Establishment and Validation of an Analytical Technique for Quantification of Trace Metallic Elements in Uranium-Zirconium Fuel Ingot Employing Time of Flight-based ICP-MS

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ABSTRACT

U-Zr alloys have potential use in low power or research reactors due to numerous advantages, while U-Pu-Zr alloys are considered a metallic fuel for fast breeder reactors. An analytical methodology was developed for the quantification of trace elements in U-Zr alloys by using inductively coupled plasma orthogonal acceleration time of flight mass spectrometry (ICP-oe-TOF-MS).

A dual solvent extraction technique was employed for matrix separation prior to analysis of the trace constituents by ICP-oe-TOF-MS. Zirconium was synergistically extracted by 2-thionyltrifluoroacetone (HTTA) in the presence of tri-butylphosphine oxide (TBPO) in 1,2-dichloroethane, while uranium was separated by the well-established tri-butylphosphate (TBP)/carbon tetrachloride (CCl_4) solvent extraction technique. In order to

validate the analytical methodology, recovery studies of the elements were carried out employing the standard addition technique, followed by analysis with ICP-MS.

Reproducible recoveries of $\geq 90\%$ were achieved for 17 elements (Al, Ba, Co, Cr, Cu, Ga, Ge, In, Mg, Mn, Ni, Rb, Rh, Sr, W, Y, and Zn) and $\geq 83\%$ for Cd and V due to their lower specification limits in the alloy. The detection limits for the interested elements were in the range $1\text{--}99\text{ }\mu\text{g kg}^{-1}$. The separation procedure was further validated for transition elements by an independent gamma spectrometry technique using carrier-free ^{51}Cr and ^{54}Mn tracers with recoveries of $>94\%$. The method was used for the determination of trace metallic elements in three U-Zr alloy samples by ICP-MS with the percentage relative standard deviation (1 σ) between 2–7 and $r^2 \geq 0.999$ for the individual element calibration plots.

stability at elevated temperatures, and ductility and malleability properties, zirconium is one of the few transition metal elements that has led to the development of U-Zr (5,6) and U-Pu-Zr (7,8) alloy fuels. U-Zr alloys are an important subset of U-Pu-Zr alloys, which are considered as metallic fuel for the fast breeder reactor (FBR) and integral fast reactor (IFR) concept (9). It has been reported that U-10 wt% Zr fuel had been irradiated in EBR II, USA (9) in early 1985.

The presence of trace impurities above certain specific limits in the fuel may affect its performance in the reactor by affecting the neutron economy and/or chemical and metallurgical properties. The possibility of forming activation products is also of concern (10). Therefore, chemical quality control (CQC) and quality assurance (QA) programs are required to meet the stringent specification needs of the fuel.

Inductively coupled plasma mass spectrometry (ICP-MS) is a well-known multi-elemental technique with high sensitivity, high throughput, low detection limits, and improved precision for trace impurity quantification of various materials (11–21). The chemistry involves quantitative dissolution of the refractory material, separation of the matrix elements, and quantitative recovery of trace elements. Sengupta et al. (22) employed inductively coupled plasma atomic emission spectrometry (ICP-AES) for the determination of trace elements in a U-Zr alloy where the total concentration of the matrices after separation was $> 0.1\%$. The

INTRODUCTION

Ideally, the most effective way of achieving high burn-up, lowering the doubling time, and increasing the breeding ratio in commercial power reactors is the use of metallic fuel with high fissile atom content. Though the use of metallic uranium fuel can serve the purpose, its use is limited due to dimensional changes occurring as a result of

irradiation and thermal cycling at elevated temperatures. Another good choice is the dispersion type of fuel (CERMET and METMET) with high uranium and/or plutonium content in the novel matrix of Zr, Ti, Al, Zr-Ti alloy, etc. (1–3). However, difficulties in fabricating dispersion fuel make their use restricted (1). Uranium-rich binary or ternary fuels (4) are the best possible candidates for reactor use to achieve the desired performance. From the point of neutron transparency, corrosion resistance, high thermal conductivity, dimensional

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reported technique utilized synthetic standard solutions of uranium and zirconium, and the validation by recovery studies was carried out without varying the concentration of the trace elements. Moreover, the detection limits of the trace elements were not mentioned in their report.

