COMPLEXATION EQUILIBRIA BETWEEN URANIUM(VI) AND 2-(2'-THIAZOLYLAZO)-4,6-DIMETHYLPHENOL AND 2-(4',5'-DIMETHYL-2'-THIAZOLYLAZO)-4,6-DIMETHYLPHENOL. EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

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2-(2'-Thiazolylazo)-4,6-dimethylphenol (TADMP) and 2-(4',5'-dimethyl-2'-thiazolylazo)-4,6-dimethylphenol (DMTADMP) have been synthesized and their ionization constants determined by spectrophotometric methods and graphical and numerical calculation methods. Both reagents form UO_2R^+ and UO_2R_2 complexes with uranium (TADMP: $\log \beta_{101} = 9.18 \pm 0.02$, $\log \beta_{102} = 17.64 \pm 0.01$; DMTADMP: $\log \beta_{101} = 8.38 \pm 0.02$, $\log \beta_{102} = 18.78 \pm 0.14$) in a 40% (v/v) ethanol–water medium at $I = 0.25$ ($NaClO_4$). An extraction-spectrophotometric method for the determination of 1.35—9.45 ppm uranium based on its extraction into toluene with TADMP from a pH 6.5 buffered medium has been developed ($\varepsilon = 1.6 \cdot 10^4 \ 1 \ mol^{-1} \ cm^{-1}$ at 580 nm), and applied to its determination in sulphuric acid leaching residues.

The need for the determination of trace uranium is becoming important in the industry and environmental problems. The best known methods for the spectrophotometric determination of uranium are based on reactions with bisazo derivatives of chromotropic acid: Arsenazo I (refs[1,2]), Arsenazo III (refs[3,4]), and Chlorophosphonazo III (ref.[5]).

In the last years, various selective heterocyclic azo phenols have been synthesized and examined as reagents for uranium. Of these compounds, pyridylazophenols that have an alkylamino group in the *p*-position to the azo group in the phenol ring are the most sensitive, but most of them are sparingly soluble in water[6-10]. Recently Oshita et al.[11] synthesized and studied several N-sulphoalkyl derivatives of pyridyl-5-aminophenol. The introduction of the sulphoalkyl group made these reagents extremely soluble in water and increased their sensitivity. Besides, several thiazolylazo-phenol derivatives have been also used as reagents for uranium[12-17], but only in a few cases the equilibria involved have been studied, usually by application of graphical analysis of the absorbance–$[H^+]$ dependences.

In the present study 2-(2'-thiazolylazo)-4,6-dimethylphenol (TADMP) and 2--(4',5'-dimethyl-2'-thiazolylazo)-4,6- dimethylphenol (DMTADMP)
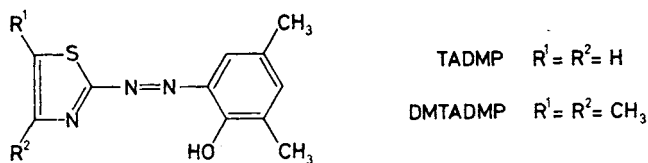
have been synthesized and their dissociation constants as well as complexation equilibria with uranium(VI) studied by spectrophotometric methods, and graphical and numerical calculation methods are used to calculate the corresponding equilibrium constants. Besides that an extraction-spectrophotometric determination method for uranium using TADMP as the reagent has been developed and applied to its determination in sulphuric acid leaching method residues.

EXPERIMENTAL

Apparatus

Beckman 25 (Fullerton, California) and Hitachi Perkin–Elmer 200 (Tokyo, Japan) recording spectrophotometers with 1 cm path length glass cells, Radiometer PHM64 digital pH meter (Copenhagen, Denmark) with glass–calomel combination electrode, Heidolph rotary shaker (Kelhein, F.R.G.), constant speed Gerber M80A centrifuge (Zürich, Switzerland) and Phaxe-2000 digestion bomb (Fairlawn, N.J., U.S.A.) were used. Calculations were performed on a Digital VAS/VMX 11/780 (V.4.0) computer (Maynard, Ma, U.S.A.).

