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DETERMINATION OF URANIUM IN NATURAL WATERS BY SOLID PHASE SPECTROMETRY

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A microdetermination method (at the $\mu\text{g.l}^{-1}$ level) for uranium has been developed, based on Solid-Phase Spectrophotometry (SPS). The uranium reacts with pyridylazo-resorcinol in the presence of fluoride to form a 1:1:1 red ternary complex, which is fixed on an anion-exchange resin. The resin absorbance is measured directly, and allows the determination of uranium in the range of 1-10 $\mu\text{g.l}^{-1}$, with an RSD of 4%. The method has been applied to the determination of U(VI) in natural waters from wells located near the deposits of industrial wastes from a uranium mineral plant in Andujar (Spain).

KEY WORDS Solid phase spectrometry, uranium analysis, 4-(2-pyridylazo)resorcinol, natural waters.

INTRODUCTION

The analysis of uranium in natural waters demands highly sensitive methods, due to its very low content in this medium. Many methods have been reported for the spectrophotometric analysis of uranium, several of which have a molar absorptivity greater than $2 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$.¹⁻⁹ However, they lack the sensitivity to solve the problem of determining uranium in natural waters. Therefore, preliminary enrichment and separation of uranium from the water matrix are usually required. The inherent suitability of spectrophotometric methods induced us to explore the possibilities of Solid Phase Spectrophotometry (SPS) in order to solve the problem.

SPS methodology combines the preconcentration of the species of interest on a solid matrix, usually an ion-exchanger, with the aid of a complexing agent and subsequent measurement of the absorbance of the complex in the resin phase.¹⁰⁻¹² In many cases the complexing system used for fixation is a mixed ligand complex, formed with a chromogenic agent and an auxiliary, usually a masking agent. This provides an increase in selectivity and sensitivity to SPS methods.^{11,12}

On account of its high sensitivity, 2-(4-pyridylazo)-resorcinol (PAR) is a good chromogenic reagent for the determination of traces of uranium in solution. In the presence of fluoride no reaction is observed other than the PAR-uranium one; fluoride is even used as a masking agent in the solution method for uranium.²

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However, when an anionic resin is present, another new species is formed and fixed on the resin, viz. a mixed ligand complex. This system, studied in this paper, is the basis of a new method to analyze uranium in water. It has been applied to the determination of uranium in well water from a leaching of industrial wastes from a uranium mineral plant.

EXPERIMENTAL

Reagents

Ion exchanger Dowex 1-X8 (200–400 and 100–200 mesh) anion-exchange resins were used in the chloride form. The resins were washed several times with doubly distilled water, then treated with 2 M HCl and finally with distilled water until the washings were free from chloride. They were air-dried and stored in a polyethylene container.

Uranyl nitrate stock solution (4.30×10^{-3} M; $f=0.995$) Prepared by dissolving 2.1590 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and diluting to 1000 ml with water. The solution was standardized by precipitating ammonium diuranate and igniting it, forming U_3O_8 . The solution was diluted as required.

4-(2-Pyridylazo)resorcinol (PAR) 1000 $\text{mg} \cdot \text{l}^{-1}$ (3.92×10^{-3} M) A 0.263 M sodium fluoride solution and a 0.2 M acetic acid/acetate buffer pH 4.8, were prepared.

All chemicals used were of analytical grade; water was doubly distilled. All experiments were carried out at room temperature.

Apparatus

A Bausch and Lomb Spectronic 2000 spectrophotometer with 1 mm cells was used. Other apparatus consisted of an Agitaser 2000 rotating bottle agitator, an Emas desk centrifuge and a Crison Model 501 pH meter with a combined glass-saturated calomel electrode for pH measurements.

Absorbance Measurements

The absorbance of the complex species sorbed on the resin was measured in a 1 mm cell at 550 and 800 nm (the latter is in the range 700–850 nm where only the resin absorbs light), compared with a 1 mm cell packed with resin and equilibrated with water. The net absorbance was calculated as in a previous report.¹⁰

Procedures

General procedure To a 500 ml sample placed into a 1-l polyethylene bottle and

containing $0.0084\text{--}0.1512\ \mu\text{mol.l}^{-1}$ of U(VI) ($2\text{--}36\ \mu\text{g.l}^{-1}$), $0.70\ \text{ml}$ of $3.92 \times 10^{-3}\ \text{M}$ PAR solution, $3\ \text{ml}$ of $0.263\ \text{M}$ fluoride solution, $5\ \text{ml}$ of pH 4.8 acetate buffer solution, and $0.15\ \text{g}$ of Dowex 1-X8 (200–400 mesh) resin were added. The mixture was stirred for 10 min and the coloured resin beads were collected by filtration under suction and, with the aid of a pipette, packed into a 1 mm cell together with a small volume of the filtrate. The cell was centrifuged for 1 min at $280 \times G$. A blank solution containing all reagents except uranium was prepared and treated in the same way as the sample. The absorbance at 550 and 800 nm for both sample and blank were measured against a 1 mm reference cell, similarly packed with resin equilibrated with water. The absorbance difference between sample and blank provides an estimation of the net absorbance.¹⁰

