Preseparation of uranium by reversed-phase partition chromatography

Application to the determination of trace elements in nuclear-grade uranium compounds by inductively coupled plasma atomic emission spectrometry

ASSAD S. AL-AMMAR*, H. A. HAMID, B. H. RASHID and H. M. BASHEER

Chemistry Department, Nuclear Research Centre, Iraqi Atomic Energy Commission, P.O. Box 765, Baghdad (Iraq)

(First received March 9th, 1990; revised manuscript received May 15th, 1990)

ABSTRACT

The chromatographic behaviour of a tri-*n*-butyl phosphate (TBP)-impregnated macroporous Amberlite XAD-4 column was investigated for the separation of uranium from impurity elements in nuclear-grade uranium compounds prior to analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES). The parameters affecting separation with this column were optimized. The proposed separation method proved to be rapid and efficient. High recovery factors for all the impurity elements were obtained. The procedure is suitable for routine application to the determination of the impurity elements Mo, Zr, Cd, Co, Ni, Ba, B, Mg, Mn, Fe, Cr, Al, V, Be, Cu, Ti, Se, Zr, Sr, Ca and As.

INTRODUCTION

Nuclear-grade uranium compounds, such as yellow cake and UO_2 powder, must have certain specifications in order to be suitable for the industrial production of nuclear reactor fuel.

The determination of impurity elements in uranium compounds represents a major part of the quality control programme used to determine the chemical specifications. The impurity elements contents are responsible for corrosion of the nuclear fuel and some act as nuclear poisons, as they have high neutron cross-sections.

Several techniques have been used to determine impurity elements, including spectrochemical analysis [1], atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-AES) [2,3]. The last technique is very convenient owing to its high sensitivity, reproducibility, wide dynamic range, relative freedom from matrix interferences and multi-element measurement capability. However, if ICP-AES is to be used, the uranium must be separated prior to the determination of the impurities because the dense uranium spectrum will severely interfere with

the spectral lines of the analytes. Therefore, several workers have used liquid–liquid extraction methods to separate uranium from the impurities [4–7].

Recently, ion-exchange chromatography [8] and reversed-phase partition chromatography (RPPC) [9] were introduced to separate the impurities from uranium prior to their determination. The RPPC method has nearly the same precision and recovery factors as the liquid–liquid extraction method. However, the RPPC method has the advantages that it is faster and requires less manipulation as the number of samples become large.

One of the most successful applications of the RPPC method is that by Pan and Wang [9]; they determined 40 trace elements in uranium compounds simultaneously by end-on viewed ICP-AES after separation from uranium by RPPC using tris(2-ethylhexyl) phosphate as a uranium extractant supported on Kel-F (polychlorotrifluoroethylene). In the end-on viewed method, the plasma flame is bent from its vertical position so that the spectrometer slit will receive a higher intensity from the emitted spectrum, which increases the sensitivity. However, the method is not suitable for routine use because of the complicated arrangement required. Accordingly, the aim of this work was to modify the experimental design of the method developed by Pan and Wang [9] to make it applicable on a routine basis to the determination of the impurity elements in uranium compounds.

The modification required the use of another type of extractant–support combination, such that the resulting separtion column would have a higher capacity for uranium extraction. Therefore, a larger amount of sample could be used to obtain a final solution containing higher concentrations of impurity elements, so that it could be analysed by a normal ICP-AES technique. Accordingly, it was decided to investigate the use of tri-*n*-butyl phosphate (TBP) as a uranium extractant, supported on the macroporous styrene–divinylbenzene polymer Amberlite XAD-4.

The reasons are that TBP is the most commonly used extractant for the purification of uranium on an industrial scale, extracting uranium selectively into the organic phase and leaving the impurities totally in the aqueous phase. TBP is also very stable in highly acidic media where the extraction of uranium usually takes place. Amberlite XAD-4 is often used as a support for different extractants for the separation and preconcentration of trace metal ions by reversed-phase adsorption chromatography [10] and has been used as a support for TBP for the separation of some fission products [11,12] using RPPC. It is used as a support because of its high surface area [750 m^2/g, according to the manufacturer's data (Aldrich)], and high affinity for organic extractants; this allows it to absorb strongly more than its own weight of the organic extractant. Accordingly; the prepared column wil have high efficiency and a long life.

