

Determination of Trace Metals in Uranium Oxide by Inductively Coupled Plasma Mass Spectrometry Combined With On-line Solvent Extraction

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An on-line solvent extraction technique for the determination of trace elements in uranium by inductively coupled plasma mass spectrometry is described. An aqueous solution containing uranium (2% m/v) in 1 mol dm⁻³ nitric acid and an organic solvent that can effectively extract uranium, *viz.*, trioctylphosphine oxide in cyclohexane (0.2 mol dm⁻³), are pumped alternately through a poly(tetrafluoroethylene) (PTFE) tube where they mix thoroughly. The organic phase containing the extracted uranium is removed on-line by allowing the solution to pass through a microporous PTFE tube which, being hydrophobic, selectively allows the organic phase to permeate through its walls. This technique facilitates rapid and sensitive determination of trace elements in uranium with detection levels in the range 1–45 ppb for La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Ag, Ba, Cd, Co, Cr, Cu, In, Li, Mn, Ni, Pb, Sr, Ti, V and Y, 0.1 ppm for Al and 0.5 ppm for Fe.

Keywords: On-line solvent extraction; inductively coupled plasma mass spectrometry; uranium determination; trioctylphosphine oxide; phase separator

Uranium, an important constituent of nuclear fuels, frequently has to be characterized for its trace metal content. Optical emission spectroscopic methods^{1,2} have commonly been employed for this purpose, but they suffer from spectral interference and low sensitivity. Inductively coupled plasma mass spectrometry (ICP-MS) has distinct advantages such as spectral simplicity and very high sensitivity.

A procedure for determining trace metals in uranium by directly aspirating a uranyl nitrate solution into the ICP-MS instrument has been described previously.³ However, as uranium was found to suppress the analyte signals in ICP-MS, its removal was found to be essential in order to obtain adequate detection limits.³ The use of a common batch-type solvent extraction procedure was found to be time consuming and incompatible with the intrinsic speed of ICP-MS analysis. Therefore, an on-line solvent extraction technique has been developed making use of microporous poly(tetrafluoroethylene) (PTFE) tubing prepared in-house as a phase separator.

On-line separation techniques making use of PTFE membranes have been reported previously.^{4–7} The present method is similar to that used by Yamamoto *et al.*,⁸ who employed commercial microporous PTFE tubing as a phase separator for the determination of beryllium by flow injection in ICP atomic emission spectrometry. In the proposed method, an aqueous solution containing the uranium sample to be analysed and an organic solvent, *viz.*, 0.2 mol dm⁻³ trioctylphosphine oxide (TOPO) in cyclohexane, which can effectively extract uranium,^{9–11} are allowed to mix thoroughly during their passage through a PTFE coil. The organic phase containing the extracted uranium is subsequently removed on-line by allowing the solution to pass through a microporous PTFE tube which, being hydrophobic, selectively allows the organic phase to permeate through its walls.

Experimental

Instrumentation

All the measurements were carried out using an Elan 250 inductively coupled plasma mass spectrometer supplied by SCIEX (Thornhill, Ontario, Canada).

The instrumental operating conditions are given in Table 1. Mass spectrometric measurements were made by peak jumping using the sequential scanning mode. Ion counts were measured and integrated at three points per mass peak

Table 1 Instrumental operating conditions

Coolant argon flow rate	12 dm ³ min ⁻¹
Auxiliary argon flow rate	1.4 dm ³ min ⁻¹
Injector argon flow rate	0.4 dm ³ min ⁻¹
Nebulizer pressure	38 psi (6892 Pa)
Sampling depth	23 mm
<i>Lens settings—</i>	
B	5.24 V
E ₁	–17.0 V
P	–10.17 V
S ₂	– 3.47 V
<i>Resolution—</i>	
Low resolution	1 ± 0.1
High resolution	0.6 ± 0.05

(central mass plus two adjacent points). The measurement time was 0.5 s per point on the mass peak. The entire scanning process was repeated ten times for final integration. Generally the measurements were made in the low-resolution mode (peak width at 10% of peak height is 1 ± 0.1 u), but for Fe and Al the high-resolution mode (peak width at 10% of peak height is 0.6 ± 0.05 u) was employed.

Reagents

Distilled water and analytical-reagent grade acids were further purified by sub-boiling distillation in a quartz apparatus for use in these studies. For the preparation of stock standard solutions, Specpure-grade metals or chemicals (Johnson Matthey) were used. Uranium nitrate solution was prepared from nuclear-grade uranium oxide supplied by Nuclear Fuel Complex (Hyderabad, India).

