Pergamon

0039-9140(94)00176-6

Talanta, Vol. 41, No. 12, pp. 2173–2175, 1994
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0039-9140/94 $7.00 + 0.00

SHORT COMMUNICATION

A HIGHLY SELECTIVE PHOTOMETRIC METHOD FOR URANIUM(VI) USING A PYRIMIDYL AZO DYE IN THE PRESENCE OF EDTA

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(*Received* 18 *February* 1994. *Revised* 19 *May* 1994. *Accepted* 25 *May* 1994)

Summary—The sodium salt of 2,4,6-tris(1-hydroxy-4-sulphonaphthyl-2-azo)pyrimidine gives a 1:1 violet coloured complex with uranyl(II) at pH 5.5–6.5 in the presence of EDTA absorbing maximum at 560 nm, where no other metal, including lanthanides, forms a complex. The Sandell's sensitivity of colour reaction is 6.14 ngU(VI)/cm^2. The developed method has been applied to the determination of uranium(VI) in synthetic samples corresponding to mineral monazite and some uranium alloys.

Uranium is a very important metal, with its alloys also finding numerous uses, *viz.* the uranium alloyed copper[1] has good tensile properties, particulate uranium[2] is used for making liners suitable for penetrating more than 15 inches into rocks during deep well drilling and there are diverse uses cited in the literature.[3–5] While numerous methods are reported for micro analysis of uranium, most of them are unselective.[6–8] We propose a simple and highly selective spectrophotometric method using a new reagent, the sodium salt of 2,4,6-tris(1-hydroxy-4-sulphonaphthyl-2-azo)pyrimidine (THPm-4S) in the presence of EDTA.

EXPERIMENTAL

Equipment

A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for absorbance measurements and a Backman pH meter (model Φ 60) was used for pH adjustments.

Reagents

The synthesis of the dye is given elsewhere[9] and its 1 m*M* solution was prepared by dissolving 0.896 g/l. in double distilled water.

A stock solution of uranyl(II) ions was prepared by dissolving an appropriate amount of uranyl nitrate(AR) in double distilled water. The solution was standardized as uranyl oxinate.

Buffer solution: acetate buffer of pH 5.9 was prepared by mixing acetic acid (2.5 ml, 0.2*N*) and sodium acetate (47.5 ml, 0.2*N*).

Procedure

To an aliquot containing 10–80 μg of uranyl(II) was added 0.5 ml of 1 m*M* THPm-4S followed by 1 ml of 25 m*M* EDTA solution. Acetate buffer (1 ml) was added and the contents diluted to 10 ml with water. The absorbance was measured at 560 nm against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

Under the conditions used, uranyl(II) forms a violet coloured complex with THPm-4S. The uranyl(II) complex exhibits maximum absorption at 560 nm (against reagent blank) whereas that of reagent is at 470 nm (against water). The absorption spectra of THPm-4S and its uranyl(II) complex against water are shown in Fig. 1.

Reaction conditions

The optimum pH range for constant and maximum colour development is 5.5–6.5. An acetate buffer (1 ml) of pH 5.5 gave the best results. Only six-fold molar excess of THPm-4S was required for complete colour development.

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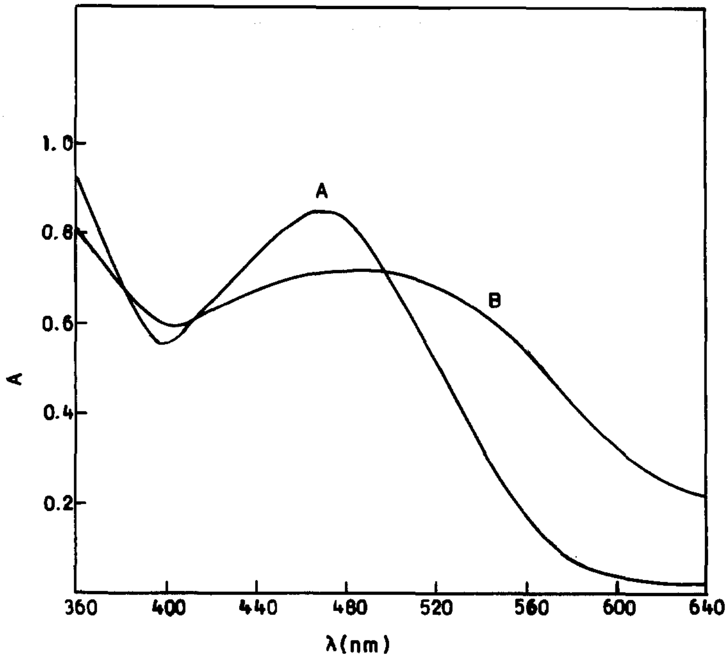

Fig. 1. Absorption spectra of (A) THPm-4S alone; (B), UO_2^{2+}-THPm-4S complex *vs.* water. Conditions = $UO_2^{2+} = 1 \times 10^{-5} M$, THPm-4S = $5 \times 10^{-5} M$, pH 5.5.

