Determination of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U in Zirconium Matrix by Inductively Coupled Plasma Mass Spectrometry Employing Microwave-Assisted Digestion and Matrix Separation by Synergistic Solvent Extraction

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INTRODUCTION

Zirconium is a valuable engineering material and used as a secondary metal for carrying out certain kinds of industrial processes (1). Its other widespread application is in the manufacture of nuclear reactor core components (2-5). Zirconium alloys are preferred as a clad both for boiling water and pressurized heavy water reactors/pressurized water reactors (BWRs/PHWRs/PWRs). Calandria vessels and coolant channels in PHWRs are based on certain unique properties widely discussed in the literature (6-8).

Zircaloy-2 contains Sn, Fe, Cr, and Ni as alloying elements and is used as a clad material in PWRs due to its excellent corrosion resistance in oxygenated high temperature water environment. In BWRs/PHWRs, under the reducing conditions with hydrogen over pressure, zircaloy-4 is preferred where the amount of Ni is reduced and compensated by Fe and Cr. Though the presence of these alloying elements increases the corrosion resistance properties of zirconium, their specification arises from the fact that these elements may deteriorate the performance of the alloy with time in reactor operating conditions if their concentration exceeds a certain limit (9-10). For instance, the formation of transition metal intermetallics (Zr_2Ni) accelerates the deuterium/hydrogen pickup, the presence of excess copper

ABSTRACT

This paper describes the development of an analytical methodology for the quantification of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U in a nuclear-grade zirconium matrix (ZrO_2 and zircaloy-2) by inductively coupled plasma mass spectrometry (ICP-MS). The samples were dissolved using microwave-assisted digestion. These nine elements were quantitatively separated from the zirconium matrix by synergistic solvent extraction using HTTA and TBPO in 1,2-dichloroethane.

To ascertain and establish the analytical procedure and its applicability in the concentration range of interest, recovery studies were carried out by standard addition for each of these elements so as to cover their specification range in nuclear-grade zirconium alloys. The analytical methodology was further validated by analyzing SRM NIST 360b.

Recoveries of >90% were achieved for the nine elements in the specification range of nuclear-grade zirconium alloys. The percentage relative standard deviation ($N=10$) of these determinations was 6.0, 9.0, 8.0, 10.0, 7.0, 8.0, 7.0, 4.0, and 6.0 for V, Cr, Mn, Fe, Ni, Cu, Cd, Pb and U, respectively. The three sigma detection limits ($N=10$) were 1.93, 1.81, 1.98, 3.15, 2.06, 1.76, 1.13, 0.86, and 0.77 $\mu g\ Kg^{-1}$ for the respective elements.

enhances radiation embrittlement and sometimes the presence of alloying elements above a specified concentration may affect the ductility, strength, weldability, and hardness, etc., of the material. Although zircaloy-2 and zircaloy-4 have been used as structural materials in nuclear reactors, there is mounting evidence that these alloys show accelerated oxidation/high hydrogen pickup (hydrogen embrittlement) over long exposures in the reactors. This led to the development of Zr-Nb alloy, with Zr-2.5% Nb alloy being used as a structural material for pressure tubes of PHWRs and Zr-1% Nb as fuel cladding materials in PWRs. Absence of any significant transition metal intermetallics in Zr-Nb is probably one of the primary reasons for the low uptake of hydrogen.

It is known that impurities at parts per million (ppm) level concentrations in the bulk material could result in a significant reduction of material strength and transition of fracture mode from ductile to brittle (11). Due to the stringent specifications imposed by reactor chemistry on the components used from the point of sustaining the neutron economy, corrosion resistance, and mechanical properties, it is essential to limit the impurity/alloying elements within the stipulated range (12-16). Recently, we reported the quantification of rare earth elements in a zirconium matrix by ICP-MS (17). This paper extends the work to other important elements in a zirconium matrix whose accurate and precise determination is imperative.

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Numerous techniques have been reported for the determination of trace or alloying elements in zirconium matrices (6, 18-31). The detection limits employing spectroscopic techniques are often limited by the spectral interferences from the line-rich spectrum of the zirconium matrix.