For 1000 ml samples, placed in a 2-l polyethylene bottle, solutions containing $0.0042\text{--}0.0420\ \mu\text{mol.l}^{-1}$ of U(VI) ($1\text{--}10\ \mu\text{g.l}^{-1}$), $0.40\ \text{ml}$ of $3.92 \times 10^{-3}\ \text{M}$ PAR solution, $3\ \text{ml}$ of $0.263\ \text{M}$ fluoride solution, $10\ \text{ml}$ of pH 4.8 acetate buffer solution, and $0.15\ \text{g}$ of Dowex 1-X8 (200–400 mesh) resin were added. The mixture was shaken mechanically for 15 min, operating as indicated in the above procedure.

Procedure for natural water To a 500 ml water sample, previously adjusted with NaOH to pH 4–5; $5\ \text{ml}$ of $10^{-2}\ \text{M}$ 1,2-cyclohexanediaminetetraacetic acid solution, the same volume of the other reagents and the same weight of resin as in the general procedure were added, operating as indicated in the general procedure. The standard addition method was used for calibration except in mineral water.

Treatment of sample Natural water was preserved with conc. HNO_3 ($0.25\ \text{ml}/1000\ \text{ml}$), filtered through a $0.45\ \mu\text{m}$ membrane filter paper (Millipore) and collected in a polyethylene container carefully cleaned with nitric acid. The samples were stored at 4°C until analysis. The analyses were performed with the least possible delay. The usual general precautions were taken to avoid contamination.¹³

RESULTS AND DISCUSSION

Absorption Spectra of the System

The PAR is fixed on an anionic resin, giving a yellow-orange colour with an absorption maximum at 409 nm, compared with 415 nm in solution. The presence of uranium (VI) shifts the absorption maximum to 527 nm in solution, and to 549 nm in the resin phase. The addition of fluoride to a solution of PAR–U(VI) effects a hypsochromic shift (to 505 nm) in the absorption spectrum (Figure 1b). In the resin phase, the presence of fluoride in solution causes a slight shift in the absorption maximum of the complex in the resin phase, viz. to 551 nm colouring the resin red. A significant hyperchromic effect was also observed (Figure 1a).

OPTIMIZATION OF VARIABLES

pH dependence The optimum pH for the formation and fixation of the species is 4–5. At pH values below 4 or above 5 the absorbance decreases. The complex is