There was a need to carry out exhaustive studies so as to establish an analytical methodology for the quantification of trace amounts of metallic elements in actual U-Zr fuel ingot samples. It has been reported that zirconium, from HNO₃ medium, can be extracted by 2-thionyltrifluoroacetone (HTTA) in the presence of tri-butylphosphine oxide (TBPO) in 1,2-dichloroethane (23); the same method was extended for separating trace elements from the zirconium matrix in U-Zr alloy. The uranium content was reduced by the well-known tri-butylphosphate (TBP) /carbon tetrachloride (CCl₄) solvent extraction technique (24).

In the present work, systematic studies were carried out by taking a real sample of U ~6 wt% Zr fuel ingot and applying the dual separation procedure to bring down the overall matrix concentration to <50 µg mL⁻¹. The proposed method was used for the quantitative determination of 19 elements: Al, Ba, Cd, Co, Cr, Cu, Ga, Ge, In, Mg, Mn, Ni, Rb, Rh, Sr, V, W, Y, and Zn. As per IUPAC (25), and an important step in the process of introducing a new analytical procedure is its validation. For this purpose, recovery studies (spike recovery) for all of the elements were carried out employing the standard addition technique (26-30). Moreover, the separation procedure was further validated for transition elements by an independent gamma spectrometric technique (28, 31-32) employing the carrier-free radiotracers ⁵¹Cr and ⁵⁴Mn. The instrumental and method detection limits for the 19 analytes were also determined. The method was extended to the quan-

tification of trace impurities in three real samples by ICP-MS.

EXPERIMENTAL

Instrumentation

Inductively Coupled Plasma Mass Spectrometer

A Model Optimass 8000R inductively coupled plasma orthogonal acceleration time of flight mass spectrometer (ICP-oa-TOF-MS) (GBC, Australia) was used for the determination of trace elements in the U-Zr matrix. The mass analyzer has a mass range of 5-225 amu with a resolution (m/Δm at FWHM) of 500 in the low mass range and 1800 in the high mass range. The mass range has been calibrated for the time of arrival of singly charged species to the detector by taking standard solutions of the elements of m/e values 7.016(Li), 88.906(Y), 114.904(In), and 208.980(Bi). The mass spectrometer has a provision of deflecting the unwanted ions by the use of a 'smartgate' so that they do not reach the detector (21).

Sample introduction was carried out by pneumatic nebulization using a Meinhard® nebulizer together with a cyclonic-type baffled spray chamber and a Fassel-type quartz torch. The solution

flow rate was controlled by a peristaltic pump with a sample uptake rate of 1 mL min⁻¹. The instrumental operating conditions are given in Table I. The monitored isotopes of the analytes under consideration are tabulated in Table II.

To minimize instrumental drift, data acquisition was done 1 hour after plasma ignition (33).

Gamma Spectrometer

A 3"x3" NaI(Tl) well-type detector coupled to a Multichannel Analyzer (Electronic Corporation of India Limited) was used to quantify the tracers in the final raffinate. The detector has a resolution of 46.2 keV (FWHM) at 661 keV of ¹³⁷Cs.

Reagents and Solutions

Suprapur® acids (Merck, Darmstadt, Germany) and de-ionized water, obtained with a Milli-Q™ system (18 MΩ, Millipore Corporation, Bedford, MA, USA), were used for preparation of the standards and sample solutions. Stock solutions of individual elements, each of 1000 mg L⁻¹ (Alfa Aesar, Ward Hill, MA, USA), were used for preparing the multi-element standard solutions and for standard additions by appropriate dilution with 1%

TABLE I
ICP-MS Operating Parameters

Nebulizer	Meinhard (pneumatic/concentric)
Spray chamber	Baffled (cyclonic type)
RF power	1220 W
Frequency	27.2 MHz
Cool gas flow rate	11.5 L min ⁻¹
Auxiliary gas flow rate	0.55 L min ⁻¹
Nebulizer gas flow rate	0.9 L min ⁻¹
Sample uptake rate	1.0 L min ⁻¹
Integration time	30 ns
Detector mode	Dual (PC/Analog)
Acquisition time	5 sec
Reflected power	2 W
Plasma intensity	98.8%

HNO₃, HTTA (Sigma-Aldrich, Germany), TBPO (Sigma-Aldrich, Germany), and TBP (Merck, Darmstadt, Germany) were used as organic extractants in the solvents 1,2-dichloroethane (Merck, Darmstadt, Germany) and CCl₄ (Merck, Darmstadt, Germany) for matrix separation. Two carrier-free tracers (⁵¹Cr and ⁵⁴Mn) were obtained from the Board of Radiation and Isotope Technology (BRIT, Mumbai, India) on request in solution form. Eppendorf® micropipettes were used for handling the solutions. Teflon® PFA beakers and Nalgene Teflon® PFA funnels were used for preparation of the sample solutions. The solutions were made up in Nalgene® PP volumetric flasks.

