

**SPECTROPHOTOMETRIC DETERMINATION OF URANIUM
IN NATURAL WATERS AFTER PRECONCENTRATION
ON TBP-PLASTICIZED
DIBENZOYLMETHANE-LOADED POLYURETHANE FOAMS**

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A method is presented for the spectrophotometric determination of uranium in natural waters after a preconcentration step involving percolation of a suitable aliquot of the water sample whose pH is adjusted to 6.0–6.5 through a TBP-plasticized dibenzoylmethane-loaded polyurethane foam bed. Uranium on the foam is eluted with 0.6M HCl solution and then determined spectrophotometrically using arsenazo III as a chromogenic reagent.

Uranium is a relatively mobile element in many surface or near surface environments and hence geochemical exploration methods can often be based on the measurement of trace quantities of the metal in waters.^{1,2} In the sea, uranium occurs in a remarkably uniform distribution at a concentration of only 3.3 mg/m³,^{3–5} but the average content of uranium in surface or ground water is below 1 µg/l.⁶

The most acceptable method for determining trace amounts of uranium is based on measuring the fluorescence of the uranyl ion in alkali metal fluoride glass beads.⁷ 0.01–1 µg uranium should be present, but 0.001 µg may be measured.⁸ Obviously, preconcentration is mandatory when the metal ion is present at very low concentration as it is the case with surface and ground waters. Also, because the fluorometric procedure involves evaporation of the sample in a fluorometric tray, fluorometry cannot be used for the determination of uranium in sea water or in water containing a high salt content without preliminary separation of uranium. This is because large residues from water cannot be dissolved in the usual quantities of flux.⁶ Preliminary separation is also essential for a precise determination of uranium by fluorometry due to the interference of a number of metal ions with the method.⁹ Furthermore, the accuracy of fluorometry is low, up to 20% and not better than ± 5%. Therefore, it is frequently preferred for determining uranium by spectrophotometry after adequate preconcentration.

The main purpose of this study was to develop a rapid method for the preconcentration of uranium from water samples so as the metal ion concentration in the sample can be determined spectrophotometrically.

Of the many spectrophotometric methods for the determination of uranium(VI),^{7,10-13} the most popular appear to be those that use dibenzoylmethane (DBM), thiocyanate or arsenazo III as chromogenic reagents. DBM and thiocyanate have poor sensitivity. Arsenazo III reacts with the uranyl ion¹³ to form several complex compound, depending on the acidity of the medium. The determination is reported¹³ to be selective, especially in strong acid solution and therefore the arsenazo III method in the present work is based on that of NEMODRUK and GLUKHOVA,¹⁴ which involves the use of 6M HNO₃ solution for color development.

Various methods have been described for the preconcentration of uranium in natural waters prior to its determination. In the present work, a method for the preconcentration of uranium present in natural waters on TBP-plasticized DBM-loaded polyurethane foams prior to the spectrophotometric determination of the metal ion by the arsenazo III method, is described. The proposed combined preconcentration-spectrophotometric determination procedure may also find application for the determination of uranium in waters from various nuclear reactor circuits.

The technique of the use of organic reagent-loaded polyurethane foams for metal ions separation and preconcentration was first introduced by BRAUN and FARAG in 1972.^{15,16} Two years later the same authors¹⁷ could immobilize chelating agents on polyurethane foams by the aid of plasticizers. Both non-plasticized and plasticized reagent-loaded polyurethane foams have found extensive application for enrichment for metal ions and many review papers and books have appeared in the field.¹⁸⁻²³

In previous work,²⁴ studies on the application of non-plasticized and TBP-plasticized DBM-loaded polyurethane foams for the concentration of uranium present at low concentration levels in aqueous media, have been reported. The optimum pH for uranium(VI) extraction has been found to lie in the pH range of 6.0-6.5. In accordance with findings using other cations,²⁵⁻²⁷ it was observed that the rate of uranium extraction by plasticized DBM-loaded foams is much faster than that obtained by non-plasticized ones and, therefore, only TBP-plasticized DBM-loaded foams are used in the present work.

Experimental

Materials and reagents. The polyurethane foam used in this study was of the same batch (PU 3152 slab-Nr WAV 212, polyol type, kindly provided by Bayer Co.) used in earlier investigations.²⁴

Dibenzoylmethane (DBM) was purchased from Alpha Co. and is claimed to have a purity of about 98%.

Tri-n-butyl phosphatate (TBP), a BDH product, was purified²⁸ before use.