Sample Preparations

A known mass of uranium oxide (U₃O₈) (1.1795 g) was accurately weighed into an acid digestion bomb (Parr Model T347), 3.2 ml of quartz-distilled nitric acid were added and the bomb was heated at 150 °C for about 2 h. The resulting clear solution was diluted to 50 cm³ so as to have a 2% m/v uranium solution with an acid concentration of 1 mol dm⁻³. The acidity was checked by a method reported previously.¹² For the International Atomic Energy Agency (IAEA) SR-54 U₃O₈ sample, in addition to the nitric acid the addition of one drop of hydrofluoric acid was required to facilitate complete dissolution. Experimental blanks were prepared similarly.

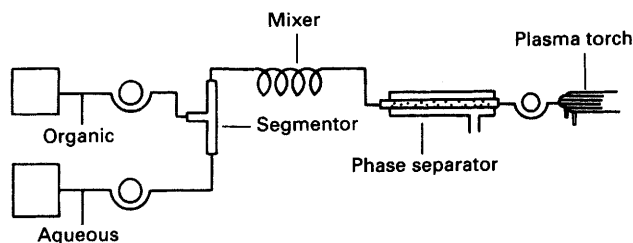


Fig. 1 Schematic diagram of the on-line solvent extraction system

On-line Extraction

The microporous PTFE tubing used as a phase separator was prepared by manually puncturing the PTFE tube (1.1 mm i.d.) with a fine needle. The tube, when examined under an optical microscope, showed the holes to have an average diameter of 200 μm and they were distributed fairly uniformly. The porosity, calculated as the percentage of the surface area occupied by the pores, was found to be approximately 10%.

The configuration for the on-line solvent extraction of uranium is shown schematically in Fig. 1. Two peristaltic pumps were used to pump the uranium solution and the solvent, *viz.*, 0.2 mol dm^{-3} TOPO in cyclohexane, separately into a T-shaped glass capillary tube (350 μm i.d.) which acted as a segmenter. The segmented stream with the alternating aqueous and TOPO segments then passed through a spiral PTFE tube (1.1 mm i.d.) which was mechanically shaken for efficient extraction. Subsequently the solutions passed through the microporous PTFE tube (24 cm \times 1.1 mm i.d.) phase separator which effected continuous phase separation. The organic solvent containing the uranium selectively permeated through the pores into an outer glass jacket from where it was drained off. The aqueous phase containing only the trace metals not extracted by the TOPO was continuously pumped by another peristaltic pump into the ICP-MS system.

Experimental Conditions

In order to obtain the optimum experimental conditions for an efficient separation of the uranium matrix from the trace metals, the following experimental parameters were varied: concentration of nitric acid (from 0.5 to 2 mol dm^{-3}); aqueous to organic ratio (from 1:1 to 1:3); length of the mixer (from 1 to 3 m); and length of the phase separator (12 and 24 cm). Known amounts of trace metals were added to nuclear-grade uranium nitrate solution (2% m/v uranium) and the recoveries were checked to assess the applicability of the extraction procedure for the determination of these metals.

In the determination of rare earth elements (REE), the oxides of the lighter REE are known to interfere spectrally in the determination of the heavier REE.¹³ Hence for the determination of REE, only isotopes free from such spectral interferences were employed, as recommended by Longerich *et al.*¹³ In the standard additions studies, the interference mentioned above was avoided by studying the REE as two separate groups, *viz.*, La, Ce, Pr, Nd, Sm, Eu and Yb and Gd, Dy, Ho, Er and Y. Iron and Al were determined in the high-resolution mode. Gallium was used as the internal standard for Al, Co, Cr, Cu, Fe, Li, Mn, Ni, Ti, V and Sr, Tm for Ag, Ba, Cd, In, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb and Tl for Pb. An IAEA standard reference material of U_3O_8 (SR-54) and two secondary U_3O_8 standards (Bhabha Atomic Research Centre, Bombay, India) were analysed by the procedure described above in order to check the accuracy of the method.