Matrix Separation for Trace Element Quantification by ICP-*oa*-TOF-MS

The U-Zr alloy turnings were first washed with CCl₄ and acetone and dried to remove any organic contamination which may have originated during scraping of the ingots to prepare turnings. Then, about 0.3 g of U-Zr alloy sample in duplicate was accurately weighed and transferred to the Teflon® PFA beakers. The sample was dissolved using concentrated HNO₃ + 0.05% HF under an IR lamp. Then, the solution was evaporated to near

dryness and made up to 10 mL volume in 6M HNO₃. This solution was subjected to 1:1 solvent extraction using 0.3M HTTA + 0.3M TBPO in 1,2-dichloroethane. The extraction was repeated three times to ensure that the zirconium concentration in the aqueous solution is minimized. The resulting solution was diluted to 15 mL with Milli-Q™ water so that the nitric acid concentration in the resulting solution was 4M. Consequently, the uranium content in this solution was reduced by conventional 1:2 solvent extraction using 30% TBP in CCl₄ by employing three contacts. Finally, the raffinate was made up in 25 mL 1% HNO₃ for analysis of the trace constituents (Ba, Be, Co, In, Ga, Ge, Rb, Rh, Sr, V, Y, Zn) and further diluted to 25 times for analyzing Al, Cr, Cu, Mg, Mn, Ni, and W by ICP-MS. The need for further dilution arose from the fact that these latter seven elements are present at higher levels in the alloy. The uranium and zirconium content in the final raffinate was qualitatively determined after appropriate dilution by VG Plasma Quad PQ II (V.G. Elemental, Winsford, Cheshire, England) inductively coupled plasma quadrupole mass spectrometer (ICP-QMS).

Recovery Studies of the Trace Elements by ICP-*oa*-TOF-MS Employing the Standard Addition Technique

The standard addition method was utilized to investigate any loss or uptake of the analytes during the chemical separation process. About 1.5 g of ingot turnings was dissolved and made up to 50 mL in 6M HNO₃. Equal volumes (10 mL) of this stock solution were taken in four separation funnels. Varying amounts of the elements under investigation were added from their individual stock solutions to the three separation funnels, while one served as the matrix blank. The standard additions were carried out in such a way so as to vary the concentration of the elements around their specification range. The specifications of 10 elements (Al, Cd, Co, Cr, Cu, Mg, Mn, Ni, V, and W) were arrived at for the metallic fuels based on the experience attained from operating thermal (Pressurized Heavy Water Reactors) and fast (Fast Breeder Test Reactor) reactors in India. For elements, which have not been specified in the alloy, the addition was done in such a manner that it corresponds to a value around the vicinity of the matrix blank; the upper limit was fixed between four to 10 times that of the lower limit.

The solutions were subjected to the dual solvent extraction procedure, followed by analysis of the raffinate five times by ICP-*oa*-TOF-MS. Two such duplicate measurements were carried out.

Recovery Studies by Gamma Spectrometry

Gamma spectrometry is an independent analytical technique which does not suffer from isobaric interferences like ICP-MS. Carrier-free radiotracers, namely ⁵¹Cr and ⁵⁴Mn, were employed to further validate the separation procedure. Three stock solutions were prepared by

TABLE II
Elemental Isotopes Monitored by ICP-*oa*-TOF-MS

Element	Isotope Selected	Abundance (%)	Element	Isotope Selected	Abundance (%)
Al	²⁷ Al	100	Mn	⁵⁵ Mn	100
Ba	¹³⁸ Ba	71.70	Ni	⁶⁰ Ni	26.1
Cd	¹¹¹ Cd	12.8	Rb	⁸⁵ Rb	72.17
Co	⁵⁹ Co	100	Rh	¹⁰³ Rh	100
Cr	⁵² Cr	83.8	Sr	⁸⁸ Sr	82.58
Cu	⁶³ Cu	69.17	V	⁵¹ V	99.75
Ga	⁶⁹ Ga	60.1	W	¹⁸² W	26.3
Ge	⁷² Ge	27.4	Y	⁸⁹ Y	100
In	¹¹⁵ In	95.7	Zn	⁶⁶ Zn	27.9
Mg	²⁴ Mg	78.9			