A stock solution of uranyl nitrate in 0.01M nitric acid solution was prepared from an analytical reagent BDH salt. The exact concentration of uranium(VI) in this stock solution was determined gravimetrically by the oxinate method.²⁹

Foam pretreatment. The foam was first cut either in the form of small cubes of about 5 mm edges, or as cylinders of about 13 mm diameter and 10 cm length for use in batch equilibration and column experiments, respectively, and then washed and dried as described elsewhere.³⁰

Preparation of TBP-plasticized DBM-loaded foams. The specified weight of dry foam cubes or cylinders was soaked, for 2 hours, in a 2.5% solution of DBM in TBP at a foam: DBM in TBP solution ratio of 1 : 10 (w/v) with occasional vigorous shaking. The foam pieces were then drained and squeezed between 2 layers of filter paper.

Preparation of foam columns. DBM-loaded foam cylinders were placed at the bottom of glass columns (12 mm diameter) with enough water or washing solution to completely immerse them. Air in the foams was expelled by pressing them with a glass plunger. The foams were then allowed to expand and next washed with the specified volume of washing solution. The washing solution was completely drained from the column and the foam was compressed several times to remove any residual solution. Enough sample solution was then introduced into the column, air expelled as mentioned before and the foams were allowed to expand before percolating the sample solution.

Analysis of uranium(VI). Analyses were generally run on samples of the aqueous solution before and after extraction. The solution sample to be analyzed was evaporated with a few drops of a concentrated solution of hydrochloric acid, ignited to destroy any organic matter then evaporated several times with a few drops of hydrochloric or of nitric acid for fluorometric and spectrophotometric¹⁴ determination, respectively. Fluorometry was used for the determination of uranium when present at trace concentration levels. Higher concentrations were determined spectrophotometrically.

Recommended preconcentration and spectrophotometric determination procedures. Through a foam bed of 2.5 g or more of dry foam loaded with a solution of DBM in TBP and washed with 1 litre of distilled water of pH 6.0–6.5 presaturated with TBP is percolated a suitable aliquot (up to 20 l) of the water sample after adjusting its pH to 6.0–6.5 with hydrochloric acid or sodium hydroxide solution. The column is next washed with 1 l of double distilled water of pH 6.0–6.5. Uranium on the column is then eluted with 120 ml of 0.6M HCl solution at a flow rate of 10 ml/min. The eluate or a suitable aliquot of it is gently evaporated in a silica dish, heated on a wire-gauze and finally ignited on a bare flame to get rid of organic matter, if any. The residue in the dish is dissolved in a few ml of 1 : 1 HNO₃ solution and evaporated several times with a few drops of conc. nitric acid. To the cooled dish is then added exactly 4 ml of 8M HNO₃ solution presaturated with urea^{13,31} to dissolve the residue in the dish. 1 ml of 1.5% solution of arsenazo III is next added and the solution is well stirred and its optical

density measured at 656 nm.¹⁴ The exact concentration of uranium in the sample is obtained from a calibration curve built in exactly the same manner as used to prepare the sample.

Results and discussion

Elution of uranium from uranium(VI)-loaded foams

In this study hydrochloric acid was tried as an eluent. This acid was preferred to other ones because it can easily be evaporated and hence, if required, the eluate can further be concentrated by mere evaporation.

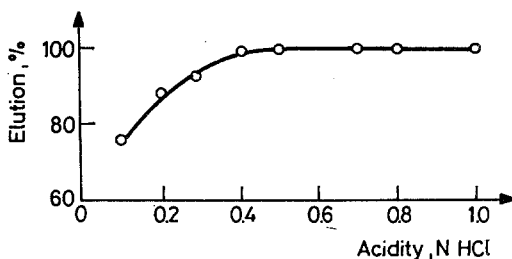


Fig. 1. Effect of HCl concentration on the back-extraction of U(VI) from U(VI)-loaded TBP-plasticized DBM-loaded foam batches. Organic phase: 0.2 g of dry foam batches treated with DBM + TBP and loaded with 23.8 μg of U(VI). Back-extraction conditions: twice equilibration with 10 ml aliquots of solutions of various HCl concentrations

Batch equilibration experiments were first run to find out the optimum acidity required for successful elution. A series of 0.2 g dry foam batches treated with DBM in TBP and loaded with exactly known amounts (23.8 μg) of U(VI) were prepared. The foam batches were then subjected to back extraction of uranium by equilibrating twice with 10 ml aliquots of HCl solutions of known concentrations. The results (Fig. 1) indicate that almost quantitative elution can be achieved at acidities of 0.4M HCl and above.