Reagents

10^{-3}M ethanolic solutions of TADMP and DMTADMP; standard 10^{-1}M solution of uranium-(VI) perchlorate in 0·1M perchloric acid, prepared from uranium(VI) nitrate by perchloric acid treatment and standardized complexometrically; pH 5·30 (pyridine–perchloric acid) and pH 6·20 and 6·50 (hexamine–perchloric acid) buffer solutions were used as indicated; 0·1M-NaClO$_4$ solution was used to control the ionic strength to 0·25.

Analytical reagent grade chemicals and doubly distilled water were used throughout with no further purification.

Synthesis of the Reagents

The reagents were synthesized in the usual way by coupling 2-aminothiazole or 4,5-dimethyl-2--aminothiazole with 2,4-dimethylphenol. Crude products (yield 75 and 70%, resp.) were purified by column chromatography on silica gel Merck (70—230 mesh) using petroleum ether–ethyl acetate mixtures of increasing polarity as the eluents. After purification, m.p. 83 ± 1°C and 92 ± 1°C for TADMP and DMTADMP, resp.

Both reagents are soluble in methanol, ethanol, DMSO, DMF, and alkaline solutions and scarcely soluble in water.

High resolution mass spectrometry showed the parent molecular ions (M$^+$) at 233 and 261 m/z and $C_{11}H_{11}N_3OS$ and $C_{13}H_{15}N_3OS$ as the most probable compositions. NMR spectra (C^{2}HCl$_3$, TMS, 200 MHz) were as follows: TADMP: 2·22 s and 2·42 s, 6 H (4,6-CH$_3$);

6·67 d, 6·89 m, 7·14 s, and 7·54 s, 2 H (H$_3$ and H$_5$); 7·39 and 7·97 m, 2 H (H$_4$ and H$_5$, $J = 3$ Hz); 11·79 s, 1 H (—OH); DMTADMP: 2·22 s, 2·24 s, 2·26 s, and 2·68 s 12 H (4,5,5',6'-CH$_3$); 6·64 m, 6·90 s, 7·09 s, and 7·48 s 2 H (H$_3$ and H$_5$); 11·75 s, 1 H (—OH).

RESULTS AND DISCUSSION

Acid-Base Behavior of TADMP and DMTADMP

The absorption spectra of both reagents recorded in dependence of the acidity of the medium as well as the absorbance–pH curves, Fig. 1, obtained at the wavelengths of the corresponding absorption maxima, show the presence of at least three species of each reagent in 40% (v/v) ethanol–water medium at $I = 0.25$ (NaClO$_4$). The corresponding dissociation constants were evaluated by applying graphical methods of analysis of the absorbance–pH dependences[18,19], taking into account that 10^{-H_0} replaces [H$^+$] when in highly concentrated perchloric acid medium; H_0 is the Hammett function for this acid in the medium used[20,21]. Values found for the corresponding pK_{ax} together with the optical characteristics of every species are listed in Table I. The values of pK_{ax} found graphically were then used

FIG. 1

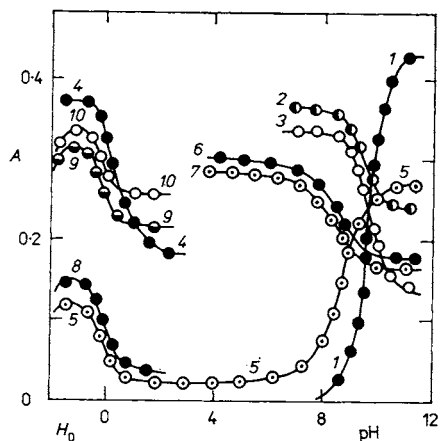Absorbances–pH dependences for DMTADMP (curves 1—5) and TADMP (curves 6—10); λ, nm: 1 560, 2 400, 3 460, 4 510, 5 550, 6 375, 7 365, 8 525, 9 410, 10 400. $c_R = 4 . 10^{-5}$ mol l^{-1}, 40% (v/v) ethanol–water, $I = 0.25$ (NaClO$_4$)

