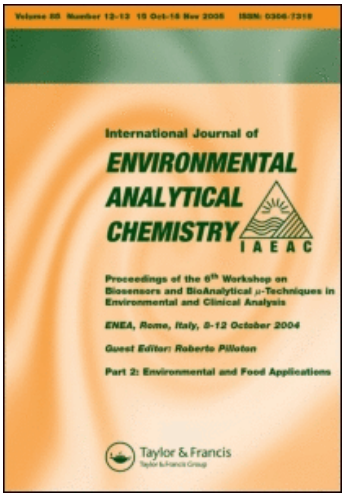

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Atomic Absorption Spectrometric and Spectrophotometric Trace Analysis of Uranium in Environmental Samples with N-p-MEthoxyphenyl-2-Furylacrylohydroxamic acid and 4-(2-Pyridylazo) Resorcinol

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To cite this Article Abbasi, S. A.(1989) 'Atomic Absorption Spectrometric and Spectrophotometric Trace Analysis of Uranium in Environmental Samples with N-p-MEthoxyphenyl-2-Furylacrylohydroxamic acid and 4-(2-Pyridylazo) Resorcinol', International Journal of Environmental Analytical Chemistry, 36: 3, 163 — 172
To link to this Article: DOI: 10.1080/03067318908026869
URL: http://dx.doi.org/10.1080/03067318908026869

Intern. J. Environ. Anal. Chem., Vol. 36, pp. 163–172
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ATOMIC ABSORPTION SPECTROMETRIC AND SPECTROPHOTOMETRIC TRACE ANALYSIS OF URANIUM IN ENVIRONMENTAL SAMPLES WITH N-p-METHOXYPHENYL-2-FURYLACRYLOHYDROXAMIC ACID AND 4-(2-PYRIDYLAZO) RESORCINOL

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Methods are presented for the determination of uranium in presence of various anions and cations which are usually associated with it in rocks, waters, minerals, nuclear fission products and biological materials. The methods are based on the solvent extraction of uranium(VI) as its complex with N-p-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA) in chloroform, or methyl isobutyl ketone (MIBK) at pH 4.5–5.1. The uranium in the orange-yellow chloroform extract is either directly determined spectrophotometrically or back-extracted into 0.01 M HCl solution and determined as its intensely red coloured complex ($\varepsilon = 3.94 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ at 530 nm) with 4-(2-Pyridylazo) resorcinol (PAR). The metal in the MIBK extract is determined atomic absorption spectrometrically by the aspiration of the extract in nitrous oxide-acetylene flame and measuring the absorbance at 358.5 nm resonance line. Both the methods are highly sensitive and selective, and were applied to the determination of uranium in waters, plants and animal tissues.

KEY WORDS: Uranium, atomic absorption spectrometry (AAS), spectrophotometry, trace analysis, environmental samples.

INTRODUCTION

Uranium in the Environment

Uranium occurs at the average of $2\,mg\,kg^{-1}$ in the earth's crust. The uranium levels in the plants and animals are very low;[1] typical examples are: $0.01–0.18\,mg\,kg^{-1}$ (wet weight) in clam *Mactra sachalinensis*, and $0.04–0.42\,mg\,kg^{-1}$ (wet weight) in long-tailed ducks *Glanquia hyemalis* L. However, in some animals which are probably exposed to higher than natural uranium levels, the metal may be present in abnormal concentrations ($1.6–8\,mg\,kg^{-1}$, wet weight), as typified by reports on aquatic bryophytes[2] and the moss *Scorpidium scorpiodes*.[3] In humans, about 25% of the ingested uranium gets accumulated in

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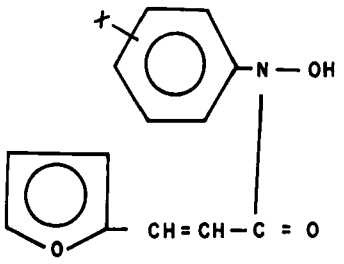

X = meta or para H, CH_3, OCH_3, Cl, Br, I, NO_2

Figure 1 N-phenyl-2-furylacrylohydroxamic acid ($X = H$) and its analogues explored in the present study.

the bone, about 60% is excreted in the urine and the remainder is either bound to plasma protein or solubilised, with the potential of causing acute renal damage.[4] The metal has chemical toxicity in addition to the hazard it presents due to its radioactivity.

