 0.1 to 10 μg of U/L. The correlation coefficient is higher than 0.999, the intercept is 0.0011 and slope is 0.04 A/ppm; so the sensitivity of the method is 0.25 μg of U/L. The parameters obtained are better than other methods used (γ-spectroscopy and neutron activation spectroscopy) and the sensitivity achieved is satisfied not only for geophysical anomalies, but also for the determination of trace values of uranium in water and seawater samples, using 20 to 50 mL of sample. The content of uranium in seawater samples from Albanian coast are 3.4 to 4.2 μg of U/L.

The reproducibility of the method

To assess the reproducibility of the method we have done the analysis of the same sample ten times (n = 10, P = 95%), keeping all conditions constant. We have used three natural samples (N-1, N-2 and N-3) to assess the reproducibility of the method. The results are listed in Table 1.

Table-1 shows that good accuracy and reproducibility of the method is achieved. The standard error is smaller than 0.83 and F-ratio value is satisfied ($F_{tab.} = 2.32$). The data of Table 1 show, too, that no significant differences exist between our results and those obtained from γ-spectroscopy and neutron activation spectroscopy. It shows, too, that all x values obtained from chemical analysis are smaller than those obtained from γ-spectroscopy and neutron activation spectroscopy. May be it is due to two causes:

1. The presence of interference in γ-spectroscopy and neutron activation spectroscopy method.
2. The losses during the chemical treatment of the sample

Sample distribution

We have used the results of about 800 samples from Nimce region to find the distribution of uranium concentration. We have mainly chosen the samples without radioactive equilibrium between uranium (U) and radium (Ra). The rest of the samples the analyzed by γ-spectroscopy method. There are two cases, we have reached the non-radioactive equilibrium samples:

1. For the content of uranium smaller than 500 ppm
2. On the mineralized troops paced near the groundneath surface, which is due to the nonstability of uranium in oxidizing milieu.

We have used the data of chemical and γ-spectroscopy analysis to draw the histogram of the disribution of uranium concentration *via* the coefficient of redioactive equilibrium (c) of the samples in monzonite rocks of Nimce region (Fig. 5).

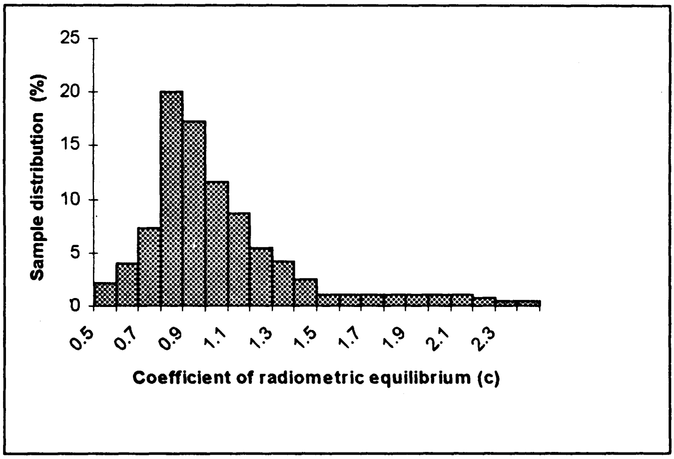

Fig. 5. The histogram of the distribution of uranium concentration *via* the coefficient of radioactive equilibrium (c)

Fig. 5 shows that for the same geological milieu, the values of the coefficent of radiometric equilibrium varied from 0.5 to 2.4. It is due to different behaviours of uranium and radon for different positions of the mineralized troops. Most of the cases (n > 68%) have c = 0.8 to 1, which show that this region is close to the radiometric equilibrium conditions. We have verified the red/ox situation of the mineralized troop, using the criteria of the coefficent of radiometric equilibrium. We found a good relationship between red/ox situation and the position of the mineralized troops, with the tendency of smaller coefficient of radiometric equilibrium near the groundneath surface. The situation explained above is a good proof of the accuracy of the analytical method used.

Conclusions

1. Arsenazo III spectrophotometric method is an accurate method to determine the content of uranium in various natural samples, such as water, soils and sediments. This methods has low cost, high yield, good selectivity and accuracy; so it is useful in geochemical research and environmental surveys. Good detection limit and sensitivity is obtained.
2. We propose to use 20% TBP in benzene solution to separate uranium from other interfering elements, such as rare earth elements, thorium, zirconium or niobium. and to preconcentrate it, instead of ion exchange method. NaF and EDTA additions are used to avoid the interferences of iron and calcium.
3. A good relationship is obtained between the content of uranium and the position of the mineralized troop, which proves the accuracy of the analytical method used.

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