

Thin Film-XRF Determination of Uranium Following Thin-Film Solid Phase Extraction

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Foi desenvolvido um método sensível baseado na pré-concentração de urânio em papel de filtro modificado (filme fino) para a determinação deste elemento em amostras de águas e de solos, usando a técnica de fluorescência de raios-X de comprimento de onda dispersivo. Para a extração de urânio (VI), 100 mL de amostra reagiram com tri-octil fosfina (TOPO) em presença de ácido nítrico. O efeito da concentração de ácido nítrico e de TOPO, bem como da retenção do metal em função do volume de amostra foram avaliados neste estudo. O método proposto mostrou boa linearidade entre 7 e 1000 µg de urânio (VI) e o limite de detecção (LOD), calculado com a relação sinal-ruído (S/N) igual a 3 foi de 2,5 µg.

A sensitive method based on the preconcentration of uranium on modified filter paper (thin film) has been developed to determinate this element in water and soil samples by wavelength dispersive X-ray fluorescence. Uranium (VI) extraction from nitric acid medium by trioctyl phosphine (TOPO) from 100 mL of sample was carried out. The effects of nitric acid concentration, TOPO concentration and sample breakthrough on uranium extraction were investigated in this study. The proposed method provided good linearity from 7 to 1000 µg and the limit of detection (LOD), based on a signal-to noise ratio (S/N) of 3, was 2.5 µg.

Keywords: uranium, thin film, X-ray florescence, preconcentration

Introduction

Uranium is an element that naturally presents various oxidation states (namely +2, +3, +4, +5 and +6), but uranium appears mostly in its hexavalent form. Usually in nature, uranium is associated with oxygen, forming the uranyl ion UO_2^{2+} . In the terrestrial crust, uranium has an average concentration of 4 µg g⁻¹ and, in order of magnitude, is more abundant than other heavy metals, such as mercury and silver.¹ The growing exploitation and use of uranium in recent decades has attracted the concern of the analytical community because it is an inorganic pollutant that spreads easily in the environment and presents both chemical and radiological effects to living beings. Thus, there is an increasing need for the development of simple and quick methods for the monitoring of this element in the environment. A variety of techniques have been used

for the determination of uranium concentrations: alpha-spectrometry² inductively coupled plasma optical emission spectrometry (ICP-OES),^{3,4} inductively coupled plasma mass spectrometry (ICP-MS)^{5,6} and X-ray fluorescence spectrophotometry (XRF)⁷ and spectrophotometry.⁸

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples.⁹⁻¹¹

There are comparatively few methods to detect low level concentrations of uranium, and usually these techniques are complex and require extensive and laborious separation or preconcentration steps.¹²

The uranyl ion can be viewed as the end result of extensive hydrolysis of the highly charged, hypothetical, U^{6+} cation. In fact, the aqueous uranyl ion is a weak acid. As pH increases, polymeric species with stoichiometry $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ and $[(\text{UO}_2)_3(\text{OH})_5]^+$ are formed before the

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hydroxide $\text{UO}_2(\text{OH})_2$ precipitates. The hydroxide dissolves in strongly alkaline solution to give hydroxo complexes of the uranyl ion.

In uranyl nitrate, $[\text{UO}_2(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$, for example, there are six donor atoms in the equatorial plane, four from bidentate nitrato ligands and two from water molecules. The structure is described as hexagonal bipyramidal. Other oxygen-donor ligands include phosphine oxides and phosphate esters. The complexes formed by the uranyl ion in aqueous solution are of major importance both in the extraction of uranium from its ores and in nuclear fuel reprocessing.¹³

In industrial processes, uranyl nitrate is extracted with tributyl phosphate, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_3\text{PO}$ (TBP) as the preferred second ligand, and kerosene the preferred organic solvent. Later in the process, uranium is stripped from the organic solvent by treating it with strong nitric acid, which forms complexes such as $[\text{UO}_2(\text{NO}_3)_4]^{2-}$ which are more soluble in the aqueous phase. Uranyl nitrate is recovered by evaporating the solution. In the last few years, organophosphorous compounds have found wide application in nuclear establishments for the extraction, enrichment and reprocessing of uranium, thorium and plutonium.¹⁴ Trioctylphosphine oxide is an organophosphorus compound with the formula $\text{OP}(\text{C}_8\text{H}_{17})_3$. Frequently referred to as TOPO, this compound is used as an extraction or stabilizing agent. It is an air-stable white solid at room temperature. The main use of TOPO is in solvent extraction of metals, especially uranium. The high lipophilicity and high polarity are key properties to this application. Its high polarity, which results from the dipolar phosphorus-oxygen bond, allows this compound to bind to metal ions. The octyl groups confer solubility in low polarity solvents such as kerosene. Trioctylphosphine oxide (TOPO) is one of the neutral organo-phosphorous solvating reagents, although having the highest extractive power. TOPO contains a strong dipole moment centered on the phosphorus-oxygen bond. The oxygen being more electronegative is the end that will provide the unshared pair of electrons for bonding with the vacant orbitals of a metal ion. The long side chains of this molecule help to increase the size of the complexed metal ion, thus decreasing the charge density and making it appear closer to zero charge. This hydrophobic end also aids in the dissolution in organic solvents.