EXPERIMENTAL

Instrumentation and operating parameters
    A Hilger Model E974 MK.1 Polyvac direct-reading spectrometer with a Hilger 2.5-kW ICP lightsource equipped with a Meinhard Model TR-30 concentric glass nebulizer was used. The argon flow-rates were 11, 0.8 and 0.4 l min^{-1} for the plasma, auxiliary and nebulizer, respectively.
    A Hilger E92B argon humidifier was used. The incident power was 1.7 kW for

the extraction method and 1.25 kW for the RPPC method.

The nebulizer pressure was 35 p.s.i.g. The observation height was 16 mm above the induction coil. The emission intensity was integrated for 15 s.

The following analytical lines were used: Mo 2020.3, Ti 3372.8, Ni 2316.0, Zr 3438.2, Ba 2335.3, Se 1960.3, B 2497.7, Bi[a] 2230.1, Sc[b] 2552.3, Zn 2138.6, Fe 2599.4, Be 3130.4, Mn 2576.1, Cd 2266.0, Mg 2795.5, Co 2286.2, Cr 2835.6, As 1972.6, Al 3082.2, Sr 4077.7, V 3110.7, Ca 3968.5 and Cu 3247.5 Å.

Reagents

Amberlite XAD-4 was purchased from Aldrich with 20–50 mesh size, average particle size 0.5 mm and surface area 750 m^2/g. It was washed with 10% (v/v) hydrochloric acid in methanol, water, methanol, dichloromethane and finally diethyl ether, then dried overnight at 80–90°C under 1.0–0.5 mmHg pressure.

TBP was purified [13] by equilibration with 5% sodium carbonate solution. High-purity acids and deionized water were used throughout. The argon used was of 99.999% nominal purity. All other reagents were of analytical-reagent grade. Standard solutions were prepared from Merck Titrisol standards.

Preparation of the separation column

A 10-g amount of the washed Amberlite XAD-4 was impregnated with 12 g of TBP by adding the TBP dropwise and with continuous mixing to ensure its uniform distribution over the XAD-4. The mixture was allowed to stand for at least 2 h to ensure good diffusion of the TBP inside the polymeric material. The loading of TBP on XAD-4 was 120% (w/w).

The slurry packing technique was adopted for packing the impregnated Amberlite XAD-4 inside a PTFE column (50 cm × 0.8 cm I.D.). The column was conditioned before use with 10 ml of 4 M nitric acid[c] at a flow-rate of 2 ml/min.

Sample treatment

A sample of uranium oxide or yellow cake containing 1.25 g of uranium was dissolved by heating it gently with 5 ml of 8 *M* nitric acid. After complete dissolution, 5 ml of water were added and the resulting solution was transferred to the column for uranium separation. The separation was performed at a flow-rate of 0.5 ml/min. The column was then washed with about 12 ml of 4 *M* nitric acid at a flow-rate of 1.5 ml/min. The wash solution was combined with the sample solution in a 25-ml volumetric flask. A 1-ml volume of a solution containing 500 ppm of scandium and 500 ppm of bismuth (internal standards) was added and the mixture was diluted to volume with 4 *M* nitric acid.

The sample solution was analysed for impurity elements by measuring it together with standard solutions by ICP-AES. The concentrations of the analytes in the

---

[a] Bi was used as internal standard for the elements Mo, Ba, Al, Cu, Ca, Se, Zn, Cd, As and Sr.

[b] Sc was used as internal standard for the elements Fe, Co, Cr, Ni, V, Ti, Zr, Mg, Be, Mn and B.