THE PRESENT METHODS

N-phenyl benzohydroxamic acid (PBHA) is a versatile complexing agent and has been extensively utilised for the separation and determination of a great number of metal ions.[5] The first detailed examination of PBHA as a reagent for uranium was carried out by Agrawal.[6] It was found that in the extraction of U(VI) several cations interfered and the colour of the extracted U(VI)-PBHA complex was suitable only for the determination of milligram quantities of uranium, the molar absorptivity at λ_{max} (510 nm) being as low as 230. The selectivity was also low and no attempt was made to counter the interference of various common and less-common metals which are associated with uranium in rocks, minerals and fission products. Subsequently N-phenyl-2-naphthohydroxamic acid (PNHA) was prepared and tried as a reagent for U(VI)[7] but it proved only a marginal improvement on PBHA in terms of both sensitivity and selectivity. We had earlier introduced N-o-methoxynaphthoyl-N-p-tolylhydroxylamine (MNTHA) for extractive separation and spectrophotometric determination of uranium(VI).[8] This method was significantly more sensitive and selective than the previous methods but the sensitivity (0.01 mg l^{-1}) was still not good enough for the determination of the usually low levels of uranium in the environmental samples. We have recently synthesised heterocyclic analogues of PBHA (Figure 1) which have proved significantly more sensitive and selective than PBHA and its other analogues reported previously. We have utilised the new series of reagents in the trace analysis of palladium,[9] vanadium,[10] titanium,[11] molybdenum[12] and germanium.[13] When tried for the selective extraction of uranium the new reagents proved equally effective, as detailed in this paper. Besides hydroxamic acids, the commonly used methods of solvent extraction-spectrometric determination of uranium(VI) are:

tributyl phosphate extraction and determination with dibenzoyl methane ($\varepsilon = 2.1 \times 10^3$ l mole^{-1} cm^{-1} at λ_{max} 415 nm);[14, 15] chloroform extraction with 8-hydroxyquinoline and determination at 390 nm or 430 nm ($\varepsilon = 4 \times 10^3$ l mole^{-1} cm^{-1});[15] ethyl methyl ketone extraction with sodium diethyldithiocarbamate determination at 420 nm ($\varepsilon = 3.8 \times 10^3$ l mole^{-1} cm^{-1});[16] and benzene extraction with thenoyltrifluoroacetone and determination at 430 nm ($\varepsilon = 1.95 \times 10^3$ l mole^{-1} cm^{-1}).[15, 17] The sensitivities of these methods are very low. Greater sensitivity is possible in the method involving extraction with 1-(2-pyridylazo)-2-naphthol (PAN) in o-dichlorobenzene ($\varepsilon = 2.3 \times 10^4$ l mole^{-1} cm^{-1} at 570 nm)[18] but the selectivity is low; EDTA, cyanide, and fluoride are to be used as masking agents but large amounts of EDTA compete with PAN for complexation. The lack of suitable chelation-extraction system for uranium(VI) has also adversely affected the atomic absorption spectrophotometric determination of the metal; the atomisation of the metal from aqueous media is very poor and the detection limit of the most sensitive determination in a fuel-rich nitrous oxide-acetylene flame, at the 358.5 nm resonance line,[19] is only 120 mg l^{-1}. With electrothermal atomisation techniques this limit is improved[20, 21] to 30 mg l^{-1}. Considering that atomisation is greatly facilitated as well as matrix interferences are considerably reduced when metals are aspirated or electrothermally atomised as chelates after prior extraction from aqueous matrices to suitable organic solvents,[19, 21] the uranium-MFHA extracts in chloroform and other solvents were explored for AAS determination. It was observed that significant improvement in the sensitivity of uranium determination by AAS is achieved when the metal is aspirated as its chelate with MFHA in MIBK.