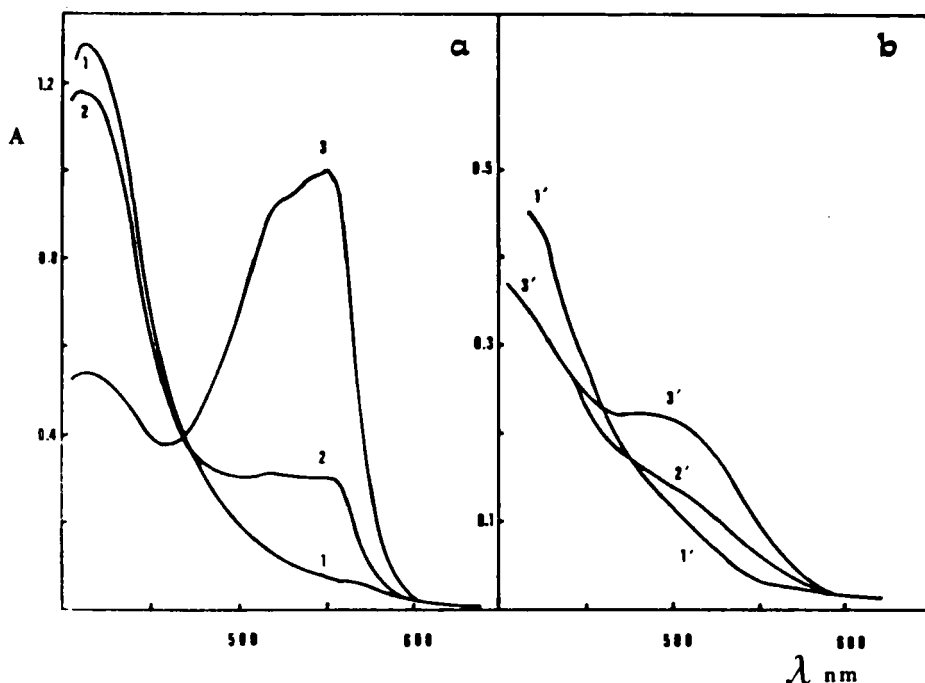


Figure 1 Absorption spectra of U(VI)-PAR species. (a) on the resin (resin as reference); (b) in solution (water as reference). Spectra 1 and 1', PAR in the presence of fluoride; spectra 2 and 2', PAR-U(VI); spectra 3 and 3', PAR-U(VI) in the presence of fluoride. Conditions: $[\text{PAR}] = 8.3 \times 10^{-3} \text{ M}$, $[\text{U(VI)}] = 6 \times 10^{-7} \text{ M}$, $[\text{F}^-] = 2.9 \times 10^{-3} \text{ M}$, $\text{pH} = 4.8$, 0.2 g of Dowex 1-X8 (100–200 mesh).

not fixed on the resin for a pH above 8 or below 2. We chose pH 4.8 as the working pH, using a 0.2 M acetate buffer, in the general procedure. The optimum pH range in homogeneous solution and in the presence of fluoride is 7–9, 8.0 being the working pH.²

Reagent concentrations Absorbance increases with an increasing PAR concentration, a plateau occurring from $8.4 \times 10^{-6} \text{ M}$. The minimum molar $[\text{PAR}]/[\text{U(VI)}]$ ratio necessary was 20:1. Therefore, a concentration of $5.49 \times 10^{-6} \text{ M}$ PAR was chosen.

In the presence of fluoride, the absorbance value was increased twelve times with respect to the value obtained in its absence, which is due to U(VI)-PAR- F^- complex fixation. At a fluoride concentration higher than $1.6 \times 10^{-3} \text{ M}$ ($[\text{F}^-]/[\text{U(VI)}] = 3800$), the absorbance of the blank increases; therefore, we chose to work at this fluoride concentration (Figure 2).

Other experimental conditions The optimum stirring time is 30 min for the 100–200 mesh resin and 10 min for the 200–400 mesh resin. The fixed complex is stable for at least one day after equilibration. The best order of addition of reagents, and the one used here, is: U(VI)-PAR- F^- -buffer-resin. Other sequences slightly reduce the absorbance.

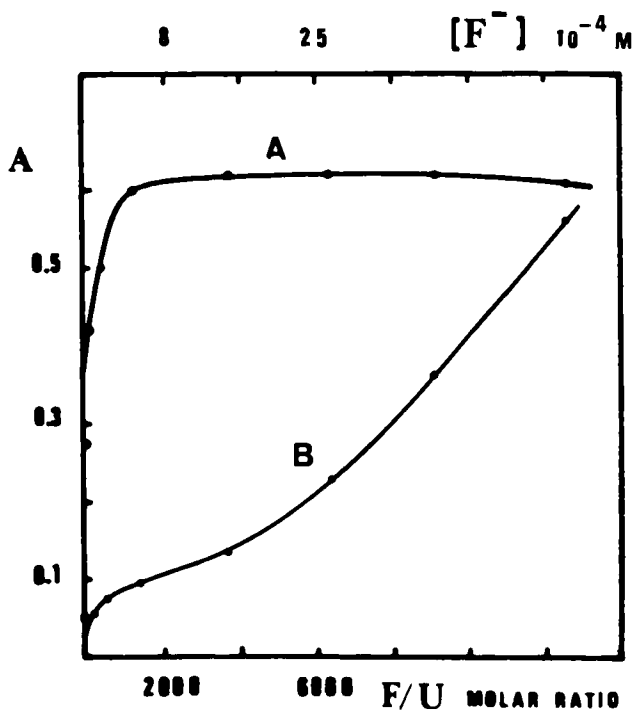


Figure 2 Dependence of net absorbance on $[F^-]/[U(VI)]$ molar ratio (Curve A). Conditions: $[PAR] = 3.16 \times 10^{-6} M$; $[U(VI)] = 4.2 \times 10^{-7} M$; $pH = 4.8$; 0.2 g of Dowex 1-X8 (100–200 mesh); stirring time, 25 min; sample volume, 500 ml. Dependence of blank absorbance with fluoride concentration (Curve B). Same conditions without U(VI).