Inductively coupled plasma mass spectrometry (ICP-MS) is a versatile multi-elemental technique with high sample throughput, high linear dynamic range, and low detection limits and has been employed for the determination of trace elements in a zirconium matrix (32-33). In conjunction with laser ablation, it has been used for the determination of Fe, Ti, and Mg in solid zircon (34). The challenge lies in quantitatively dissolving the refractory material, separating the matrix element Zr, and recovering the elements of concern quantitatively. Pandey et al. (35) employed ICP-MS for the determination of trace elements in zircaloy both in the presence of the matrix as well as after matrix removal by solvent extraction. They concluded that the results from simple sample dilution yielded inaccurate data for most of the elements, while the solvent extraction procedure for matrix removal was quantitative for some elements but poor for others.

Since zirconium alloys are refractory, conventional digestion procedures require a long time, and therefore microwave digestion with an evaporation system (Multiwave® 3000, Anton Paar, Graz, Austria) was employed in the present study. The result is complete dissolution of the matrix with minimum amount of reagent, attainment of low detection limits, and minimal method errors.

Because the concentration of certain elements in the zircaloy is in the trace/ultra-trace levels, it becomes essential to separate the zirconium matrix prior to their pre-

cise and accurate quantification by ICP-MS. There are numerous ways, such as solvent extraction, co-precipitation, ion exchange, solid phase extraction, etc. (1, 7, 36-45), to separate the matrix and reduce the total dissolved solid concentration to tolerable limits. A number of complexing agents (1, 46-48) are available for zirconium, but few would qualify for quantitative complexation with zirconium without affecting traces of these elements. Uranium is an important element which has a specification of 3.5 ppm (13-16) in nuclear-grade zirconium alloys as it undergoes fission in nuclear reactors. The fission products, especially iodine which is suspected to be the primary detrimental species (11), induce stress corrosion and cracking in zircaloy. Also, the presence of uranium above the specified limit enhances the long-term in-pile corrosion. The determination of uranium in a zirconium matrix has been reported using time-resolved laser fluorescence spectrometry, fluorimetric, volumetric techniques, etc. (23, 49-53). Its determination in a zirconium matrix by ICP-MS has, however, not yet been reported until this date.

It has been reported that titanium (IV) can be extracted from hydrochloric acid solutions by the onyltrifluoro acetone (HTTA) in the presence of tri-n-butylphosphine oxide (TBPO) in 1,2-dichloroethane (54). From this available information, and the fact that Ti and Zr belong to the same group and exhibit similar chemical characteristics, in the present study a synergistic extraction was developed for the removal of zirconium (IV) matrix from nitric acid medium using these reagents.

The proposed method was used for the quantitative determination of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U by ICP-MS in nuclear-grade zirconium dioxide and zircaloy-2 with satisfactory results. The

amount of zirconium in the extracted solution was found to be < 10 ppm, thereby making it an ideal separation technique.

Recovery studies were carried out by standard addition to ascertain and establish the analytical separation. Because the specifications of the individual elements vary not only among the different nuclear-grade zirconium alloys but, also, within each alloy, recovery studies by standard addition were conducted by adding standards of varying concentrations to these matrices to cover the entire range. The analytical methodology was further validated by using SRM NIST 360b zircaloy (National Institute of Standards and Technology, Gaithersburg, MD, USA) where the zirconium matrix was separated by the synergistic extraction discussed above, and the elements V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U were determined by ICP-MS.

EXPERIMENTAL

Instrumentation

A VG Plasma Quad PQ II (V.G. Elemental, Winsford, Cheshire, England) inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) was used. Sample introduction was carried out by pneumatic nebulization using a Meinhard concentric nebulizer, a double-pass Scott-type spray chamber cooled to 10 °C with a locally made recirculating chiller, and a Fassel-type torch. The solution flow rate was controlled by a peristaltic pump (sample uptake rate: 1 mL min⁻¹). The ICP-QMS conditions were optimized daily for maximum sensitivity and calibrated using a 100 ng mL⁻¹ tuning solution of Li, Be, Al, Ti, Co, Sr, In, La, Bi, Th, and U. A quadrupole mass analyzer having a mass range of 1-300 amu with a resolution of 0.3 amu was employed. The mass analyzer was operated in the peak hopping mode. The optimum operating

conditions of the instrument are given in Table I.