EXPERIMENTAL

Reagents and Apparatus

All chemicals were of guaranteed reagent or equivalent grades unless otherwise specified. Water was deionised and double distilled.

Hydroxamic acids were synthesised by coupling the para or meta substituted phenylhydroxylamines with the oxychloride of furan-2-acrylic acid by the general method of Tandon and Bhattacharyya.[22] The acids were repeatedly crystallised from benzene to constant, sharp, melting points and were characterised by micro analysis, IR and UV spectroscopy as detailed elsewhere.[23] Solutions of hydroxamic acids (0.01 M) were made in chloroform (for spectrophotometric studies) and in MIBK (for AAS studies). PAR was employed as its 2 g l^{-1} aqueous solution. Uranium(VI) solution was prepared by dissolving 0.5 g uranyl nitrate in 1000 ml water and standardising volumetrically.[14]

The pH adjustments were done with Radiometer model PHM 29 and Industrial Electronics Corporation model 092 pH meters after precalibration with standard buffers of pH 4 and 9. The spectrophotometric measurements were carried out on Perkin–Elmer model 402 and Hitachi model 220 spectrophotometers using matched quartz cells. For atomic absorption spectrometric studies Techtron model

AA-3 and Instrumentation Laboratory model IL 951 instruments equipped with hallow cathode lamps for uranium (358.5 nm line) were used.

Procedure for Extraction and Determination

a) For spectrophotometric analysis: A portion (15–20 ml) of the sample containing 2–50 μg of uranium(VI) was adjusted to pH 4.5–5.1 with the help of dilute NaOH or HNO_3 and transferred to a 50 ml separatory funnel. To it 5 ml of MFHA solution in chloroform was added and the phases equilibrated for 5 min. After phase separation the chloroform layer was transferred to a test tube containing anhydrous sodium sulphate. The aqueous layer was retained in the separatory funnel and re-extracted with a fresh 5 ml portion of MFHA for 3 min. The extract, after phase separation, was combined with the first extract and transferred to another separatory funnel. To ensure that no uranium gets trapped in the sodium sulphate matrix, the latter was washed with a 2 ml portion of MFHA solution and the washing combined with the previous extracts. Next 5 ml of 0.01 M HCl was added to the extracts and the mixture equilibrated for 5 minutes to back-extract uranium in the aqueous phase. After phase separation and collection of aqueous layer in a 25 ml calibrated flask, the process was repeated with another 5 ml portion of 0.01 M HCl to ensure complete recovery of uranium. Finally 5 ml of 0.018 M NaOH (to neutralise HCl), 5 ml of triethanolamine buffer (pH 8) and 2 ml of aqueous PAR solution were added to the 25 ml calibrated flask, achieving a final pH of 7.9–8.1. The contents were mixed and diluted to the mark with water. The absorbence was measured at 530 nm against a blank treated in the same manner as the sample solution but omitting uranium.

b) For atomic absorption spectrometric analysis: For AAS analysis, uranium(VI) was extracted with 4 ml of 0.01 M MFHA solution in MIBK for 5 minutes and the extract was transferred to a test tube containing anhydrous sodium sulphate. The extraction was repeated with another 3 ml portion of reagent solution for 3 minutes. The two extracts were combined and transferred to a 10 ml calibrated flask. The sodium sulphate was washed with a 2 ml portion of the reagent solution and the washing combined with the two previous extracts in the calibrated flask. The contents were diluted to 10 ml with MFHA-MIBK solution and aspirated into nitrous oxide-acetylene flame for AAS determination at 358.5 nm line using a uranium hallow cathode lamp. The light beam was 10 mm above the burner head and the flow rates of nitrous oxide and acetylene were set at 3.5 l min^{-1} and 4.5 l min^{-1} respectively. The MFHA-MIBK reagent solution was used as blank.