Results and Discussion

A previous study³ showed that at a concentration of 20 mg dm^{-3} and below, uranium does not pose any problem as a matrix interferent. Hence, the solvent extraction conditions were standardized so that the uranium concentration in the aqueous phase was reduced to a satisfactory level ($<20 \text{ mg dm}^{-3}$), whereas the other trace metals remained quantitatively in the aqueous phase without undergoing any

Table 2 Optimization of on-line solvent extraction conditions

Variation of parameter	Conditions			
	Nitric acid concentration/mol dm^{-3}		Uranium concentration in aqueous phase/ mg dm^{-3}	
Acid concentration	0.5		6	
	1		12	
	2		43	
Aqueous to organic ratio	Solution flow rate/ $\text{cm}^3 \text{ min}^{-1}$	Organic flow rate/ $\text{cm}^3 \text{ min}^{-1}$	Uranium concentration/ mg dm^{-3}	
	1	1	12	
	1	2	21	
	1	3	24	
Mixer tubing length	Length of mixer/m		Uranium concentration/ mg dm^{-3}	
	1		46	
	2		12	
	3		10	
Solution flow rate <i>versus</i> mixer length	Solution flow rate/ $\text{cm}^3 \text{ min}^{-1}$	Mixer length/m	Washout time/s	Uranium concentration/ mg dm^{-3}
	1	2	195	12
	0.7	1	225	15
	0.5	1	300	11

Table 3 On-line solvent extraction conditions adopted

Nitric acid concentration	1 mol dm ⁻³
Aqueous to organic ratio	1:1
Solution flow rate	1 cm ³ min ⁻¹ with 2 m length of mixer tubing or 0.7 cm ³ min ⁻¹ with 1 m length of mixer tubing
Length of phase separator	24 cm

extraction with TOPO. For this purpose a 2% m/v uranium (as nitrate) solution containing known amounts of different trace metals was used and the extraction behaviour was studied. The following experimental conditions were used initially: sample and solvent flow rates, 1 cm³ min⁻¹; length of the mixer tubing, 2 m; and length of the phase separator, 24 cm. The sample flow rate (1 cm³ min⁻¹) was kept the same as that which is generally used in the present ICP-MS work. The other parameters, *viz.*, mixer length and phase separator length, were selected arbitrarily. The extraction behaviour of TOPO was studied by systematically varying the different experimental conditions and the results, all of which are presented in Table 2, are discussed below.

Effect of Acid Concentration

The concentration of nitric acid in the uranyl nitrate solution was varied from 0.5 to 2 mol dm⁻³ and the results (mean of five determinations) are given in Table 2. With an acid concentration of 0.5 mol dm⁻³, uranium was extracted fairly efficiently, but the REE were also extracted to the extent of about 50%. Whereas uranium was satisfactorily extracted at an acid concentration of 1 mol dm⁻³, all the other trace metals remained quantitatively in the aqueous phase. At an acid concentration of 2 mol dm⁻³, the extraction of uranium was not satisfactory. Hence the acid concentration was kept at 1 mol dm⁻³ in subsequent experiments.

Aqueous to Organic Ratio

The extraction of uranium by TOPO at an aqueous flow rate of 1 cm³ min⁻¹ was found to decrease with the increase in the aqueous to organic ratio (1:1 > 1:2 > 1:3). The mean uranium concentrations (five determinations) in the aqueous phase are given in Table 2. This behaviour is explained as follows. For a given mixer length and sample flow rate (1 cm³ min⁻¹) an increase in the flow rate of the organic solvent results in a decrease in the residence time or contact time in the mixer where the extraction takes place. Hence, uranium was less efficiently extracted as the flow rate of the solvent was increased. Both the aqueous and organic flow rates were therefore fixed at 1 cm³ min⁻¹.

Length of the Mixer

The extraction efficiency with lengths of 1, 2 and 3 m of the mixer tubing was studied. The flow rates of uranium solution (2% m/v) and the solvent were maintained at 1 cm³ min⁻¹. The concentration of the uranium in the aqueous phase and the sample washout time were studied (Table 2). The washout time is the time taken for the analyte signals to return to blank levels between two determinations with the aspiration of 1 mol dm⁻³ nitric acid. With washing of the system with 1 mol dm⁻³ nitric acid for 3 min, no memory effects or cross-contamination problems were observed. Based on these studies, the optimum length was found to be 2 m. As the extraction efficiency is dependent on the contact time between the aqueous and organic phases, it was considered that the

lengths of the mixer tube could be reduced if lower solution flow rates were employed. Hence, the extraction efficiency was also tested at reduced flow rates of 0.7 and 0.5 cm³ min⁻¹ (Table 2). It was found that the performance of a 2 m length of mixer tubing with a flow rate of 1 cm³ min⁻¹ was comparable to that of a 1 m length of mixer tubing with a flow rate of 0.7 cm³ min⁻¹. However, the use of a flow rate of 0.5 cm³ min⁻¹ was found to enhance the washout time (5 min).