[c] The solutions used for column conditioning, washing, regeneration and sample dissolution must be previously saturated with TBP to minimize the loss of TBP from the impregnated Amberlite XAD-4, thus extending the life of the column.

sample were obtained by using the standard curves, which were constructed from the measurements of the standard solutions by ICP-AES. The standard solutions were prepared by mixing the required volumes of stock standard solutions of the elements to be determined and making the final solution 4 M in nitric acid. The final standard solutions contained scandium and bismuth as internal standards. The results of the measurements were corrected using recovery factors previously determined as decribed in the next section. The concentrations of the impurity elements in the standard solution were taken in accordance with the specifications for nuclear-grade UO_2 powder and nuclear-grade uranium ore concentrate [14,15].

Determination of impurity element recovery factors

The recovery factors were measured by preparing a standard solution containing 300 μg of each analyte and 1.25 g of uranium per 10 ml of the solution (except for B and Cd, for which the solution contained 2 μg of B and 2 μg of Cd per 10 ml; this solution is a simulation of a solution obtained by dissolving UO_2 powder containing the maxium allowable concentrations of the impurity elements according to the specifications for nuclear-grade UO_2 powder [14]. This standard solution is 4 M in nitric acid. A 10-ml portion of this solution was passed through the column to separate uranium from the impurity elements. The concentrations of the impurity elements in the resulting solution were determined using the same procedure as used for the sample.

Column regeneration

The used column was freed from absorbed uranium by passing 30 ml of 30% (w/w) ammonium acetate solution through the column at a flow-rate of 1 ml/min, followed by washing with 10 ml of water at a flow-rate of 2 ml/min. The TBP-impregnated Amberlite XAD-4 of the column was stored in water for further use.

RESULTS AND DISCUSSION

The chromatographic behaviour of uranium on a column prepared as described above was examined quantitively by separating the uranium from 10 ml of 4 M nitric acid containing 1.25 g of uranium. It was found that the yellow uranium band occupies about one third of the total length of the TPB-impregnated XAD-4 column charge. This band spread to two thirds of the column when washed with 12 ml of 4 M nitric acid.

The eluate was collected and analysed for uranium. The uranium concentration in the eluate was found to be 4 ppm for a freshly prepared column and 4–10 ppm for a regenerated column. This low concentration of uranium will not interfere with the determination of the impurity elements.

The validity of the proposed method with respect to the accuracy, precision and recovery was tested by applying it together with the liquid–liquid extraction method [16], involving extraction of the impurity elements from a 6 M nitric acid solution with 30% (v/v) TBP in carbon tetrachloride, to the analysis of a synthetic standard solution containing the impurity elements and uranium. The accuracy of the proposed method can therefore be determined by comparing the results obtained by the two methods, given in Table I. The agreement between the results obtained indicates

TABLE I

COMPARISION OF LIQUID–LIQUID EXTRACTION AND RPPC METHODS FOR THE DETER-
MINATION OF IMPURITY ELEMENTS IN A SYNTHETIC URANIUM SOLUTION

Element	Concentration present (ppm)	Concentration determined (ppm)	
		Extraction method[a]	RPPC method[a]
Mo	10	9.5	9.7
Zn	5	5.2	4.9
Cd	2	1.8	1.9
Co	5	4.8	4.7
Ni	10	9.7	10.1
Ba	5	4.9	4.9
B	5	5.2	4.9
Mg	5	4.8	5.0
Mn	5	5.1	4.9
Fe	10	9.8	9.8
Cr	2.5	2.3	2.6
Al	5	5.1	5.0
V	2	2.1	2.1
Be	2	1.8	2.0
Cu	10	9.8	10.1
Ti	5	4.9	4.8
Se	10	9.8	9.7
Zr	2	1.7	1.9
Sr	2	1.8	1.8
Ca	5	5.1	4.9
As	10	9.7	9.7

[a] Average values of two determinations.

the applicability of the proposed method to the determination of impurity elements in nuclear-grade uranium compounds.

Table II shows a comparison between the proposed method and the liquid–liquid extration method [16] with respect to recovery and precision. The recovery was determined using the procedure given above for recovery factors.

The good recovery and high precision of the present method support its use for the proposed application. The detection limits for the elements determined are given in Table III, and are well below the specification values for impurities in nuclear-grade UO_2 powder [14].