FIG. 2

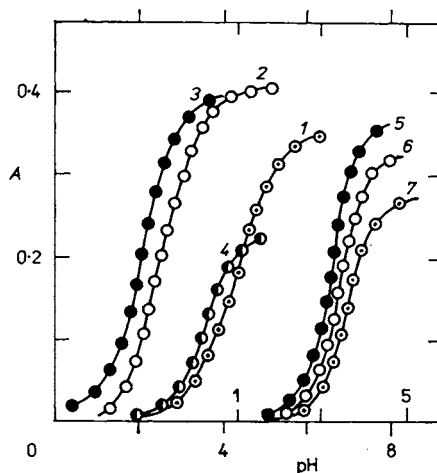Absorbance–pH dependences for U–TADMP system: 600 nm, c_U/c_R: 1 1, 2 25, 3 75 ($c_R = 4 . 10^{-5}$ mol l^{-1}), 4 1/5 ($c_R = 1 . 10^{-4}$ mol l^{-1}); U–DMTADMP system: 595 nm, c_U/c_R: 5 100, 6 50, 7 25 ($c_R = 5 . 10^{-5}$ mol l^{-1})

as starting values for further refinement using the LETAGROP-SPEFO program[22,23]. In Table I the resulting values of $\log K_{ax} \pm 3\sigma(\log K_{ax})$ as well as the molar absorptivities calculated for every species by the program are given.

On comparing the pK_{a1} values for both TADMP and DMTADMP one can see how the inductive effect of the methyl groups on the heterocycle ring may account for the change in basicity of the N-heterocyclic atom.

Complexation Equilibria Between Uranium(VI) *and* TADMP *or* DMTADMP

Uranium(VI) reacts with TADMP and DMTADMP in a wide pH range, giving greenish coloured solutions with absorption maxima at 600 and 595 nm, resp. Due to the insolubility of reagents and complexes in water the studies were carried out in a 40% (v/v) ethanol–water medium, and $I = 0.25$ (NaClO$_4$) was used.

The absorbance–pH curves for several c_U/c_R ratios at the wavelengths of the absorption maximum of each complex are shown in Fig. 2. They indicate that the complexation in both systems begins at higher acidities as that ratio increases and that the absorbances stabilize for pH $\geqq$ 4.6. The stoichiometry of the complex species, determined at pH 6.2 for the U–TADMP system and pH 5.3 for the U––DMTADMP system, as established by the continuous variations, mole ratio and slope ratio methods, show the formation of 1 : 2 U : R complexes in both systems.

TABLE I

Optical and acid-base characteristics of the reagents 2-(2′-thiazolylazo)-4,6-dimethylphenol (TADMP) and 2-(4′,5′-dimethyl-2′-thiazolylazo)-4,6-dimethylphenol (DMTADMP)

Species	λ_{max} nm	Graphical method		Numerical method	
		$\varepsilon . 10^{-4}$, 1 mol^{-1} cm^{-1}	pK_a	ε, 1 mol^{-1} cm^{-1}	pK_a
			TADMP		
R$^-$	550	1.29	8.58 $\pm$ 0.20[a]	12 500 $\pm$ 411	8.64 $\pm$ 0.05[a]
HR	550	0.89		8 700 $\pm$ 280	
H$_2$R$^+$	400	1.21	-0.29 ± 0.09[b]	8 700 $\pm$ 110	-0.07 ± 0.10[b]
			DMTADMP		
R$^-$	560	1.05	9.76 $\pm$ 0.01[a]	9 900 $\pm$ 250	9.70 $\pm$ 0.03[a]
HR	560	0.01		100 $\pm$ 75	
H$_2$R$^+$	510	0.95	0.42 $\pm$ 0.07[b]	9 600 $\pm$ 90	0.51 $\pm$ 0.03[b]

[a] pK_{a2} value; [b] pK_{a1} value.