adding these tracers to the solutions containing natural chromium and manganese so as to have a specific count rate of $3.0\text{--}5.0 \times 10^6$ CPM mL⁻¹. The overall concentrations of the individual elements were maintained at 7.5, 15, and 30 µg mL⁻¹ by varying only the natural isotope concentration. Three aliquots of 1 mL from the first, second, and third stock solutions were added to three separate U-Zr sample solutions (0.3 g in 10 mL 6M HNO₃) and treated in the same manner as discussed above for the chemical separation. The separated solutions were made up to 25 mL in 4M HNO₃. Three aliquots each of 0.25 mL from these separated solutions were taken in separate counting tubes, made up to 2 mL by adding 4M HNO₃, and taken for counting (marked as sample 1, 2, and 3). For reference, 0.01 mL was aliquoted from the individual stock solutions, taken in a separate counting tube, and diluted to 2 mL with 4M HNO₃. The reference and sample counting tubes of three sets were counted five times in the NaI(Tl) detector. Three such replicate tracer experiments were carried out. These tracers have several characteristic gamma energies, and the abundant ones were selected. The selected energies of various tracers along with their abundances are given in Table III.

RESULTS AND DISCUSSION

The use of the dual solvent extraction technique employing HTTA+TBPO in 1,2-dichloroethane and TBP in CCl₄ ensures apprecia-

TABLE III
Characteristic γ-Energies and Abundances of Radiotracers

Radio-tracer	Gamma Energy (MeV)	Gamma Ray Abundance (%)
⁵¹ Cr	0.320	9.83
⁵⁴ Mn	0.835	99.98

ble reduction of Zr and U concentration in the final raffinate with sound recoveries for the 19 elements (Al, Ba, Cd, Co, Cr, Cu, Ga, Ge, In, Mg, Mn, Ni, Rb, Rh, Sr, V, W, Y, and Zn) by ICP-oe-TOF-MS. The separated solution was also analyzed for U and Zr by ICP-MS (PQ2 plus, V.G., U.K.). It was found that the extraction reduces the total matrix concentration in the final separated solution to <50 µg mL⁻¹, yielding a decontamination factor of ~10⁵. Due to the non-availability of an appropriate certified reference material (CRM) containing the elements under examination in the U-Zr matrix, recovery studies were carried out by the standard addition technique and an independent gamma spectrometry technique using radio tracers to ascertain and establish the analytical procedure.

The recovery studies of the 19 elements by standard addition were carried out by adding appropriate amounts of the elements in an actual U-Zr alloy sample as the matrix. The results of this exercise are summarized in Table IV. The addition of the elements was done in such a way so as to vary their concentration around their specification limits which had been arrived at as a result of experience gained from research and a Fast Breeder Test Reactor operation. Due to non-uniform specification limits of these elements, some elements could be determined after the initial dilution, but further dilution was required for other elements present at higher concentrations. It can be seen from Table IV that the recoveries of all of the elements are reproducible, and the extent of recovery is ≥90% for 17 elements and ≥83% for Cd and V. Since the latter two elements have lower specifications in the alloy, loss during chemical processing and instrumental uncertainties at low concentration levels may be responsible for limiting the recovery of these two elements. The

precision indicated in the table is the overall precision calculated by propagation of error, taking into account both the external (N=2) as well as the internal (N=5) standard deviation.

From the recovery studies by standard addition it is seen that the present methodology has been validated for the quantification of 19 trace elements in the U-Zr alloy. However, it was desired to validate the separation procedure by an independent analytical technique. In this direction, recovery studies with an independent gamma spectrometric technique using ⁵¹Cr and ⁵⁴Mn as tracers was employed. The interference-free maximum abundant gamma energies of these tracers were monitored by NaI(Tl) detector. Here too the concentrations of the elements were varied, and the results are given in Table V. Recoveries of >94% were achieved, thereby enhancing our confidence in the separation procedure employed for the quantification of 19 trace elements by ICP-MS.