Reagents and Solutions

High purity reagents were used for preparation of the standards, and all solutions were prepared in de-ionized water obtained from a Milli-Q™ system (18 MΩ, Millipore, Bedford, MA, USA). Stock solutions of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U, each of 1000 mg L⁻¹ (Alfa Aesar, MA, USA), were diluted daily to obtain the working solutions. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 0.23 mol L⁻¹ HNO₃ (65% Suprapur®, E. Merck, Darmstadt, Germany). Standard solutions of diverse elements meant for instrument calibration were prepared by dilutions from 1000 mg L⁻¹ stock solutions. 40% Suprapur® hydrofluoric (Merck) was used in the sample dissolution. A 0.3M solution of theonyltrifluoroacetone (Aldrich, USA) and 0.3M tributylphosphine oxide (Aldrich, USA) in 1,2-dichloroethane (Merck) was freshly prepared for matrix separation. Eppendorf® micropipettes were used for handling of the solutions. Nalgene® PP measuring flasks and Nalgene® PP, 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.

Dissolution of the Sample and Matrix Separation

Nuclear-grade zirconium oxide powder and zircaloy-2 turnings were used. The turnings were washed with acetone followed by nitric acid for 10 seconds, rinsed with deionized water, dried in an oven at 110 °C for one hour, and then cooled in a desiccator. A microwave digestion system (Multiwave® 3000, Anton Paar, Graz, Austria), with an 8X rotor and a 100-mL Teflon vessel, was

TABLE I
ICP-MS Operating Conditions

Nebulizer	Meinhard (concentric; TR-30-A3)
Spray Chamber	Double Pass Scott-type
RF Power	1150 W
Frequency	27.12 MHz
Cool Gas Flow Rate	18 L min ⁻¹
Auxillary Gas Flow Rate	0.8 L min ⁻¹
Nebulizer Gas Flow Rate	1.0 L min ⁻¹
Sample Uptake Rate	1.0 mL min ⁻¹
Detector Mode	Dual (PC/Analog)
Integration Time	10 ms

TABLE II
Operating Conditions of Microwave Digestion System

Acid Mixture	Power (W)	Ramp (W/min)	Hold Time (min)	Cooling Time (min)
HF + H ₂ O	1200	66	30	30

employed for sample dissolution. As part of the instrument, an evaporating system with an 8EVAP rotor (connected to a scrubber system via a chemically resistant vacuum pump) was used for safe and odorless evaporation and the concentration of the aqueous sample solutions. The un-pulsed microwave power ensures soft and efficient drying without carbonization or contamination of the samples. Known weights of these samples (corresponding to ~100 mg of zirconium) in 8 replicates were taken in the Teflon vessels. The matrix was dissolved in 5 mL H₂O and 250 µL HF. The evaporating parameters of digestion are given in Table II.

After dissolution, the solutions were evaporated to near dryness, followed by addition of 1 mL concentrated HNO₃+1 mL H₂O, and evaporated again. This process was repeated twice to ensure the complete removal of hydrofluoric acid. This was followed by addition of 15 mL 6M HNO₃, then the contents were transferred from the microwave vessel to a 60-mL Nalgene PP Separating Funnel. The zirconium solu-

tion was extracted with an equal volume (15 mL) of 0.3M HTTA+0.3M TBPO in 1,2-dichloroethane after mechanical shaking of the separating funnel for about three minutes.

The extraction process was repeated three times to ensure zirconium concentration in the aqueous solution is minimized. Each matrix-free solution was evaporated to near dryness, followed by addition of 1 mL of concentrated nitric acid; the resulting solution was evaporated again. Each of the solutions was made up in a 25 mL volumetric flask in 1% nitric acid. The solutions were then subjected to quantitative analysis by ICP-MS employing external calibration standards. Recovery studies were carried out to ascertain and establish the analytical separation. The analytical methodology was further validated by using SRM NIST 360b Zircaloy. The synergistic effect is due to the formation of 1:1:1 HTTA-TBPO-Zr(IV) complex (54). After solvent extraction, the amount of zirconium left behind in aqueous solution was estimated and found to be <0.001%.