In order to calculate the equilibrium constants the method of graphical analysis of the absorbance–pH dependences of Sommer et al.[24,25] was used, from which $\log \beta_{102} = 19\cdot6$ and $\log \beta_{102} = 19\cdot5$ were calculated for the U–TADMP and U––DMTADMP complexes, resp. However, no straight lines could be obtained when dealing with equimolar solutions and with solutions of reagent excess. That suggests the presence of at least a second complex species in both systems, probably a 1 : 1 U : R species.

Next the experimental data for both systems were analyzed by applying the LETAGROP-SPEFO program. At the beginning the program was fed, as starting values, with the values obtained for β_{102} for each system by the graphical method, and then the model was modified by introducing new species in order to ascertain what out of the proposed models could fit the experimental data with a minimum sum of squares of residuals $U = \sum_{Np} (A_{calc} - A_{exp})^2$. From the values obtained for the minimal U and the standard deviation $\sigma(A)$ it is seen, Table II, that the model including the species UO_2R_2 and UO_2R^+ fits much better than models containing only one species. Calculations for the other models assuming, that in addition to the ML and ML_2 complexes, the formation of hydroxo-complexes, mixed ligand complexes, protonated complexes and/or polynuclear complexes, did not converge. Calculated values for $\log \beta_{101}$, $\log \beta_{102}$, ε_{101}, and ε_{102} for each system together

TABLE II

Results obtained by the numerical calculation method for the different models tested. 11 A–pH curves analyzed

Species	U	$\sigma(A)$	$\log \beta$	ε_{101} $l\,mol^{-1}\,cm^{-1}$	ε_{102} $l\,mol^{-1}\,cm^{-1}$
			TADMP		
UO_2R	$0\cdot406 . 10^{-1}$	$0\cdot02$	—	—	—
UO_2R_2	$0\cdot911 . 10^{-2}$	$0\cdot009$	—	—	—
UO_2R $\left.\begin{array}{}\\\end{array}\right\}$	$0\cdot295 . 10^{-2}$	$0\cdot005$	$\left\{\begin{array}{}9\cdot04 \pm 0\cdot02^a\\17\cdot37 \pm 0\cdot13^b\end{array}\right.$	$10\,059 \pm 27(600\,nm)$	—
UO_2R_2				—	$13\,868 \pm 262(600\,nm)$
			DMTADMP		
UO_2R	$0\cdot105 . 10^{-1}$	$0\cdot009$	—	—	—
UO_2R_2	$0\cdot330 . 10^{-1}$	$0\cdot01$	—	—	—
UO_2R $\left.\begin{array}{}\\\end{array}\right\}$	$0\cdot204 . 10^{-2}$	$0\cdot04$	$\left\{\begin{array}{}8\cdot75 \pm 0\cdot12^a\\19\cdot56 \pm 0\cdot02^b\end{array}\right.$	$7\,490 \pm 181(595\,nm)$	—
UO_2R_2				—	$13\,197 \pm 105(595\,nm)$

^{a} $\log \beta_{101}$ value; ^{b} $\log \beta_{102}$ value.

with their standard deviations are included in Table II. No systematic errors are present and the model containing the UO_2R^+ and UO_2R_2 species explains experimental data for both systems within a $\pm 0.1\%$ error.

The HALTAFALL[26] program was used to establish, on the basis of the equilibrium constants obtained by LETAGROP-SPEFO, in what experimental condition the UO_2R^+ complex would be the main species in the system. Results for the U–TADMP system showed that the UO_2R^+ species will account for more than 99% of the uranium when $c_U/c_R = 100$ at pH 4·2. Fig. 3 shows the spectra recorded at pH 6·0 from solutions where $c_U/c_R = 100$, 1, and 1/5, for which UO_2R^+ is 99%, 53·5%, and 0·01%, resp. No change in the wavelength of the absorption maximum can be observed and it might be concluded that species UO_2R^+ and UO_2R_2 show the same absorption maximum at ≈ 600 nm in aqueous solution, even though the respective molar absorptivities are quite different, and more in accordance with results from LETAGROP-SPEFO.