Limits of Detection

The detection limit is a key factor in any analytical technique and decides a minimum margin below which quantification of an analyte is not possible. The detection limits for both of the instruments and methods were studied under optimal experimental conditions (23). A blank solution comprising all of the reagents used for the dissolution of 0.3 g of U-Zr alloy was subjected to the separation procedures and made up to 25 mL volume in 1% (v/v) HNO₃, followed by mass spectrometric analysis. This solution was used for the determination of the method detection limit (MDL). The instrumental detection limit (IDL) for these elements was determined using 1% (v/v) HNO₃. Both the MDL and IDL, based on three times the standard deviation of the blank, are listed in Table VI (N=10). The limits of quantification

TABLE IV
Results for Recovery Studies
by Standard Addition Employing ICP-*oa*-TOF-MS
Sample solution= 25 mL;
Those further diluted 25 times are marked with ^a. (N= 10)

Element	Specifi- cation ($\mu\text{g g}^{-1}$)	Added Amount (μg)	Recovered Amount (μg)	Percentage Recovery (%)
Al ^a	150	0	19.1 $\pm$ 0.5	--
		18.75	38.0 $\pm$ 0.6	101 $\pm$ 4
		37.5	59.6 $\pm$ 1.8	108 $\pm$ 5
		75.0	96.0 $\pm$ 1.5	103 $\pm$ 2
Ba	--	0	1.05 $\pm$ 0.02	--
		1.5	2.43 $\pm$ 0.04	92 $\pm$ 3
		7.5	8.03 $\pm$ 0.30	93 $\pm$ 4
		15	14.7 $\pm$ 0.5	91 $\pm$ 3
Cd	1	0	0.15 $\pm$ 0.01	--
		0.125	0.26 $\pm$ 0.01	88 $\pm$ 11
		0.25	0.36 $\pm$ 0.02	84 $\pm$ 9
		0.5	0.58 $\pm$ 0.02	86 $\pm$ 4
Co	10	0	0.12 $\pm$ 0.02	--
		1.25	1.25 $\pm$ 0.01	90 $\pm$ 2
		2.5	2.47 $\pm$ 0.08	94 $\pm$ 3
		5.0	4.87 $\pm$ 0.20	95 $\pm$ 4
Cr ^a	75	0	4.70 $\pm$ 0.22	--
		12.5	17.1 $\pm$ 0.3	99 $\pm$ 3
		25	28.8 $\pm$ 0.8	96 $\pm$ 3
		50	53.7 $\pm$ 1.5	98 $\pm$ 3
Cu ^a	50	0	5.00 $\pm$ 0.28	--
		6.25	10.8 $\pm$ 0.1	93 $\pm$ 5
		12.5	15.7 $\pm$ 0.5	86 $\pm$ 5
		25	27.5 $\pm$ 1.3	90 $\pm$ 5
Ga	--	0	0.25 $\pm$ 0.02	--
		1.5	1.66 $\pm$ 0.08	94 $\pm$ 5
		7.5	7.14 $\pm$ 0.22	92 $\pm$ 3
		15	13.8 $\pm$ 0.24	90 $\pm$ 2
Ge	--	0	1.25 $\pm$ 0.05	--
		1.5	2.63 $\pm$ 0.06	92 $\pm$ 5
		7.5	8.31 $\pm$ 0.35	94 $\pm$ 5
		15	15.8 $\pm$ 0.6	97 $\pm$ 4
In	--	0	0.12 $\pm$ 0.01	--
		1.5	1.48 $\pm$ 0.04	91 $\pm$ 3
		7.5	7.32 $\pm$ 0.30	96 $\pm$ 4
		15	14.8 $\pm$ 0.3	98 $\pm$ 2
Mg ^a	50	0	14.6 $\pm$ 0.2	--
		6.25	21.0 $\pm$ 0.4	102 $\pm$ 7
		12.5	28.2 $\pm$ 0.8	109 $\pm$ 7
		25	40.2 $\pm$ 0.4	102 $\pm$ 2

(TABLE IV cont'd next page)

(LOQs) (10 σ) of the 19 elements for the method are listed in Table VII.

Sample Analysis

The technique was employed for the quantification of 19 trace elements by ICP-*oa*-TOF-MS in three samples collected from the different fractions of U-Zr ingots. The results of these analyses are summarized in Table VIII. The repeatability of the measurements (%RSD at 1 σ) varied between 2-7 for the elements under investigation. The regression coefficient (r^2) for the individual element calibration plots were ≥ 0.999 .