RESULTS AND DISCUSSION

Choice of Hydroxamic Acid

N-Phenyl-2-furylacrylohydroxamic acid and its ten analogues (Figure 1) were

Table 1 Spectral characteristics of the complexes of uranium with pyridylazo reagents in the aqueous phase

Pyridylazo reagent	*Wavelength of maximum absorbance, λ_{max}, nm*	*Molar absorptivity at λ_{max} $1\,mol^{-1}\,cm^{-1}$*
1-(2-pyridylazo)-2-naphthol [PAN]	–[a]	–[a]
2-(2-pyridylazo)-1-naphthol [α-PAN]	–[a]	–[a]
4-sulfo-α-PAN [4-SPAN]	540	2.7×10^4
5-sulfo-α-PAN [5-SPAN]	545	2.9×10^4
6-sulfo-α-PAN [6-SPAN]	545	3.0×10^4
2-(2-pyridylazo)-p-cresol [PAC]	–[a]	–[a]
5-(dimethylamino)-2-(2-pyridylazo)-phenol [DEPAP]	–[a]	–[a]
N,N-dimethyl-p-(2-pyridylazo) aniline [DMPAA]	–[a]	–[a]
5-(ethylamino)-2-(2-pyridylazo)-p-cresol [EAPAC]	–[a]	–[a]
PAR	530	3.95×10^4

[a]Formation of turbidity.

explored for the liquid–liquid extraction of uranium and subsequent determination with PAR. It was found that the sensitivity and selectivity of the uranium determination was maximum when MFHA was employed; the time required for extraction of uranium into organic phase and back-extraction into the aqueous phase was also the least when MFHA was used.

Choice of PAR

Several pyridylazo reagents besides PAR (Table 1) were explored for developing colour with uranium in the MFHA-chloroform extract or after stripping the metal from the organic phase. When added directly to the MFHA-chloroform phase, the pyridylazo reagents failed to replace MFHA in the uranium-MFHA complex or form ternary complexes. In the aqueous phase only PAR, 4-sulfo-α-PAN, 5-sulfo-α-PAN and 6-sulfo-α-PAN formed soluble complexes with uranium. Of these the sensitivity of the uranium-PAR complex was the highest.

Uranium could be directly determined with PAR without MFHA extraction but such determination was not selective; a large number of anions and cations interfered and the metal could not be analysed in environmental samples. Extractive separation with MFHA followed by spectrophotometric determination with PAR enabled optimum sensitivity and selectivity. MFHA extraction in MIBK also enabled significant enhancement in the sensitivity and selectivity of AAS determination.

Choice of Extracting Solvents

Chloroform, carbon tetrachloride, benzene and MIBK were studied as extracting solvents. For spectrophotometric methods chloroform was found to be the