Analytical characteristics

A calibration graph was prepared by the procedure described for the determination of a microamount of uranium(VI). Beer's law was followed up to 8.6 ppm with an optimum concentration range of 1.0 to 8.0 ppm as determined by a Ringbom plot. Sandell's sensitivity was found to be 6.14 ng U(VI)/cm^2 with a molar absorptivity (ϵ)$3.7 \times 10^4 M^{-1}$ cm^{-1}. Composition of the complex was determined by Job's method of continuous variations and uranium:THPm-4S ratio was found to be 1:1.

The precision of the proposed method was checked by establishing the concentration of 10 samples containing 4.76 μg of uranyl(II). The mean recovery was found to be 4.73 μg with a coefficient of variance of 0.67%.

Interferences

In the determination of 2.38 μg/ml uranyl(II) according to the recommended procedure, fluoride, chloride, bromide, iodide, nitrate, nitrite, oxalate, tartrate, thiosulphate, cyanide, borate, acetate and thiourea did not interfere at all. EDTA up to 80 mM was well tolerated in 10 ml of total volume and hence was used as the masking agent. EDTA prevented the formation of other metal complexes which otherwise formed with THPm-4S. However, phosphate interfered seriously. The results of tolerance limits of various ions (in folds) that caused a deviation smaller than ±2% in absorbance in the determination of uranyl(II) were: Cu(II) 52, Fe(II) 24, Co(II) 25, Ni(II) 25, Zn(27), Cd(II) 47, Hg(II) 40, Mn(II) 23, Cr(III) 50, V(V) 15, Sr(II) 40, Ba(II) 100, Sb(III) 51, Bi(III) 88, In(III) 48, Tl(III) 40, Sn(II) 50, Pb(II) 45, Ag(I) 21, Pd(II) 25, Pt(IV) 50, Th(IV) 47, Ce(IV) 150, Pr(III) 160, Nd(III) 160, Sm(III) 130, Eu(III) 165, Gd(III) 200, Dy(III) 170, Tm(III) 125, Yb(III) 140.

Analysis of synthetic samples

Synthetic samples of the same composition as mineral monazite and uranium alloys were prepared and analysed for uranium(VI) at pH 5.9 according to the recommended procedure. The results were in good agreement with known amounts of uranium(VI). The results are given in Table 1.

Comparison of sensitivity

The sensitivity of this method ($3.7 \times 10^4 M^{-1}$ cm^{-1}, 560 nm) is comparable with some well known reagents used for the determination of uranium, *viz.* arsenazo I[10] ($2.3 \times 10^4 M^{-1}$ cm^{-1}, 596 nm), arsenazo III[11] ($8.8 \times 10^3 M^{-1}$ nm^{-1}, 565 nm), thiocyanate[12] ($2.9 \times 10^3 M^{-1}$ cm^{-1}, 380 nm), PAN[13] ($2.3 \times 10^4 M^{-1}$ cm^{-1}, 560 nm), PAR[14] ($3.87 \times 10^4 M^{-1}$ cm^{-1}, 530 nm), chlorophosphonazo III[15] ($7.96 \times 10^4 M^{-1}$ cm^{-1},

Table 1. Analysis of synthetic samples of mineral monazite and alloys of uranium

Percentage composition	Conc. of metals taken ($\mu g/ml$)	U(VI) found ($\mu g/ml$)*	Coefficient of variance† (%)
Mineral monazite			
Ce earths (49–74), Y earths (1–4), ThO_2 (5–12), SiO_2 (1–2) U (in traces)	(i) Ce(25), Pr(15)+ Nd (15)+Gd(20)+Yb(2)+ Er(2)+Th(10)+U(10)	9.8	0.53
	(ii) Ce(20)+Nd(15)+ Sm (25)+Eu(15)+Yb(2) +Tm(2)+U(10)	9.8	0.83
Alloys			
1. Uranium alloyed copper[1] Cu(76), U(24)	Cu(76)+U(24)	24.5	0.29
2. U(45–50), Cu(20–35), Pb(20) (used for making liners for penetrating deep into rocks)[2]	U(45)+Cu(35)+Pb(20)	44.0	0.98
3. U(52–90), Mo(5–15), Cu(2–15), Zr(1–5), Cr(0.5–5), Fe(0–5), Ni(5–2), Nb(0.5–1.5) (used for making containers for final storage of radioactive waste)[3]	U(52)+Mo(15)+ Cu(15)+Zr(5)+ Cr(4.5)+Fe(5)+ Ni(2), Nb(1.5)	50.0	1.3
4. Th(90), U(10) (used for neutron response of several fission track detectors worn on the body)[4]	Th(180)+U(20)	20.3	1.25
5. U(55), Co(27), Th(18) (used for photoemission studies on actinide glasses)[5]	U(55)+Co(27)+ Th(18)	54.6	0.68

*Mean of three readings ($\bar{x}$).

†$C.V. = SD \times 100/\bar{x}\%$.

670 nm), potassium ferrocyanide[16] ($4.65 \times 10^3 M^{-1}$ cm^{-1}, 390 nm). Moreover, this method is highly selective since commonly interfering metals including lanthanides did not interfere in this method under experimental conditions.

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