NATURE OF THE FIXED COMPLEX

The nature of the species fixed on the resin was determined by the equilibrium shift method at the working pH. The plot of $\log A/(A_m - A)$ vs. $\log [PAR]$ at a $[F^-]/[U(VI)]$ molar ratio of 3750 gave a slope of 1.06, indicating the presence of one molecule of PAR in the fixed complex. Similarly the $\log A/(A_m - A)$ vs. $\log [F^-]$ plot at a $[PAR]/[U(VI)]$ molar ratio of 230 gave a slope of 1.02, indicating that a fluoride to uranium molar ratio of 1:1 is present in the complex. These results show that the stoichiometry is $U(VI): PAR: F^- = 1: 1: 1$.

The mixed complex is anionic in nature, due to the fact that complexation of $UO_2(II)$ with PAR requires previous dissociation of the o-OH group of the reagent. The uranium ion is coordinated through the pyridinic nitrogen, the azo group and the oxygen in the ortho position. The dissociation of the p-OH of PAR ($pK_{a2} = 5.6$ in solution)¹⁴ on the resin gives a -1 charge to the complex.

The molar ratio $PAR: U(VI)$ in the resin phase is in agreement with that found in solution by Busev *et al.*¹⁵ and Florence *et al.*,² although in the latter case, the molar ratio $PAR: U(VI)$ was described by Geary *et al.*¹⁶ as a 2:1 $PAR: U(VI)$ complex at pH 8.0.

Table 1 Analytical parameters

Parameter	Volume of sample system	
	500 ml	1000 ml
Intercept	-3.6×10^{-3}	-7.53×10^{-3}
Slope	0.025	0.051
Linear dynamic range ($\mu\text{g.l}^{-1}$)	2–36	1–10
Correlation coefficient	0.999	0.997
Detection limit ($\mu\text{g.l}^{-1}$)	0.65	0.28
RSD (%)	4.1	4.1

Table 2 Comparison of sensitivities for spectrophotometric uranium methods

Reagent	Molar absorptivity ($\times 10^4 \text{ l.mol}^{-1} \text{ cm}^{-1}$)	Reference
Eriochrome Black-T	3.0	1
PAR	3.9	2
Arsenazo III	5.3	3
PADAP	6.6	4
Malachite Green	8.3	5
3,5 diBr-PADAP+SLS	9.1	6
Chromazurol S+HDTMA	10.4	7
Chlorophosphonazo III	11.5	8
Chromal Blue G+CTA	13.0	9
Procedure 500 ml	595	present
Procedure 1000 ml	1210	method

PADAP: 2-(2-pyridylazo)-5-diethylaminophenol; SLS: Sodium Lauryl Sulphate; HDTMA: Hexadecyltrimethylammonium bromide; Chlorophosphonazo III: 3-(4-Chloro-2-phosphonophenylazo)-6-(3-trifluoromethyl phenyl azo) chromotropic acid; CTA: Cetyltrimethylammonium chloride.

ANALYTICAL DATA

The calibration graphs for the samples treated according to the procedure described above are linear for 2–36 $\mu\text{g.l}^{-1}$ of U(VI) for 500 ml, and 1–10 $\mu\text{g.l}^{-1}$ for 1000 ml samples. The analytical parameters are summarized in Table 1.

The reproducibility was established using 500 ml and 1000 ml sample solutions with a U(VI) concentration of 16 $\mu\text{g.l}^{-1}$ and 4 $\mu\text{g.l}^{-1}$, respectively. For 10 determinations, the RSD was 4.1% in both cases. We have demonstrated previously¹⁷ that one of the main contributions to the RSD comes from the variability of the packing of the ion-exchanger. Reproducibility is improved if the cells packed with the resin phase are centrifuged before spectrophotometric measurements are taken.

The sensitivity, expressed as molar absorptivity, of the proposed methods, is compared with that of spectrophotometric procedures in the literature (Table 2). Using the SPS method causes a noticeable increase in sensitivity, especially in relation to the solution methods using the same reagent.

Sensitivity enhancement through an increase in the sample volume, estimated from the slope ratio of the calibration graphs, was $S_{1000/500} = 2.03$.

The standard deviation of A^*_R , the background absorbance measured for the blank, necessary for the estimation of the IUPAC detection limit ($K = 3$), measured as the average of ten determinations and noted as RSD units, for the 500 and 1000 mL samples were 0.022 and 0.019, respectively (Table 1).