In 40% (v/v) ethanol–water medium at pH 5·3 (pyridine–HClO$_4$ buffer solution) the systems conform to Beer's law in the ranges $1·1 - 5·6$ ppm U (TADMP) and $1·2 - 4·5$ ppm U (DMTADMP) with molar absorptivities $\varepsilon_{600} = \varepsilon_{595} = 1·5$. $. 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ and optimum ranges for the determination of $2·16 - 5·4$ and $1·94 - 4·5$ ppm U, resp., as determined by Ringbom's method[27] with 1·0 and 0·9% relative error. However, many ions that interfere make the methods unsuitable for practical purposes.

Extraction of the U–TADMP *Complexes into Toluene*

In order to enhance the selectivity of the determination of uranium using TADMP as the reagent, the combination of complex formation and extraction into organic solvents from a weakly acidic medium seemed to be advantageous. Hence a direct
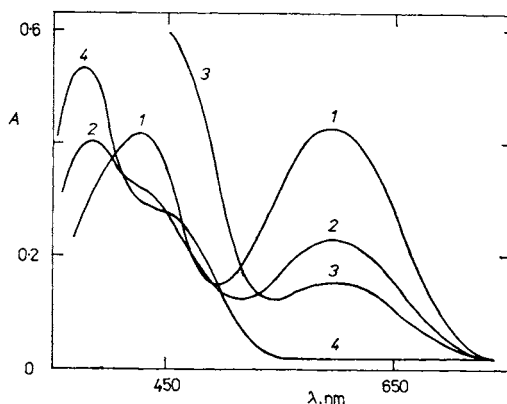
FIG. 3

Absorption spectra at pH 6·0 for the system U–TADMP at several c_U/c_R ratios: *1* 100 ($c_R = 4 . 10^{-5}$ mol l^{-1}), *2* 1 ($c_R = 4 .$. 10^{-5} mol l^{-1}), *3* 5/30 ($c_R = 1·2 . 10^{-4}$ mol . . l^{-1}), *4* reagent alone

extraction-spectrophotometric method was developed for the determination of uranium.

Previous tests showed that the complexes as well as the reagent could be extracted into chloroform, benzene, toluene, and petroleum ether. Toluene was chosen as the absorbances were higher and stable for more than 24 h and the extraction was complete after 10 min of mechanical shaking.

TADMP is extracted into toluene in a wide pH range from 0 to 9 and the extracts show an absorption maximum at 375 nm indicating that the neutral HR species of the reagent is responsible for it, and from the plot of log D vs pH (Fig. 4) log $K_D = 1·58$ could be evaluated and $pK_{a2} = 8·55$ was calculated in a good agreement with the spectrophotometric result above mentioned.

The U–TADMP complexes are extracted into toluene from solutions of reagent excess in the range $4·5 \leq pH \leq 6·5$ as can be seen in Fig. 4, and this extract shows an absorption maximum at 580 nm (Fig. 5). When the extraction is performed from an aqueous phase with uranium excess the absorption maximum is at 600 nm and the absorbances are very unstable. However, stability increases when the extraction is carried out in the presence of tributylphosphate.