CONCLUSION

The proposed matrix separation method quantitatively separates trace amounts of the 19 elements from the U-Zr matrix and was measured by inductively coupled plasma orthogonal acceleration time of flight mass spectrometry (ICP-*oa*-TOF-MS) ICP-MS. Reproducible recoveries of $\geq 90\%$ were achieved for 19 elements (Al, Ba, Co, Cr, Cu, Ga, Ge, In, Mg, Mn, Ni, Rb, Rh, Sr, W, Y, and Zn) and $\geq 83\%$ for Cd and V due to their lower specification limits in the alloy. The detection limits for the interested elements were in the range 1-99 $\mu\text{g kg}^{-1}$. The use of dual solvent extraction reduces the total matrix concentration to tolerable limits of $<50 \mu\text{g mL}^{-1}$, which is ideal for ICP-MS analysis.

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TABLE IV (cont'd)
Results for Recovery Studies
by Standard Addition Employing ICP-*oa*-TOF-MS
[Sample solution= 25 mL;
Those further diluted 25 times are marked with ^a]. (N= 10)

Element	Specifi- cation ($\mu\text{g g}^{-1}$)	Added Amount (μg)	Recovered Amount (μg)	Percentage Recovery (%)
Mn ^a	50	0	2.03 $\pm$ 0.03	--
		6.25	8.10 $\pm$ 0.12	97 $\pm$ 2
		12.5	13.7 $\pm$ 0.2	93 $\pm$ 2
		25	28.3 $\pm$ 1.0	105 $\pm$ 4
Ni ^a	100	0	9.45 $\pm$ 0.57	--
		12.5	21.9 $\pm$ 0.6	100 $\pm$ 7
		25	34.8 $\pm$ 1.3	101 $\pm$ 6
		50	57.5 $\pm$ 1.6	96 $\pm$ 3
Rb	--	0	0.52 $\pm$ 0.01	--
		1.5	1.92 $\pm$ 0.08	93 $\pm$ 5
		7.5	7.57 $\pm$ 0.35	94 $\pm$ 5
		15	14.3 $\pm$ 0.2	92 $\pm$ 1
Rh	--	0	0.14 $\pm$ 0.03	--
		1.5	1.57 $\pm$ 0.07	95 $\pm$ 5
		7.5	7.20 $\pm$ 0.16	94 $\pm$ 2
		15	14.8 $\pm$ 0.3	98 $\pm$ 2
Sr	--	0	1.13 $\pm$ 0.02	--
		1.5	2.54 $\pm$ 0.07	94 $\pm$ 5
		7.5	8.34 $\pm$ 0.18	96 $\pm$ 2
		15	14.7 $\pm$ 0.4	90 $\pm$ 3
V	3	0	0.16 $\pm$ 0.02	--
		0.375	0.48 $\pm$ 0.01	85 $\pm$ 6
		0.75	0.81 $\pm$ 0.03	87 $\pm$ 5
		1.5	1.40 $\pm$ 0.01	83 $\pm$ 1
W ^a	100	0	10.5 $\pm$ 0.2	--
		12.5	21.9 $\pm$ 0.6	91 $\pm$ 5
		25	34.1 $\pm$ 0.6	94 $\pm$ 3
		50	56.8 $\pm$ 1.7	93 $\pm$ 3
Y	--	0	8.50 $\pm$ 0.12	--
		7.5	15.7 $\pm$ 0.3	96 $\pm$ 4
		15	22.4 $\pm$ 0.5	93 $\pm$ 3
		30	36.4 $\pm$ 1.3	93 $\pm$ 4
Zn	--	0	13.5 $\pm$ 0.3	--
		7.5	20.4 $\pm$ 0.2	92 $\pm$ 5
		15	27.2 $\pm$ 0.2	91 $\pm$ 2
		30	41.6 $\pm$ 1.2	94 $\pm$ 4

TABLE V
Analytical Data Obtained From Recovery Studies Employing Gamma Spectrometry
Using Various Concentrations of the Stock Solutions (N=15)