It should be mentioned that the factors taken into consideration in preparing the TBP-impregnated XAD-4 separation column and those in performing the separation process were selected by optimizing the TBP loading, particle size, amount of TBP-impregnated Amberlite XAD-4 and solution compostion.

Regarding TBP loading, when separating uranium from impurities it is very important to have a column with the highest possible capacity for uranium extraction in order to make the separation process practical, which can be achieved by using a column with the highest possible percentage loading of the extractant on the support. TBP loadings from 70% to 190% were investigated and it was found that the efficiency of the column for uranium extraction increases linearly with loading. However

TABLE II

COMPARISON OF RECOVERY FACTORS DETERMINED BY RPPC AND LIQUID–LIQUID
EXTRACTION METHODS AND OF RELATIVE STANDARD DEVIATIONS

	Recovery factor (%)		Precision as relative standard deviation (%)[a]	
	Extraction method	RPPC method	Extraction method	RPPC method
Mo^{6+}	93	91	6	5
Zn^{2+}	98	97	3	4
Mg^{2+}	99	100	3	3
Mn^{2+}	97	98	4	3
Fe^{3+}	100	99	3	2
B^{3+}	98	97	3	2
Ni^{2+}	99	97	5	4
Cd^{2+}	96	95	4	3
Co^{2+}	99	100	5	6
Ba^{2+}	98	99	4	2
Cr^{3+}	92	90	5	3
Al^{3+}	99	100	4	4
V^{4+}	100	99	3	2
Be^{2+}	98	99	4	3
Cu^{2+}	99	98	3	3
Ti^{4+}	96	97	3	2
Zr^{4+}	74	70	5	3
As^{5+}	98	95	5	4
Se^{4+}	94	95	6	4
Sr^{2+}	99	97	5	3
Ca^{2+}	97	98	4	3

[a] $n = 5$.

at loadings higher than 120% the impregnated particles were exceedingly hydrophob-
ic and badly agglomerated, causing poor column packing. This type of agglomeration
at high TBP loadings was attributed to the presence of the extractant on the outer
surface of the beads [11,17]. Therefore, it was decided to use a column with a 120%
TBP loading as the optimum choice.

Regarding particle size, it is well know that a better column performance is
generally achieved as the particle size decreases. We investigated the performance of
150–200-mesh Amberlite XAD-4, obtained from the purchased 20–50-mesh material
by mechanical crushing followed by sieving. It was found that the separation process
using columns prepared as decribed earlier could not achieve a practical flow-rate
(i.e., 0.5 ml/min) without the aid of a pumping mechanism that delivers a pressure
higher than atmospheric. However, to simplify the proposed method, this pumping
mechanism should be avoided and the separation should be performed by gravity-
induced flow under atmospheric pressure. Hence the Amberlite used should have a
mesh size smaller than 150. Nevertheless, the column used in this work contained the
purchased well defined, nearly round 20–50-mesh Amberlite XAD-4 and no investi-
gation of the performance of a column loaded with 50–150-mesh material was made.
It is believed that no improvement in column performance would be achieved as the
50–150-mesh Amberlite has fractured particles due to the mechanical crushing and

TABLE III

DETECTION LIMITS FOR IMPURITY ELEMENTS DETERMINED BY RPPC SEPARATION WITH TBP-IMPREGNATED AMBERLITE XAD-4 FOLLOWED BY ICP-AES MEASUREMENT

Element	Detection limit ($\mu g/g$ U)	Element	Detection limit ($\mu g/g$ U)
Mo	1.3	Al	3.2
Zn	0.16	V	0.8
Cd	0.11	Be	2.4
Co	0.61	Cu	0.4
Ni	0.57	Ti	0.51
Ba	0.63	Se	4.1
B	0.13	Zr	0.58
Mg	0.02	Sr	0.05
Mn	0.12	Ca	0.12
Fe	0.36	As	4.3
Cr	0.55		

therefore the prepared column will have an irregular packing and irregular flow (channelling). This is supported by the work Louis and of Duyckaerts [11], who investigated the performance of a TBP-impregnated Amberlite XAD-4 column for the separation of americium(111). They found that the experimental results, when used to calculate the A term in the Van Deemter equation give values that are within a factor of 11–25 of the particle size of the Amberlite used. They attributed this discrepancy to the use of fractured particles obtained by the mechanical crushing of 20–50-mesh XAD-4.