The possible elution of the metal ion from uranium-loaded beds was tried next. Two foam beds consisting of 0.4 g and 1.0 g of dry foam batches impregnated with a solution of DBM in TBP and each loaded with $\sim 47.5 \mu\text{g}$ of uranium(VI) by passing 5 l of a $4 \cdot 10^{-8}\text{M}$ uranyl solution of pH 6.5 through each bed. Uranium(VI) on the columns was then eluted by passing 0.6M HCl solutions through the columns at a rate of 10 ml/min. The results are shown in Fig. 2, which indicates that uranium(VI) is almost quantitatively sorbed by the foam and can be nearly completely eluted by about 100 ml of the acid.

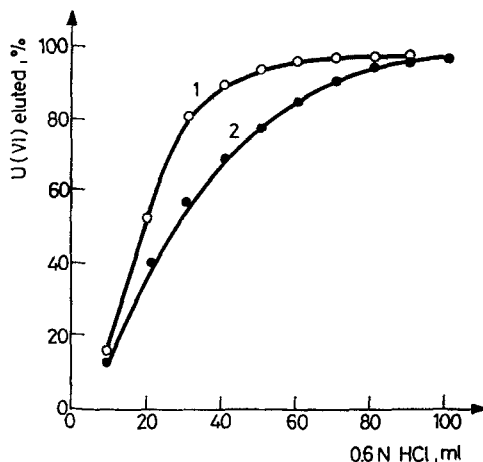


Fig. 2. Elution of U(VI) from U(VI)-loaded TBP-plasticized DBM-loaded foam beds with 0.6M HCl solution at a flow rate of 10 ml/min

Condition	Column 1	Column 2
Weight of dry foam, g	0.4	1
Prewashing	200 ml of TBP-saturated water of pH 6.5	
U(VI) loading	5 l of $1 \cdot 10^{-8}$ M U(VI) solution	
Total U(VI) loaded, μ g	47.6	
After washing	200 ml double distilled water of pH 6.5	

Effect of foreign cations

As natural waters usually contain a large number of cations (Table 1) the effect, on uranium extraction, of many of the major and some of the minor cations found in sea water was studied. The results obtained are shown in Table 2, which indicates that most of the elements tested are either poorly extracted or not extracted by DBM-loaded foams. Table 2 also shows that EDTA impairs uranium(VI) extraction and hence it cannot be used as a masking agent for adverse cations in the present case.

However, based on similarities between the chemical properties of some cations, e.g., rubidium and cesium are more or less similar to potassium and sodium, on liquid-liquid extraction data of DBM-metal ions systems³³ and also on the metal species that predominate in sea water, it would be expected that many cations other than those presented in Table 2 are not liable to extraction by DBM-loaded foams. These cations are shown in Table 1. The rest of the cations that are usually present in sea and other natural

Table 1

Major and the most predominant minor elements in ocean water for $S = 35\text{‰}$ ³² arranged in the order of decreasing concentration, the maximum permissible element/uranium ratio in the arsenazo III method^{13, 14} and the ability of metal ions for extraction by DBM-loaded foams

Element	Concentration, $\mu\text{g/l}$	Element/uranium ratio	Maximum permissible element/U ratio	Ability for extraction by DBM foam
Sodium	$11.05 \cdot 10^6$	$33 \cdot 10^5$		--ve
Magnesium	$1.326 \cdot 10^6$	$4 \cdot 10^5$	5000	--ve
Calcium	$4.22 \cdot 10^5$	$1.2 \cdot 10^5$	100	--ve
Potassium	$4.16 \cdot 10^5$	$1.2 \cdot 10^5$		--ve
Strontium	$8.5 \cdot 10^3$	$2.6 \cdot 10^3$	5000	--ve
Boron ⁺	$4.5 \cdot 10^3$	1363		-ve
Lithium	180	54.5		--ve
Rubidium	120	36		--ve
Barium	30*	9	5000	--ve
Molybdenum	10	3	500	--ve
Zinc	5	1.5	5000	--ve
Aluminium	5	1.5	5000	
Uranium	3.3			
Iron	3*	0.9	5000	
Copper	3*	0.9	100	
Arsenic ⁺⁺	2.3	0.7		
Nickel	2	0.6	5000	
Manganese	2*	0.6		
Vanadium ⁺⁺⁺	1.5	0.45		
Titanium	1	0.3	25	
Chromium	0.6*	0.18		
Cesium	0.5	0.15		--ve
Antimony	0.2	0.06	500	--ve
Tungsten	0.12	0.036	100–200	
Silver	0.1	0.03		--ve
Other elements	0.1	0.025		