EFFECTS OF FOREIGN IONS

A systematic study of the effect of foreign ions on the determination of U(VI), was undertaken. A 3000-fold w/w ratio of interfering ion to U(VI) was tested and, if interference occurred, the ratio was reduced until interference ceased to occur. Tolerance is defined as the amount of foreign ions that produces an error equal to $\pm 5\%$ in the determination of analyte. The following foreign ions were tolerated in the determination of $16 \mu\text{g.l}^{-1}$ of U(VI): Cl^- , SO_4^{2-} , NO_3^- and Ca(II) up to at least a 1250-fold ratio; Mg(II) up to a 625-fold ratio; Al(III) up to a 56-fold ratio; PO_4^{3-} up to a 25-fold ratio; Th(IV) up to a 19-fold ratio; Ti(IV) up to a 1.25-fold ratio; Zr(IV) up to a 0.6-fold ratio; Zn(II) up to a 0.4-fold ratio; Fe(III) up to a 0.2-fold ratio; Cu(II) up to a 0.09-fold ratio; Ni(II) and Co(II) up to a 0.04-fold ratio.

The interference was negative for Cl^- and positive for the other ions. The interferences could be eliminated by using CDTA (1,2-cyclohexanediaminetetraacetic acid) as masking agent. For a masking concentration of $2 \times 10^{-4} \text{ M}$ of CDTA Fe(III) up to at least 12.5-fold ratio, and Ni(II), Co(II), Cu(II) and Zn(II) up to a 2-fold ratio were tolerated, in the determination of $16 \mu\text{g.l}^{-1}$ of U(VI).

DETERMINATION OF URANIUM IN NATURAL WATERS

The method has been applied to the determination of uranium in natural waters. We have analyzed water from wells located near the town of Andújar (Jaén), which lies on the southern edge of Sierra Morena (Hesperic Massif, rocks dating from the Precambrian to the Upper Carboniferous and constituted fundamentally by gneisses, micasquists, filites and granitic rocks) and on the third fluvial terrace of the Guadalquivir river. On these fluvial terraces are the residues from a nearby treatment and separation plant for uranium minerals (Torbernite, Saleeite, Autunite, etc.). These slag heaps are protected by a thin asphaltic cover and the rain leaches uranium from the industrial wastes, carrying uranium into the subterranean aquiferous mantle linked to the fluvial terraces.

As representative samples, we selected natural water from wells placed below the industrial wastes from the uranium plant. The method used was the general procedure of the 500 ml sample system and the standard-addition method was used.

The loss of sensitivity caused by matrix effects can be evaluated by the slope's quotient between the standard calibration graph and the standard-addition

Table 3 Recovery study for uranium in natural waters

<i>Water</i>	<i>Amount added</i> ($\mu\text{g.l}^{-1}$)	<i>Amount found</i> ($\mu\text{g.l}^{-1}$)	<i>Recovery</i> (%)
Cano 1 well ^a		6.1	
	4.0	10.0	97.5
	8.0	14.1	100.0
Cano 2 well ^a		5.2	
	4.0	9.0	95.0
	8.0	13.0	97.0
Molino–Noria well ^a		4.5	
	4.0	8.7	105.0
	8.0	12.7	102.5
Menendez well ^a		5.4	
	4.0	10.0	115.0
	8.0	13.6	102.5
	12.0	17.0	96.7
Mineral water ^b (Ortigosa del Monte)	4.0	4.3	107.5

^aSample volume 10 ml. The data represent the average from three determinations.

^bSample volume 500 ml. The data represent the average from six determinations ($S_{n-1} = 0.4$).

calibration graph. The quotients found were as follows: Cano 1 well, 0.65; Cano 2 well, 0.76; Molino–Noria well, 1.01 and Menendez well, 1.06.

The average value of three determinations of the uranium found in the analysis of 10 ml of well water by the 500 ml sample method was: $6.1 \pm 0.2 \mu\text{g.l}^{-1}$ U(VI) for the Cano 1 well; $5.2 \pm 0.3 \mu\text{g.l}^{-1}$ for the Cano 2 well; $4.5 \pm 0.3 \mu\text{g.l}^{-1}$ for the Molino–Noria well; and $5.4 \pm 0.5 \mu\text{g.l}^{-1}$ for the Menendez well. The content in uranium, taking into account the dilution factor, was: 305, 260, 225 and $270 \mu\text{g.l}^{-1}$ of U(VI), respectively.

To check the accuracy of the proposed method, we carried out a recovery study in the waters mentioned above and in water whose uranium content was below the detection limit (spring water from Ortigosa del Monte (Segovia)). To do so, we added different amounts of U(VI) to water samples, obtaining a recovery acceptable to the standard conditions established. Table 3 shows the results obtained for each sample.

CONCLUSION

Uranium can be determined efficiently with pyridylazoresorcinol in the presence of fluoride using the Solid-Phase Spectrophotometry technique. The method has been applied to the determination of uranium in well water samples using the standard-addition calibration method. The method is simple, selective and sensitive as compared to others commonly used at the microgram level.

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