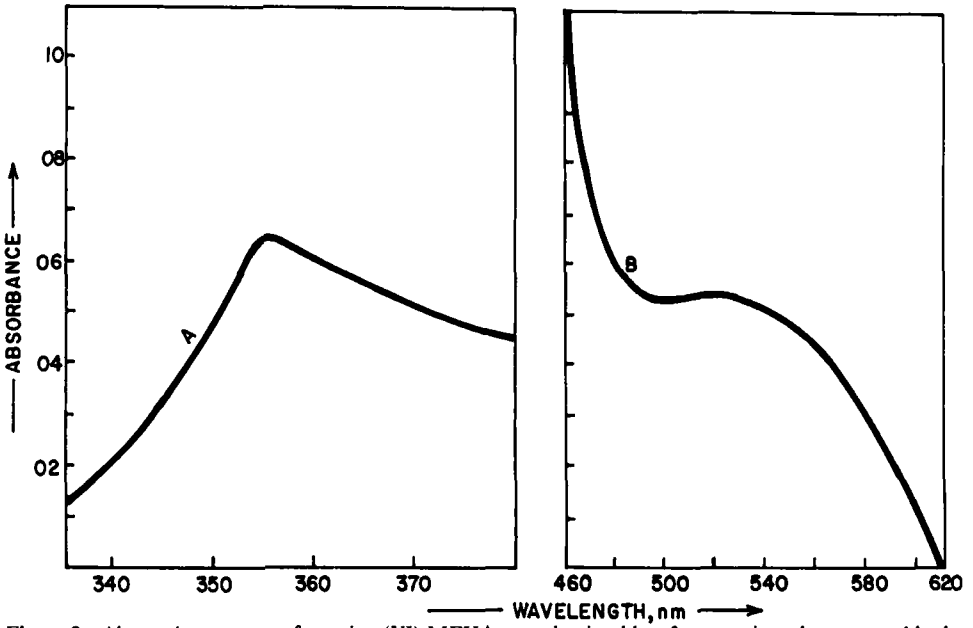

Figure 2 Absorption spectra of uranium(VI)-MFHA complex in chloroform against the reagent blank, (*a*) 0.325×10^{-3} M U(VI); (*b*) 2×10^{-3} M U(VI).

preferable solvent because it provided quantitative back-extraction and clean-cut phase separation within the shortest time. The sensitivity of the MFHA-uranium colour was also maximum in chloroform compared to other three solvents. However MIBK was preferred for AAS analysis because MIBK extracts gave the highest absorbance per unit concentration of uranium(VI) than other solvents. Furthermore, chloroform produced pungent gases in the flame and was potentially hazardous to the analyst. The superiority of MIBK over chloroform for methods based on flame AAS has been noticed by us earlier[11,13] and has also been reported by others.[14,24]

Optical Properties, Calibration Curves and Sensitivity

a) Spectrophotometric analysis: The absorption spectra of uranium extract of MFHA in chloroform against reagent (MFHA solution in chloroform) blank exhibits a sharp peak at 355 nm and a broad peak at 515–520 nm (Figure 2). Beer's law is obeyed in the range 1.5–9 mg l^{-1} of U(VI) at 515–520 nm; the molar absorptivities being 2×10^3 at 355 nm and 285 at 515–520 nm. Thus uranium, if present in concentrations less than 9 mg l^{-1} can be determined using the 355 nm peak while miligramme concentrations of uranium can be determined at 515–520 nm. On back-extraction into aqueous phase and reacting with PAR, uranium(VI) forms a red coloured complex with an absorption maximum at 530 nm. The complex obeyed Beer's law in the range 0–7 mg l^{-1} of uranium(VI), the molar absorptivity of the complex was 3.95×10^4 l mol^{-1} cm^{-1}.