The amount of TBP-impregnated Amberlite XAD-4 used was chosen as a compromise between the following effects: the efficiency of the separation of uranium from impurities increases with increasing amount of packing, and the time required for washing and column regeneration increases with increasing amount of packing.

It was found that the repeated use of the same TBP-impregnated Amberlite XAD-4 column for uranium separation led to a gradual loss of absorbed TBP and a consequent decrease in column capacity. To prevent this effect, throughout the separation procedure solutions that had been previously saturated with TBP were used. This was found to extend the life of the column to more than 80 separations.

It is worth-mentioning that the acidity of solutions passed through the column was chosen according to previous studies by Hamlin et al. [18] and Walker and Vita [19].

CONCLUSION

Reversed-phase partition chromatography with TBP-impregnated macroporous Amberlite XAD-4 column was found, after optimizing the parameters affecting the separation process, to be rapid and highly efficient for the separation of uranium from impurity elements prior to analysis by ICP-AES. The overall method is accurate, precise, free from interferences from the uranium matrix and could be applied on a routine basis to determine impurity elements in nuclear-grade uranium compounds.

REFERENCES

1 *1988 Annual Book of ASTM Standards*, Vol. 12.01, Nuclear Energy (1), American Society for Testing and Materials, Philadelphia, PA, 1988, method ASTM C 696.
2 P. M. Santoliquido, *J. Res. Natl. Bur. Stand.*, (1988) 452.
3 K. Kato, *At. Spectrosc.*, 7 (1986) 129.
4 M. A. Floyd and R. W. Morrow, *Spectrochim. Acta, Part B*, 38 (1983) 303.
5 T. J. Seshagiri and Y. Babu, *Talanta*, 31 (1984) 773.
6 R. Ko, *Appl. Spectrosc.*, 38 (1984) 909.
7 H. J. Wachtendonk and R. Baurnann, *ICP Inf. Newsl.*, 10 (1984) 277, Abstract No. 111.
8 P. Burba and P. G. Willmer *Fresenius' Z. Anal. Chem.*, 323)1986) 811.
9 F. Pan and X. Wang, *Fenxi Huaxue*, 15 (1987) 322.
10 J. N. King, *Report No. IS-T-1198*, Ames Laboratory, Ames, IA, 1986.
11 R. E. Louis and G. Duyckaerts, *J. Radioanal. Nucl. Chem.*, 81 (1984) 305.
12 R. E. Louis and G. Duyckaerts, *J. Radioanal. Nucl. Chem.*, 90 (1985) 105.
13 Z. Marczenko, *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood, Chichester, 2nd ed., 1987, p. 611.
14 *1988 Annual Book of ASTM Standards*, Vol. 12.01, Nuclear Energy (1), American Society for Testing and Materials, Philadelphia, PA, 1988, method ASTM C 753-81, p. 194.
15 *1988 Annual Book of ASTM Standards*, Volume 1201, Nuclear Energy (1), American Society for Testing and Materials, Philadelphia, PA, 1988, method ASTM C 967-87, p. 396.
16 G. P. Larson and R. E. Slagle, *Report, Y/DK-357*, Contribution to ASTM C-26-05 Task Group (1983), prepared for submission to ASTM Meeting, Quebec City, July 13, 1983.
17 E. Herrmann, *J. Chromatogr.*, 38 (1968) 498.
18 A. G. Hamlin, B. J. Roberts, W. Loughlin and S. G. Walker, *Anal. Chem.*, 33 (1961) 1547.
19 C. R. Walker and O. A. Vita, *Anal. Chim. Acta*, 43 (1968) 27.