In any experimental conditions the complexes must be formed in the auqoeus phase and then extracted into toluene. If the extraction is performed using a solution of TADMP in toluene as the extractant, the kinetics of the process becomes so slow that the method would not be of practical interest.
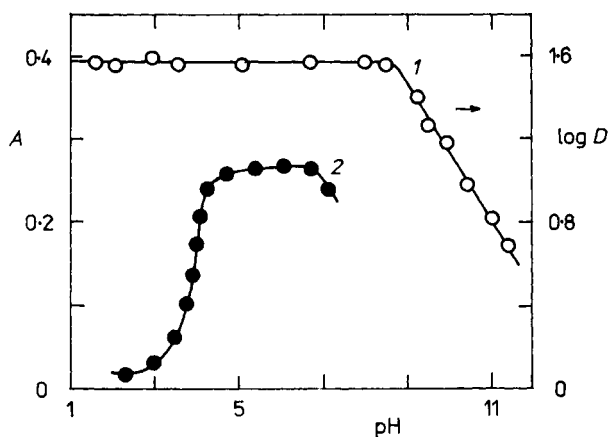

FIG. 4

Plots of log D vs pH for TADMP (curve 1) and absorbance–pH curves for the extraction of the U–TADMP system into toluene (curve 2), $c_R = 4 . 10^{-5}$ mol l^{-1}, $c_U = 2 . 10^{-5}$ mol l^{-1}, 10% (v/v) ethanol–water, $I = 0·25$ (NaClO$_4$)

The stoichiometry of the extracted species as established by the continuous varia-
tions and mole ratio methods is shown to be 1 : 1 and 1 : 2 (U : R). The later composi-
tion can be suggested when extraction takes place from solutions with the reagent
in excess and HALTAFALL shows that the UO_2R_2 species accounts for more than
99% of the uranium present in the aqueous phase when $c_U/c_R \leqq 1/6$.

Extraction-Spectrophotometric Determination of Uranium with TADMP

Using an aqueous phase buffered to pH 6·5 (hexamine–$HClO_4$) with $c_{TADMP} =$
$= 2 . 10^{-5} \text{ mol } l^{-1}$, $I = 0.25$ ($NaClO_4$) and 15% (v/v) ethanol–water medium, the
extracted complex into toluene $(V_{org} = V_{aq})$ conforms to Beer's law between 1·35 and
9·45 ppm uranium with $\varepsilon = 1.6 . 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 580 nm, and 2·70 − 9·40 ppm
uranium as optimum concentration range for the determination according to Ring-
bom's method. The statistical study carried out on eleven samples, each containing
4·76 ppm U(VI), gave 4·79 ppm as mean value, 0·06 as standard deviation and
$\pm 0.6\%$ as relative error.

A study of the effect of several ions on the determination of 4·76 ppm U was
carried out by first applying the recommended method to solutions containing
a 1 000-fold m/m excess of the interference to uranium and, if interference ocurred,
reducing this ratio until interference ceased. Higher ratios were not tested. The cri-
terion for interference was a variation in the concentration found for uranium of
more than $\pm 2\%$ from the value taken. The results are shown in Table III. In order
to mask some of the interfering cations the use of a Ca-EDTA solution[28] was tested.
Ca-EDTA did not interfere if present in amounts up to 50-fold the actual concentra-
tion of U(VI). As can be seen from Table III, in the presence of this masking agent
the tolerance for Pb(II), Cu(II), Fe(II, III), Co(II), and Ni(II) increaes up to a $c_i/c_U =$
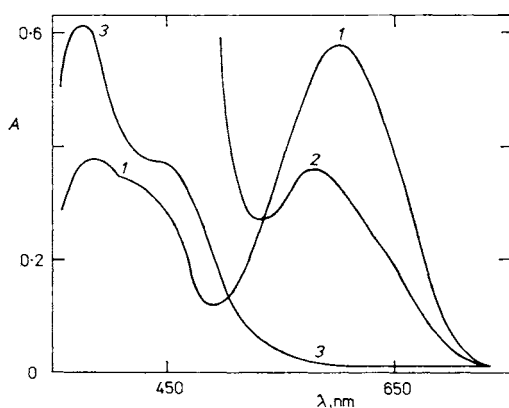$= 5$ ratio.