The sensitivities of the uranium determination directly with MFHA at 355 nm

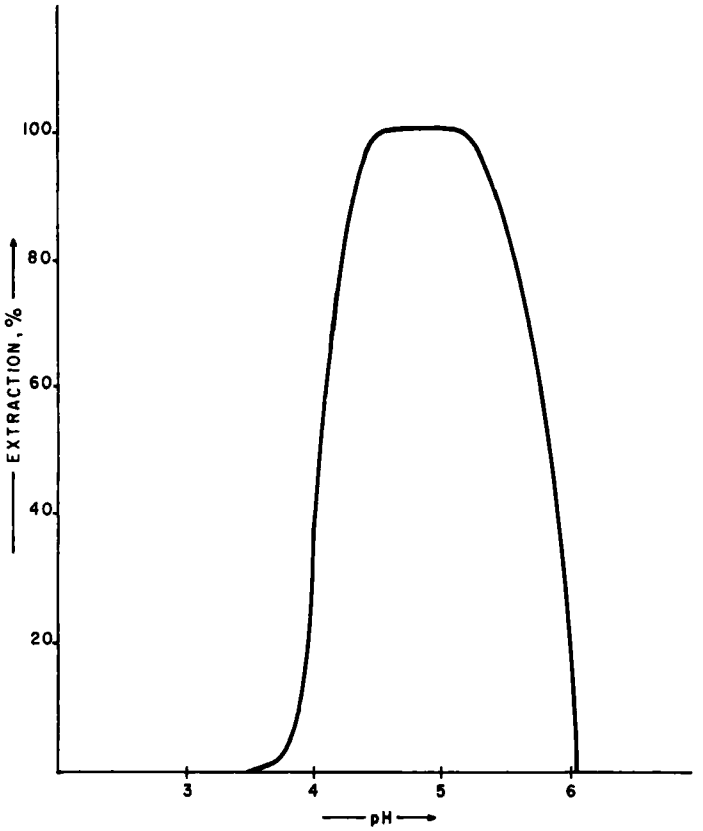

Figure 3 Extraction of uranium—MFHA chelate into chloroform/MIBK as a function of pH.

and 515–520 nm, as per Sandell's definition,[25] were 0.12 mg l^{-1} and 1.0 mg l^{-1} respectively while the sensitivity of the method when PAR was used for colour development after back-extraction of uranium from MFHA-chloroform was 0.0062 mg l^{-1} of uranium. The direct determination lacked sensitivity and was not adequate for determining uranium at trace levels.

b) Atomic absorption spectrometric analysis: The concentration-absorption curve was linear for 0.1–10 mg l^{-1} of uranium(VI) at the 358.5 nm line. The sensitivity for 1% absorption was 0.08 mg l^{-1}. The sensitivity could be enhanced 15-fold, to 0.005 mg l^{-1}, through enrichment by solvent extraction.

Optimisation of Conditions for the Extraction

Effect of pH: With chloroform as well as MIBK, the extraction commenced at pH ~3.9 and became quantitative in the pH range 4.5–5.1. Above pH 5.1 the percentage extraction declined rapidly (Figure 3).

Effect of reagent concentration and the time of equilibration: MFHA solutions 0.01 M in chloroform or MIBK enabled quantitative extraction of uranium(VI)

within 5+3 minutes of equilibration. Higher concentrations of MFHA did not expedite the extraction while the lower concentrations necessitated significantly longer equilibration times. Likewise for back extraction 5+5 minutes of equilibration with 0.01 M HCl was optimal.

Enrichment Studies A fixed amount of uranium (50 μg) was extracted from 25–500 ml solutions and determined spectrophotometrically by the present method. It was found that a change in ratio of volumes of aqueous to MFHA-chloroform phase from 1–15 does not adversely affect the uranium recovery within 5+3 minutes. The extraction system thus has the potential of enriching the sample upto 15 times, thereby enhancing the effective sensitivity of the method 15-fold.

Similar results were achieved with MFHA-MIBK extraction and AAS determination.

Effect of Diverse Ions To study the effect of foreign ions on the extractive determination of uranium and to find the concentration limits of the ions that are "tolerated" without adversely affecting the recovery of U(VI), different amounts of foreign ions were added to 25 ml aliquots of U(VI) solution containing 50 μg of uranium. The tolerance limit was set at the amount required to cause $\pm 2\%$ error in the uranium recovery. It was observed that the presence of Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(II), As(III), Ga(III), Ge(IV), Ni(II) and Co(II), in 100-fold the amount of uranium has no influence. Mg(II), Pb(II), Mn(II), La(III), perchlorate, nitrate, sulphate, bromide, iodide and alkali metal ions are tolerated in the ratio 1:500 or more. There was no interference from EDTA or chloride.

Determination of U(VI) in Presence of Bismuth, Thorium and Cerium (III)

To a solution of uranium containing bismuth, thorium or cerium(III) a composite solution containing 10 ml of 0.25 M EDTA and 5 ml of 0.5 M magnesium chloride was added and the extraction of uranium was carried out for spectrophotometry or AAS as described before. This method is efficient for masking bismuth, thorium and cerium(III) in 1000:1 concentration ratios with uranium.