Solid phase extractants are composed of a solid matrix and a chelating component (molecule or functional group). In this study, a sensitive method based on the preconcentration of uranium on modified filter paper (thin-film solid phase extraction) has been developed to determinate this element in water and soil samples by X-ray fluorescence.

Experimental

Apparatus

A Philips wavelength dispersive X-ray fluorescence spectrometer, with a rhodium tube operated at 40 kV and 30 mA, a LiF crystal and a scintillation counter were used for the determination of uranium in filter paper. The uranium measurement in solution was performed with a Varian 735 (700 series) simultaneous ICP-OES coupled to a pneumatic nebulizer and equipped with a charge coupled device (CCD). A 300 ANALYSER pH meter was used to measure pH values.

Table 1. Operating parameters for X-ray fluorescence spectrometer and ICP-OES instrumental parameters employed for uranium determination

	XRF		ICP-OES	
Channel	U	Power / kW		1.2
Line	LA	Plasma flow rate / (L min ⁻¹)		15
X-tal	LiF200	Auxiliary flow rate / (L min ⁻¹)		1.5
Collimator	150 mm	Nebulizer flow rate / (L min ⁻¹)		0.7
Detector	Scint.	Viewing configuration		radial
Tube filter	None	Viewing height / mm		10
KV	60	Replicate read time / s		30
mA	66	Instrument stabilization delay / s		30
Angle	26.1172	Replicate		3
PHD	25-75	Wavelength / nm		409.013

Reagents

All reagents were of analytical grade unless otherwise stated. Trioctyl phosphine was obtained from Sigma-Aldrich. Uranium stock standard solutions (1000.0 mg mL⁻¹) each were prepared from uranyl nitrate hexahydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in nitric acid and was diluted daily to obtain working solutions.

General procedure

Throughout this study, the influence of HNO_3 sample volume and TOPO concentration was firstly investigated. The experimental flat-round type cellulose hydrophobic filter papers are used at the obtained optimum parameters. Thus, 1.0 mL of 0.1 mol L⁻¹ TOPO in *n*-hexane was sprayed onto the surface of filter paper and dried in ambient temperature (10 min). A convenient aliquot of solution (50 mL) containing 8.0 mg L⁻¹ uranium (VI) and 2.0 mol L⁻¹ nitric acid was passed through modified filter paper. After drying, the filter paper analyzed by XRF and

the filtrate was analyzed by ICP-OES and the concentration of uranium was determined.

Method of Sample Preparation

Water

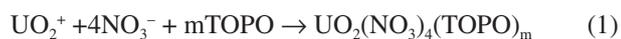
Water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. One hundred milliliters of water sample was transferred to a beaker and the concentration of nitric acid was adjusted to 2.0 mol L⁻¹ and was passed through modified filter paper. After drying, the filter paper analyzed by XRF and the filtrate were analyzed by the ICP-OES and the concentration of uranium was determined.

Soil

Each rock sample was grinded, homogenated and quartered. A representative sample was then grinded to ca. 200 mesh. The samples were dried overnight at 80 °C. 0.500 g of each sample was weighed and digested according to ASTM D4698-2. Briefly, the sample was digested in HNO₃, HF, HClO₄, and HCl by stirring on a hot plate at 80 °C for 4 h till near dryness. After cooling, the solution of each sample was centrifuged and filtered. The filtered solution was diluted with 2.0 mol L⁻¹ nitric acid in 50.0 mL volumetric flask and was passed through modified filter paper. After drying, the filter paper was analyzed by XRF and the filtrate was analyzed for uranium (VI) by ICP-OES and the concentration of uranium was determined.

Results and Discussion

The extraction of uranyl ions from aqueous nitrate media to an organic solution containing a neutral ligand (TOPO) can be described by means of following extraction equilibrium:



Some of our preliminary experiments showed that while the filter paper itself extracts 25% of uranium ions, the filter paper modified by TOPO was capable of retaining uranium ions in the sample solution quantitatively (the test solution contained 400 μg uranium in 50 mL solution).