VALIDATION OF THE PROPOSED METHOD

Recovery Studies by Standard Addition Method

For recovery studies, the matrices employed were nuclear-grade zirconium oxide powder and zircaloy-2 turnings. A known amount (corresponding to ~ 500 mg of zirconium) of each was taken in the six microwave vessels. The remaining two vessels contained only the acid solutions without the matrix and served as the process blank. The dissolution was carried out in the microwave digestion system, and the solutions were then brought into the 6M HNO₃ medium. The contents of the two vessels were mixed together and made up to 100 mL in 6M HNO₃, corresponding to 1000 mg of zirconium. Equal volumes (10 mL) of the solution were taken in six Teflon beakers. The recovery studies were designed to take into account the fact that the specifications of the individual elements not only vary among the different zirconium alloys but also within each alloy. This was done by adding varying amounts of each individual element in the corresponding matrices from 1, 10, 100 and 1000 µg/mL individual standard solutions of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U to the five beakers, while one was used as a matrix blank. Because the specification of cadmium in ZrO₂ and zircaloy-2 is very low (0.3–0.5 ppm), the recovery study for this element was carried out separately by taking 1 g of zirconium sample. For other elements, 100 mg (corresponding to the mass of zirconium) of the matrix was used for this exercise. All six solutions were subjected to a three-stage solvent extraction with 0.3M HTTA + 0.3M TBPO in 1,2-dichloroethane. The separated solutions were converted to 1% nitric acid medium (25 mL) and analyzed six times by ICP-MS. Percentage recoveries were then calculated and are listed in Tables III and IV

for zirconium oxide powder and zircaloy-2 turnings matrix. The precision (1σ) indicated in the table is the overall precision calculated by error propagation taking into account the external as well as the internal standard deviation.

Effect of Zirconium Concentration on Recovery

Recovery of the eight elements (V, Cr, Mn, Fe, Ni, Cu, Pb, and U) by ICP-MS was found to be reasonably good when 100 mg of the matrix was considered. However, it was necessary to take 1 g of the matrix for studying the recovery of Cd since its specification in nuclear-grade zirconium alloys is very low. This involved two separate analyses: one for Cd and another for other elements, thus consuming time and effort. With a view to avoiding duplication, it was therefore necessary to study the recovery of the eight elements when the zirconium matrix concentration was increased so that it is possible to quantitatively determine the nine elements in a single run. This was done by taking 1 g of nuclear-grade ZrO₂ and adding varying concentrations of these elements, followed by matrix separation and analysis. The results of the recoveries are listed in the Table V.

Analysis of SRM NIST 360b Zircaloy by Proposed Method

Approximately 1 g of SRM NIST 360b zircaloy was cleaned, dissolved, and the zirconium matrix separated by the process discussed above. The separated solution (1% nitric acid; 25 mL) was directly analyzed by ICP MS for Cd. Then, 2.5 mL of this solution was diluted to 25 mL for quantification of the other elements. The results of the analysis of the CRM are listed in the Table VI.

RESULTS AND DISCUSSION

The use of solvent extraction by HTTA and TBPO in 1,2-dichloro-

ethane ensures the quantitative extraction of zirconium into the organic phase. It was found that the extraction reduces the matrix concentration in the final separated solution to <10 µg mL⁻¹, yielding a decontamination factor of 10³. Since zirconium dioxide and its alloys are highly refractory, the use of conventional dissolution techniques may lead to the addition of contaminants. The use of microwave digestion for sample dissolution and the evaporator system for converting the solution medium followed by synergistic solvent extraction of zirconium resulted in the near quantitative (>90%) recovery of the nine elements V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U. The following isotopes of the nine elements were monitored by ICP-MS: ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁶⁰Ni, ⁶³Cu, ¹¹⁴Cd, ²⁰⁸Pb, ²³⁸U. Isobaric interference at mass number 56 due to ArO⁺ was corrected using the following interference correction equations:

Total Counts at mass No. 58 =

$$\begin{aligned} & \text{Counts due to } ^{40}\text{Ar}^{18}\text{O} + \\ & \text{Counts due to } ^{58}\text{Ni} \end{aligned}$$

Counts due to ⁵⁸Ni =

$$\frac{68.08}{26.22} \times \text{Counts at mass No. 60}$$

Counts due to ⁴⁰Ar¹⁸O =

$$\begin{aligned} & \text{Total Counts at mass No. 58} - \\ & \frac{68.08}{26.22} \times \text{Counts at mass No. 60} \end{aligned}$$

Counts due to ⁴⁰Ar¹⁶O =

$$\frac{99.76}{0.2} \times \text{Counts due to } ^{40}\text{Ar}^{18}\text{O}$$

Counts due to ⁵⁶Fe =

$$\begin{aligned} & \text{Total Counts at mass No. 56} - \\ & \text{Counts due to } ^{40}\text{Ar}^{16}\text{O} \end{aligned}$$

To minimize instrumental drift, data acquisition was done one hour after plasma ignition (55).

TABLE III
Results of Recovery Study by Standard Addition in ZrO₂
(Amount of matrix = 100 mg -- with the exception of Cd, where 1 g of matrix was taken;
Volume = 25 mL in 1% HNO₃; N = 30.)