FIG. 5

Absorption spectra of the toluene extract
in the system U–TADMP, obtained from
a pH 6·5 aqueous phase with different con-
centrations c_R and c_U, resp. (in mol l^{-1}): *1*
$4 . 10^{-5}$, $1 . 10^{-3}$; *2* $1.5 . 10^{-4}$, $2 . 10^{-5}$;
3 $4 . 10^{-5}$, 0

TABLE III

Ionic interferences in the extraction-spectrophotometric method for uranium using TADMP

Interferent	[Interferent]/[U]^a	Relative error, %
NO_3^-, SO_4^{2-}	500^b	0
Ca, Ce(IV)	100	0
Mg, Ba	100	−2·0
Sr, Li, Na, K, Tl(I)	100	−0·7
Cl^-, Br^-, I^-	100	+1·1
F^-	100	−1·5
Ca-EDTA	50	+0·6
EDTA	50	−1·2
W(VI), Zn	10	−2·0
Mo(VI), Cd, HPO_4^{2-}	10	+2·0
Cr(III)	5	−0·7
Zr(IV), Mn(II), Pb^c, Cu^c	5	+1·1
Sn(II), Al^c	5	−2·0
Th(IV), Fe(II, III)^c	5	+0·2
V(V), La(III), Co^c, Ni^c	5	+2·0
Ga(III), Bi(III)	1	−2·0
V(V), Fe(II, III), Al, Pb, Cu, Co, Ni	1	>10
Acetate, $S_2O_3^{2-}$, $C_2O_4^{2-}$	1	>10

^{a} 4·76 ppm U; ^{b} maximum amount tested; ^{c} in the presence of Ca-EDTA.

TABLE IV

Extraction-spectrophotometric determination of uranium in sulphuric acid leaching residues

U_3O_8, %	
Present^a	Found^b (range)
4·76 . 10^{-4} ^{c}	4·80(4·77−4·82) . 10^{-4}
0·004	undetected
1·00	0·98(0·97−0·99)
2·00	1·99(1·97−2·01)

^{a} Fluorimetric; ^{b} mean of three determinations; ^{c} synthetic sample: 4·76 ppm U, 20 ppm Fe(II), 14 ppm Al, 9·5 ppm Cr(III), 5 ppm Cu, 20% SiO_2.

The sensitivity of TADMP reagent for uranium is one half of PAR (ref.[29]) or TAR (ref.[14]), one third of Br-PADAP (ref.[6]) and of the same order as TAMH and TAMR (ref.[16]). However, there is less interference by other ions in the extraction-spectrophotometric determination of uranium using TADMP.

The developed extraction-spectrophotometric method for uranium using TADMP as the reagent was applied to a synthetic sample and to a residue $(U_3O_8 \leq 0.004\%)$ from the sulphuric acid leaching process of low-grade uranium ores, spiked by known amounts of U_3O_8 (Merck, nuclear grade). Results are shown in Table IV.

Procedure for the Extraction-Spectrophotometric Determination of Uranium with TADMP

To the sample solution, containing 13·5 to 94·5 µg of uranium, in a screw-cap centrifuge tube, add 1·5 ml of 10^{-3}M ethanolic solution of TADMP, 1 ml of 1M-$NaClO_4$, 2·5 ml of pH 6·50 hexamine–$HClO_4$ buffer solution, 1 ml of 10^{-3}M Ca-EDTA solution and make up to 10 ml with distilled water. Then add 10 ml of toluene and shake vigorously for 10 min, centrifuge for 10 min and measure the absorbance of the organic layer at 580 nm against a reagent blank prepared in a similar way.

Determination of Uranium in Sulphuric Acid Leaching Residues

Weigh accurately 0·5 g of the sample and wet it well in the digestion bomb with 1 ml aqua regia, then add 10 ml of hydrofluoric acid, close the digestion bomb and heat at 150°C for 150 min. Once the digestion bomb is cold and opened, 50 ml of saturated boric acid solution are added, heating if necessary for complete dissolution of any precipitate present. Transfer to a calibrated flask and make up to 100 ml with distilled water. Aliquots of this solution are analyzed for uranium according to the above-mentioned procedure.

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