Phase Separator

Two different lengths of the phase separator, *viz.*, 12 and 24 cm, were tried. Most of the organic phase was found to be removed in the first 5–6 cm of the phase separator. With the use of a 12 cm tube, it was found that occasionally a few droplets of organic phase were present in the aqueous phase, which led to serious instability in the plasma, whereas with the use of a 24 cm tube, this problem never occurred. Hence a 24 cm phase separator was chosen for subsequent measurements.

The set of experimental conditions finally adopted for the on-line solvent extraction of uranium are given in Table 3.

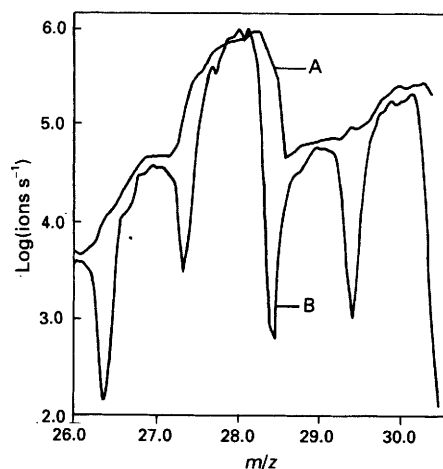


Fig. 2 Mass spectrum of Al in A, low- and B, high-resolution mode (the ²⁷Al peak is well separated from N₂⁺ in the high-resolution mode)

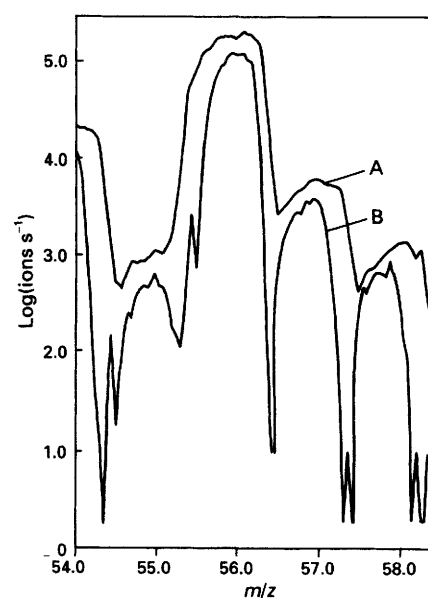


Fig. 3 Mass spectrum of Fe in A, low- and B, high-resolution mode (the ⁵⁷Fe peak is well separated from ArO⁺ in the high-resolution mode)

Table 4 Standard additions data for on-line solvent extraction of uranium from 20 g dm⁻³ uranium solution with 0.2 mol dm⁻³ TOPO in cyclohexane

Element	Relative atomic mass	Amount added/ μg g ⁻¹	Mean amount recovered (n=6)/ μg g ⁻²	Recovery (%)	RSD (%)	Detection limit/ ng g ⁻¹
Ag	107	1.0	0.97	97	3.5	17
Al	27	10.0	10.03	100	1.4	0.1 ppm
Ba	138	1.0	1.03	103	4.6	5
Cd	114	1.0	0.99	99	3.6	18
Ce	140	0.5	0.49	97	3.9	2
Co	59	1.0	0.99	99	2.7	9
Cr	52	1.0	1.06	106	5.7	42
Cu	63	1.0	0.99	99	3.5	10
Dy	163	0.5	0.49	98	4.4	7
Er	167	0.5	0.50	101	2.1	4
Eu	153	0.5	0.49	97	2.9	3
Fe	57	10.0	9.97	100	5.2	0.5 ppm
Ga	69	2.5	2.44	98	1.9	—
Gd	157	0.5	0.49	98	3.8	5
Ho	165	0.5	0.48	97	2.1	2
In	115	1.0	0.98	98	3.8	4
La	139	0.5	0.49	98	3.7	1
Li	7	1.0	0.99	99	3.9	7
Mn	55	1.0	1.03	103	4.9	9
Nd	146	0.5	0.5	100	3.2	4
Ni	58	1.0	0.95	95	3.2	33
Pb	208	1.0	1.04	104	3.3	13
Pr	141	0.5	0.50	100	2.6	1
Sm	147	0.5	0.49	99	3.3	8
Sr	88	1.0	1.06	106	3.6	45
Ti	48	1.0	0.99	99	5.4	15
Tl	205	2.5	2.37	95	2.6	—
Tm	169	1.0	0.97	97	2.1	—
V	51	1.0	1.02	102	3.0	11
Y	89	0.5	0.51	101	2.1	2
Yb	173	0.5	0.50	99	2.1	9