Analytes	Specification (ppm) in ZrO ₂	Added (µg)	Found (µg)	(%) Recovery*
V	50	0	0.1±0.04	-----
		0.5	0.6±0.02	100±9
		1	1±0.1	90±10
		2.5	2.4±0.1	92±4
		5	4.9±0.2	96±4
		10	9.5±0.4	94±4
Cr	100-200	0	1±0.1	-----
		5	5.5±0.3	90±6
		10	10±1	90±10
		20	20±1	95±5
		40	38±1	93±3
		50	49±2	96±4
Mn	50	0	0.4±0.04	-----
		1	1.3±0.1	90±10
		2.5	2.7±0.1	92±4
		5	5±0.3	92±6
		10	9.8±0.5	94±5
		20	19±1	93±5
Fe	150-1500	0	3.7±0.4	-----
		10	14±1	103±11
		50	53±4	98±8
		100	98±7	94±7
		150	155±7	100±5
		200	195±10	96±5
Ni	20-70	0	1.1±0.1	-----
		1	2.1±0.1	100±12
		2.5	3.5±0.1	96±5
		5	5.6±0.3	90±6
		10	11±0.6	99±6
		20	20±1	95±5
Cu	50	0	0.5±0.04	-----
		1	1.4±0.1	90±11
		2.5	2.8±0.2	92±8
		5	5.2±0.2	94±4
		10	10±1	95±10
		20	20±1	97±5
Cd (In this case, 1 g of ZrO ₂ was taken)	0.3-0.5	0	0.1±0.02	-----
		0.3	0.4±0.04	100±14
		0.5	0.6±0.03	100±10
		0.75	0.8±0.05	93±9
		1	1.0±0.1	90±10
		1	1.1±0.1	-----
Pb	26-100	0	1.1±0.1	-----
		1	2.0±0.1	90±14
		2.5	3.4±0.2	92±9
		5	5.5±0.3	88±6
		10	10±1	89±10
		20	19±1	90±5
U	3.5	0	0.1±0.01	-----
		0.1	0.2±0.01	100±14
		0.2	0.3±0.01	100±7
		0.5	0.6±0.02	100±4
		1	1.0±0.04	90±4
		1.5	1.5±0.1	93±7

*Recoveries after blank (from Zr matrix) correction.

TABLE IV
Results of Recovery Study by Standard Addition in Zircaloy-2
(Amount of matrix = 100 mg -- with the exception of Cd, where 1 g of matrix was taken;
Volume = 25 mL in 1% HNO₃; N = 30.)

Analytes	Specification (ppm) in ZrO ₂	Added (µg)	Found (µg)	(%) Recovery*
V	50	0	0.1±0.04	-----
		0.5	0.6±0.03	100±10
		1	1±0.1	90±10
		2.5	2.4±0.1	92±4
		5	4.9±0.2	96±4
		10	9.7±0.4	96±4
Cr	500-1500	0	0.9±0.09	-----
		10	10±1	91±10
		50	49±3	96±6
		100	93±5	92±5
		150	145±4	96±3
		200	187±4	93±2
Mn	50	0	0.4±0.03	-----
		1	1.4±0.1	100±10
		2.5	2.7±0.2	92±8
		5	5.2±0.3	96±6
		10	9.8±0.4	94±4
		20	19±1	93±5
Fe	700-2000	0	89±6	-----
		50	136±6	94±17
		100	179±9	90±10
		150	226±11	91±8
		200	282±11	97±6
		250	342±21	101±9
Ni	300-800	0	0.9±0.06	-----
		10	10±1	91±10
		20	20±1	95±5
		50	49±2	96±4
		75	71±3	93±4
		100	96±4	95±4
Cu	50	0	0.4±0.02	-----
		1	1.3±0.1	90±10
		2.5	2.7±0.2	92±8
		5	5.1±0.3	94±6
		10	9.6±0.4	92±4
		20	19±1	93±5
Cd (In this case, zircaloy-2 was taken)	0.3-0.5	0	0.1±0.01	-----
		0.3	0.4±0.03	100±10
		0.5	0.6±0.03	100±6
		0.75	0.8±0.04	93±5
		1	1.1±0.1	100±10
		1	1±0.04	-----
Pb	130	1	1.9±0.1	90±10
		2.5	3.3±0.1	92±4
		5	5.8±0.2	96±4
		10	10±1	90±10
		20	20±1	95±5
		0	0.1±0.01	-----
U	3.5	0.1	0.2±0.01	100±14
		0.2	0.3±0.03	100±15
		0.5	0.6±0.04	100±8
		1	1±0.06	96±6
		1.5	1.5±0.1	93±6

*Recoveries after blank (from Zr matrix) correction.