Effect of nitric acid concentration

In the extraction of hexavalent uranium with an organic solvent, the extraction coefficient is a function of the species

in which the uranium ion exists. For this reason, either nitric acid or nitrate ion in other form is usually added to facilitate the extraction of uranium. Indeed, in the case of most solvent extractions, the addition of nitrate to the extraction medium was imperative for quantitative application. The concentration of nitric acid was investigated in the range of 0.002-6 mol L⁻¹ (Figure 1). The results show that the extraction efficiency was increased up to 2 mol L⁻¹ and then decreased.

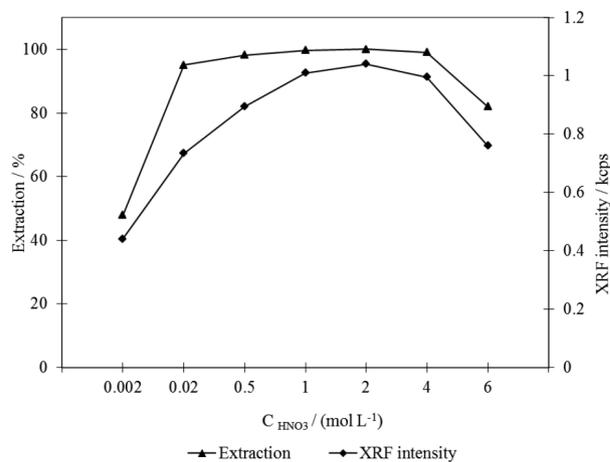


Figure 1. Percentage of extraction efficiency as a function of nitric acid concentration. Conditions: volume of sample: 50.0 mL, amount of uranium: 400.0 μg , amount of TOPO: 0.025 mmol.

Effect of breakthrough volume

The breakthrough experiment is simply a measure of the volume of sample that may be passed through the sorbent before the analyte is no longer retained. In order to explore the possibility of concentrating low concentration of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose 20, 50, 100 and 200 mL of the sample solutions containing 400.0 μg of uranium were extracted. Figure 2 shows the breakthrough curve obtained for uranium. The breakthrough volume of uranium occurred when 100.0 mL of solution had passed through the filter (extraction > 80%).

Amount of TOPO

The effect of TOPO concentration on the extraction of uranium (VI) was studied. The studies were performed over a concentration range of 0.0 to 0.05 mmol TOPO. Generally, an increase in TOPO concentration produces an increase in uranium extraction. It can be seen that an increase in TOPO concentration up to 0.025 mmol leads to an increase in extraction efficiency (Figure 3).

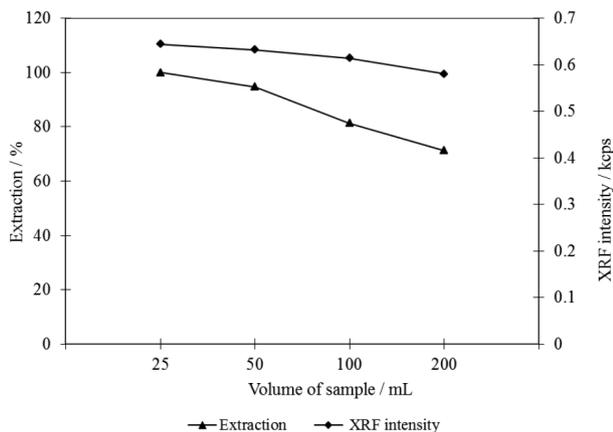


Figure 2. Breakthrough curve for filter paper modified with TOPO. Conditions: amount of TOPO: 0.025 mmol, amount of uranium: 400.0 μg , concentration of nitric acid: 2 mol L^{-1} .

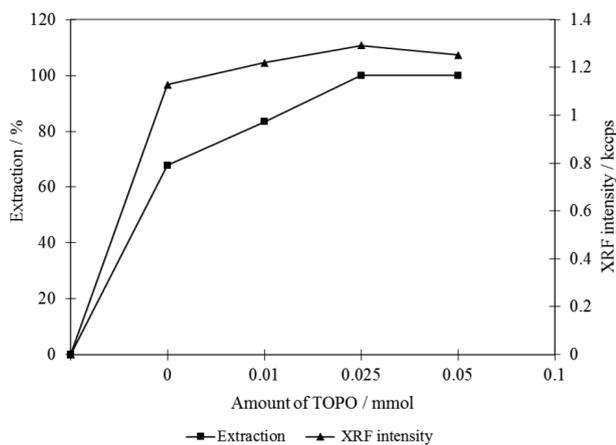


Figure 3. Percentage of extraction efficiency as a function of TOPO concentration. Conditions: volume of sample: 50 mL, amount of uranium 400.0 μg , concentration of nitric acid 2 mol L^{-1} .