Table 5 Analysis of U₃O₈ standard reference material (IAEA SR-54) for common impurities

Element	Mean concentration measured (n=6)/μg g ⁻¹	RSD (%)	Certified concentration/μg g ⁻¹	Confidence interval/μg g ⁻¹
Al	71.4	4.9	71.3	54.8–82
Co	4.1	3.1	4.2	4.0–4.3
Cr	4.0	4.1	3.6	3.1–4.3
Cu	4.9	2.5	5.0	4.2–6.7
Fe	65.7	1.9	64.7	46.0–77.5
Mn	15.3	2.7	15.6	14.3–16.9
Ni	14.2	2.6	11.4	8.4–13.9
Ag*	0.63	12.3	0.42	—
Cd*	0.18	27	0.1	0.06–0.11
Pb*	1.8	4.8	1.03	0.32–2.15
Ti*	1.05	5.5	0.98	—

*Non-certified information values.

Table 6 Analysis of U₃O₈ (secondary standard) for REE

Element	Standard 1				Standard 2			
	Mean concentration by ICP-MS (n=6)/μg g ⁻¹	RSD (%)	Mean concentration by SSMS (n=6)/μg g ⁻¹	RSD (%)	Mean concentration by ICP-MS (n=6)/μg g ⁻¹	RSD (%)	Mean concentration by SSMS (n=6)/μg g ⁻¹	RSD (%)
Sm	0.17	2	0.24	21	0.43	5	0.59	24
Eu	0.11	6	0.11	27	0.42	6	0.42	26
Gd	0.34	1	0.16	40	0.67	3	0.50	21
Dy	0.1	5	0.15	52	0.36	5	0.36	45

Choice of Internal Standards

Internal standards were mainly used to compensate for the instrumental drift. As there is mass-dependent ion transmission through the sampling interface in ICP-MS,¹⁴ a single element cannot serve as a good internal standard for

all the elements in the Periodic Table. Hence the analytes were divided into the following three groups: low relative atomic mass elements (Al to Sr), medium relative atomic mass elements (Ag to Yb) and a high relative atomic mass element (Pb). The mass discrimination effects are expected to be small within a given group, as the mass range covered

is not very large. Thus Ga ($M_r=69$) was chosen as the internal standard for Al, Co, Cr, Cu, Fe, Li, Mi, Ni, Ti, V and Sr, Tm ($M_r=169$) for Ag, Ba, Cd, In, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb and Tl ($M_r=205$) for Pb. These three elements were selected as internal standards because they are present in very low concentrations and are not required to be determined in uranium. Standard additions studies on these three elements showed that they were not extracted by TOPO and that they remained quantitatively in the aqueous phase. With the use of internal standards, good precision, of the order of 5% [relative standard deviation (RSD)], was routinely obtained despite some instrumental drift.

Standard Additions Studies

Good recoveries were obtained for La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Ag, Ba, Cd, Co, Cr, Cu, In, Li, Mn, Ni, Pb, Sr, Ti, V, Y, Ga, Tl, Fe and Al. Six additions were employed for each analyte and the mean recovery and RSD calculated (Table 4). The results show that this method is applicable to the determination of these trace metals in uranium. The detection limit was calculated as the concentration equivalent to three times the standard deviation obtained with the experimental blank (1 mol dm⁻³ nitric acid) for the different analytes, and expressed as concentration with respect to the mass of uranium in the U₃O₈ sample. The experimental blanks obtained with the nitric acid were found to have common impurities of the order of 0.2–6 ng cm⁻³ and the rare earths less than 0.1 ng cm⁻³.

Detection limits are given in Table 4. The detection limits for the different elements were found to be at the ppb level, except for Fe and Al, for which they were at the sub-ppm level. In the determination of Fe and Al, the ICP-MS instrument was operated in the high-resolution mode to avoid spectral interference from ArO⁺ and N₂⁺, respectively (Figs. 2 and 3), and this resulted in poor sensitivities. For Fe, because ⁵⁷Fe, a minor isotope, was used for the measurement, the detection limit was poorer.

The results of the analysis of an IAEA standard reference material of U₃O₈ (SR-54) are given in Table 5, and show

good agreement with the certified values. Two secondary U₃O₈ standards prepared at the Bhabha Atomic Research Centre for use in spark-source mass spectrometry (SSMS) were analysed for the presence of REE and the results compared well with the SSMS values (Table 6).

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