Determination of Uranium in Presence of Titanium, Zirconium, Molybdenum, Iron, Tungsten and Vanadium

Tungsten, vanadium, zirconium, molybdenum and titanium were removed from solutions containing uranium by prior extraction with 0.1 M MFHA in chloroform or MIBK from solutions made, respectively, 20 N, 4 N, 2.5 N, 1 N or 0.15 N in HCl.

Iron (dipositive or tripositive) was removed by prior extraction with 0.1 M MFHA in MIBK at pH 1.5–5.2.

Table 2 Determination of uranium(VI) in environmental samples

Sample	*Uranium added*	*Uranium found*			
		Spectrophotometry (MFHA–PAR)		*AAS*	
		Average of eight determinations	*Standard deviation*	*Average of eight determinations*	*Standard deviation*
Seeds of black gram (*Cicer acretinium*)	nil	$0.013\,mg\,kg^{-1}$	0.004	$0.016\,mg\,kg^{-1}$	0.011
	$1.000\,mg\,kg^{-1}$	$1.015\,mg\,kg^{-1}$	0.011	$1.018\,mg\,kg^{-1}$	0.013
Fodder grass (*Melilotus indica*)	nil	$0.007\,mg\,kg^{-1}$	0.006	$0.009\,mg\,kg^{-1}$	0.007
	$1.000\,mg\,kg^{-1}$	$1.010\,mg\,kg^{-1}$	0.012	$1.011\,mg\,kg^{-1}$	0.011
Liver of squirrel (*Funambulus sp*)	nil	$0.277\,mg\,kg^{-1}$	0.006	$0.031\,mg\,kg^{-1}$	0.012
	$1.000\,mg\,kg^{-1}$	$1.025\,mg\,kg^{-1}$	0.009	$1.028\,mg\,kg^{-1}$	0.013
Ground water	nil	nil[a]	–	nil[a]	–
	$1.000\,mg\,l^{-1}$	$0.994\,mg\,l^{-1}$	0.010	$0.989\,mg\,l^{-1}$	0.014
	$2.000\,mg\,l^{-1}$	$1.997\,mg\,l^{-1}$	0.013	$1.992\,mg\,l^{-1}$	0.112
Lake water	nil	nil[a]	–	nil[a]	–
	$0.500\,mg\,l^{-1}$	$0.497\,mg\,l^{-1}$	0.008	$0.488\,mg\,l^{-1}$	0.009

[a]Below the detection limits of the methods.

Composition of the U(VI)-MFHA Complex

Job's method of continuous variation and the molar ratio method[14,16] were employed to study the composition of the U(VI)-MFHA complex in chloroform/MIBK. The study revealed that U(VI) and MFHA are combined in a molar ratio of 1:2 in both the solvents. Potentiometric studies on analogous U(VI)-nicotinohydroxamic acid (NHA) system in aqueous media had revealed that U(VI) is chelated to NHA as a 1:2 complex at pH 3.9.

Likewise, the studies on uranium-PAR system revealed that the colour system involves a 1:1 uranium-PAR chelate.

Determination of Uranium in Animal Tissues, Plant Tissues and Natural Waters

The tissue and water samples were processed as described earlier.[11–13] Replicate analysis were performed by the spectrophotometric and AAS methods. The results are summarised in Table 2. To ensure that the matrices are not influencing the analysis, uranium was determined with and without standard addition. The results reflect the reliability of both the methods.

Acknowledgements

Author is grateful to IIT Bombay and CWRDM Kozhikode for facilities; to Mr. P. P. Venkitachalam of M/s Techno Instruments for arranging the author to do AAS analysis; and to Ms. B. Kanchana and Tasneem Abbasi for secretarial assistance.

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