Analytical performance

Seven aqueous solutions (50.0 mL) containing uranium from 25.0 μg to 1000.0 μg were submitted to the whole analytical procedure. 1.0 mL of 0.1 mol L^{-1} TOPO in *n*-hexane was carefully sprayed onto surface of filter paper in order to ensure its homogeneity and dried in ambient temperature (10 min). A convenient aliquot of solution (50 mL) containing 8.0 mg L^{-1} uranium (VI) and 2.0 mol L^{-1} nitric acid was passed through modified filter paper. After

Table 3. Recovery of uranium obtained from proposed method for water and soil samples

Sample	Certified value / (mg L^{-1})	U found / (mg L^{-1})	Recovery / %
Spiked water	0.100	< LOD	–
Spiked water	1.0	0.82	82
Spiked water	2.0	1.86	93
Spike soil	200.0	194	97
SDO-1	49	44	90

drying, the filter paper was analyzed by XRF. The results obtained showed that linearity was excellent for uranium with correlation coefficient of 0.9998 which indicates that a good linear regression was established between intensity and the concentrations. The enrichment factor for soil, which was calculated, based on the slopes for the calibration curves after and before the extraction step was 28. The limit of detection (LOD), based on the signal-to noise ratio (S/N) of 3, was 2.5 μg . The relative standard deviation (RSD) of the method, determined by analyzing the standard solution at 100 μg ten times, was 5% (Table 2).

Table 2. Figure of merits obtained for uranium determination

Equation	DLR ^a / μg	R ²	LOD / μg	PF ^b
Intensity = 0.0257C – 0.0109	7-1000	0.9998	2.5	28

^aDLR: linearity; ^bPF: preconcentration factor.

Different amounts of uranium (VI) ions were spiked in tap water and mineral water to estimate the accuracy of the procedure. The resulting solutions were submitted to the presented procedure (solutions were passed through modified filter paper), and after drying, the filter paper was analyzed by XRF. The results are given in Table 3. Good agreement was obtained between the added and found uranium content using the recommended procedure. The validation of the presented procedure is performed by the analysis of certified reference material (CRM) (SDO-1). The certified and observed values for SDO-1 are given in Table 3. The results found were in good agreement with the certified values of CRM.

Conclusion

The proposed method shows advantages such as: it is simple, rapid and low analysis cost. The effect of HNO_3 , volume of sample and TOPO concentration was investigated and optimized. The concentration factor was determined as 28. The possibility to determine uranium in water and soil by using XRF with direct measurement on modified filter paper indicates an excellent advantage of this proposed procedure over existing methods.

References

1. Rathore, D. P. S.; *Talanta* **2008**, *77*, 9.
2. Tsuey-Lin, T.; Chun-Chih, L.; Tieh-Chi, C.; *Appl. Radiat. Isot.* **2008**, *66*, 1097.
3. Yongsheng, Z.; Chunxia, L.; Miao, F.; Zhen, C.; Shuqiong, L.; Gan, T. L. W.; Jingbo, H.; Shoujian, L.; *J. Hazard. Mater.* **2010**, *176*, 119.
4. Nasab, M. E.; *Fuel* **2014**, *116*, 595.
5. Gautier, C.; Coppo, M.; Caussignac, C.; Laszak, I.; Fichet, P.; Goutelard, F.; *Talanta* **2013**, *106*, 1.
6. Aydin, F. A.; Soylak, M.; *Talanta* **2007**, *72*, 187.
7. Santos, J. S.; Teixeira, L. S. G.; Santos, W. N. L.; Lemos, V. A.; Godoy, J. M.; Ferreira, S. L. C.; *Anal. Chim. Acta* **2010**, *674*, 143.
8. Camel, V.; *Spectrochim. Acta, Part B* **2003**, *58*, 1177.
9. Dadfarnia, S.; Haji-Shabani, A. L.; *Anal. Chim. Acta* **2010**, *658*, 107.
10. Anthemidis, A. N.; Ioannou, K. I. G.; *Talanta* **2009**, *80*, 413.
11. Sadeghi, S.; Sheikhzadeh, E.; *Microchim. Acta* **2008**, *163*, 313.
12. Bayou, N.; Arous, O.; Amara, M.; Kerdjoudj, H.; *C. R. Chimie* **2010**, *13*, 1370.
13. Alibrahim, M.; Shlewit, H.; *Chem. Eng.* **2007**, *51*, 57.
14. Ghag, S. M.; Pawar, S. D.; *J. Serb. Chem. Soc.* **2010**, *75*, 1549.

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