--ve – elements that were experimentally found to be non-extractable by DBM-loaded foams;

-ve – elements that are expected to be non-extractable;

⁺present as H_3BO_3 and $\text{B}(\text{OH})_4^-$;

⁺⁺present as HAsO_4^- ;

⁺⁺⁺present as $(\text{H}_2\text{V}_4\text{O}_{13})^{4-}$, HVO_4^{2-} , VO_3^- ;

*variations occur.

waters are either tolerated by the arsenazo III spectrophotometric method (Table 1)^{13,14} or found at very low metal ion/uranium ratios so that, if they are extracted, they should not significantly affect uranium(VI) determination by the arsenazo III method. This is demonstrated in the following section.

Table 2
Percentage extraction of foreign cations and
of U(VI) in the presence and absence of EDTA

Cation	Extraction, %
Sodium	0.0
Potassium	0.0
Magnesium	0.0
Calcium	0.0
Iron(III) ⁺	83.5
Cobalt(II)	12.4
Zinc(II)	2.6
Aluminium ⁺	40.2
Zirconium(IV) ⁺	44.6
Cerium(III) ⁺	17.3
Thorium(IV) ⁺⁺	86.1
Uranium(VI)	98.8
U(VI) + EDTA (average of 5 expts.)	89.5 ± 4

Foam phase: 0.2 g of dry foam batches loaded with DBM in TBP.

Aqueous phase: 25 ml of $1 \cdot 10^{-4}$ M metal ion solution of pH 6.5;

⁺25 ml of $1 \cdot 10^{-5}$ M metal ion solution of pH 6.5;

⁺⁺25 ml of trace concentration of the metal ion of pH 6.5; EDTA $5 \cdot 10^{-4}$ M.

Preconcentration, elution and spectrophotometric determination of U(VI) in different types of water

Column experiments were conducted to test the applicability of the proposed extraction, elution and spectrophotometric procedures for the determination of uranium naturally present or added to distilled (Table 3), tap, canal and sea waters (Table 4). The conditions of the experiments and the results obtained are summarized in the tables, which indicate the applicability of the proposed preconcentration and determination procedures for uranium analysis. However, taking the value $3.3 \mu\text{g/l}^{3-5}$ as a basis for uranium concentration in sea water, the yield by the present method is calculated to be 84% (Table 4). This yield is considered acceptable, especially when compared with the yields: 74%,³⁴ 82%³⁵ and 90%³⁶ obtained by other preconcentration and determination methods.

It is worth mentioning that the selectivity of the method can be significantly increased by evaporating the eluate, dissolving the residue in 0.1M HNO₃ solution

Table 3
Results of analysis of uranium(VI) in solutions of the metal ion in doubly distilled water

Parameter	Experiment No.						
	1	2	3	4	5	6	7
Weight of dry foam, g	0.4	0.4	1	1	1.5	1.5	1.5
Volume of sample, l	0.5	5	10	10	25	25	25
Flow-rate, ml/min	18	18	18	35	18	35	18
Total U(VI) added μg	47.6	47.6	23.8	23.8	23.8	23.8	–
U(VI) found, %	96.8	97.0	98.2	98.4	98.8	98.7	–
95% confidence level (N = 5)	± 1.6	± 1.2	± 1.1	± 1.0	± 0.8	± 0.8	–

Table 4
Results of determination of uranium in tap, canal and sea waters

Parameter	Experiment, No.							
	Tap water					Canal water		Sea water
	1	2	3	4	5	1	2	
Weight of dry foam, g	1	1	1.5	1.5	1.5	2	2	2.5
Volume of sample, l	10	10	25	25	25	14	14	12
Flow-rate, ml/min	18	35	18	35	35	35	35	35
Uranium naturally present, $\mu\text{g/l}$	*	*	*	*	*	*	*	3.3
Total U(VI) added, μg	23.8	23.8	23.8	23.8	–	–	14	–
U(VI) found, %	97.9	98.1	97.3	96.8	–	–	95.0	83.9
95% confidence level (N = 5)	± 0.9	± 1.8	± 1.3	± 2.0			± 2.3	± 4.2

*Uranium was determined fluorometrically after extraction with methyl isobutyl ketone.¹² The lower determination limit was 0.05 $\mu\text{g/l}$.

containing NH_4NO_3 and EDTA. Uranium in the solution is then extracted by TBP in benzene or toluene and re-extracted from the organic phase by arsenazo III solution with subsequent photometric determination.¹³

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