Using 7.5 µg mL ⁻¹ stock solution				
	Counts (min.) ⁵¹ Cr	(%) Recovery	Counts (min.) ⁵⁴ Mn	(%) Recovery
Reference	36630±250	—	30930±360	—
Sample 1	35970±320	98	29130±250	94
Sample 2	34850±410	95	29870±440	97
Sample 3	36210±230	99	30220±210	98
Using 15 µg mL ⁻¹ stock solution				
Reference	38270±310	—	30660±410	—
Sample 1	36650±290	96	30020±210	98
Sample 2	37150±270	97	30110±300	98
Sample 3	37090±320	97	29480±330	96
Using 30 µg mL ⁻¹ stock solution				
Reference	36140±240	—	31440±290	—
Sample 1	34860±320	96	30260±230	96
Sample 2	35380±270	98	30490±330	97
Sample-3	35130±420	97	29710±290	94

TABLE VI
Instrument Detection Limits (IDL) and Method
Detection Limits (MDL) (N=10)

Element	IDL (ng L ⁻¹)	MDL (µg kg ⁻¹)	Element	IDL (ng L ⁻¹)	MDL (µg kg ⁻¹)
Al	74	99	Mn	22	16
Ba	15	15	Ni	200	56
Cd	32	8	Rb	19	4
Co	32	22	Rh	10	1
Cr	50	6	Sr	10	6
Cu	42	47	V	22	8
Ga	22	4	W	150	7
Ge	54	4	Y	12	2
In	12	1	Zn	20	9
Mg	17	23			

TABLE VII
Limits of Quantification (LOQ)
of the Analytes

Element	LOQ (µg kg ⁻¹)	Element	LOQ (µg kg ⁻¹)
Al	330	Mn	53
Ba	50	Ni	187
Cd	27	Rb	13
Co	73	Rh	3
Cr	20	Sr	20
Cu	157	V	27
Ga	13	W	23
Ge	13	Y	7
In	3	Zn	30
Mg	77		

TABLE VIII
Results of Three Different U-Zr Alloy Samples

Element	Sample I ($\mu\text{g g}^{-1}$)	Sampe II ($\mu\text{g g}^{-1}$)	Sample III ($\mu\text{g g}^{-1}$)	Element	Sample I ($\mu\text{g g}^{-1}$)	Sample II ($\mu\text{g g}^{-1}$)	Sample III ($\mu\text{g g}^{-1}$)
Al	65.2 $\pm$ 2.1	67.9 $\pm$ 2.4	65.3 $\pm$ 1.7	Mn	11.3 $\pm$ 0.4	9.14 $\pm$ 0.2	9.27 $\pm$ 0.34
Ba	3.67 $\pm$ 0.12	4.22 $\pm$ 0.14	4.63 $\pm$ 0.09	Ni	36.8 $\pm$ 2.2	34.3 $\pm$ 2.3	40.3 $\pm$ 2.9
Cd	0.64 $\pm$ 0.03	0.82 $\pm$ 0.05	0.84 $\pm$ 0.03	Rb	1.26 $\pm$ 0.05	1.83 $\pm$ 0.07	1.30 $\pm$ 0.07
Co	0.37 $\pm$ 0.02	0.34 $\pm$ 0.01	0.67 $\pm$ 0.04	Rh	0.52 $\pm$ 0.02	0.67 $\pm$ 0.04	0.48 $\pm$ 0.02
Cr	12.8 $\pm$ 0.6	14.7 $\pm$ 0.9	13.2 $\pm$ 0.9	Sr	3.77 $\pm$ 0.14	3.58 $\pm$ 0.24	3.14 $\pm$ 0.2
Cu	18.4 $\pm$ 1.2	17.7 $\pm$ 0.8	18.8 $\pm$ 1.1	V	1.04 $\pm$ 0.04	0.80 $\pm$ 0.02	1.25 $\pm$ 0.04
Ga	1.06 $\pm$ 0.03	0.88 $\pm$ 0.03	1.02 $\pm$ 0.03	W	33.6 $\pm$ 1.2	36.9 $\pm$ 1.9	32.7 $\pm$ 1.3
Ge	3.26 $\pm$ 0.14	3.16 $\pm$ 0.22	2.82 $\pm$ 0.17	Y	25.3 $\pm$ 0.8	28.4 $\pm$ 1.0	23.5 $\pm$ 1.5
In	0.45 $\pm$ 0.02	0.51 $\pm$ 0.01	0.44 $\pm$ 0.02	Zn	45.3 $\pm$ 1.3	46.1 $\pm$ 1.4	45.2 $\pm$ 2.0
Mg	44.7 $\pm$ 1.3	47.6 $\pm$ 1.2	45.5 $\pm$ 1.9				

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