TABLE V
Results of Recovery Study by Standard Addition in ZrO₂
(Amount of matrix = 1 g, Volume = 25 mL in 1% HNO₃; N = 15.)

Analytes	Specification (ppm) in ZrO ₂	Added (μg)	Found (μg)	(%) Recovery*
V	50	0	1.3±0.1	-----
		5	6.1±0.3	96±6
		10	11±1	97±10
		25	25±2	95±8
		50	49±3	95±6
		100	95±5	94±5
Cr	100-200	0	10±1	-----
		50	56±4	92±8
		100	102±6	92±6
		200	200±10	95±5
		400	377±18	92±5
		500	485±19	95±4
Mn	50	0	3.2±0.2	-----
		10	13±1	98±10
		25	27±2	95±8
		50	50±3	94±6
		100	95±6	92±6
		200	195±10	96±5
Fe	150-1500	0	4.2±0.3	-----
		100	102±8	98±8
		500	484±30	96±6
		1000	1014±90	101±9
		1500	1443±100	96±7
		2000	1964±118	98±6
Ni	20-70	0	9.3±0.8	-----
		10	18±1	87±12
		25	32±2	94.8±9
		50	55±4	91±8
		100	105±8	96±8
		200	199±10	95±5
Cu	50	0	4.3±0.3	-----
		10	13±1	87±10
		25	27±2	91±8
		50	50±3	91±6
		100	98±6	94±6
		200	192±10	94±5
Cd	0.3-0.5	0	0.1±0.02	-----
		0.3	0.4±0.04	100±15
		0.5	0.6±0.03	100±7
		0.75	0.8±0.06	93±8
		1	1±0.05	90±5
Pb	20-100	0	9.8±0.6	-----
		10	19±1	92±12
		25	33±2	93±8
		50	56±3	92±6
		100	105±5	95±5
		200	197±8	94±4
U	3.5	0	1±0.05	-----
		1	1.9±0.1	90±11
		2	2.8±0.2	90±10
		5	5.8±0.3	96±6
		10	10±1	90±10
		15	15±1	93±7

*Recoveries after blank (from Zr matrix) correction.

The recovery studies of the nine elements by standard addition were carried out in zirconium dioxide and zircaloy-2; the results are summarized in Tables III and IV. The concentration of these elements was not only varied in the same matrix but also among the matrices. This was done to study the recovery of these elements in the specification range of nuclear-grade zirconium matrices as these elements have different specifications in ZrO_2 and zircaloy-2. To ascertain the effect of zirconium on the recovery of analytes and to that the technique is effective in reducing the matrix concentration to <0.001%, recovery studies were carried out for Cd (having low specification) by taking 1 g of zirconium. For other elements (having high specification), a 100-mg sample was taken. It was found that the recovery of these nine elements was on average >90% after matrix separation. Thereafter, the recovery studies of these nine elements were carried out by taking 1 g of the matrix. The results are listed in Table V where it can be seen that the recovery of all these elements is appreciably good and the method is applicable irrespective of sample size.

The analytical methodology was further validated by analyzing SRM NIST 360b zircaloy by ICP-MS after dissolution and removal of the matrix by the synergistic solvent extraction employing HTTA and TBPO in 1,2-dichloroethane. The results obtained are summarized in Table VI. It can be concluded that the proposed method is suitable for the determination of V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U in a zirconium matrix with satisfactory precision.

In CRM NIST 360b zircaloy, the concentrations of V, Pb, and U have not been certified but merely indicated. In the present investigation using a sensitive analytical methodology, it is now possible to assign

concentration values to the elements V, Pb, and U in CRM NIST 360b zircaloy. Using the present method, the concentration of Pb in NIST 360b zircaloy was $3.94 \pm 0.27 \mu\text{g g}^{-1}$. Pandey et al. (35) reported the value of Pb as $3.45 \pm 0.35 \mu\text{g g}^{-1}$ which is close to the one obtained in the present investigation, confirming the authenticity of our result. Further, the elements V and U were quantified by the present analytical methodology as 26.44 ± 1.31 and $1.9 \pm 0.1 \mu\text{g g}^{-1}$ which were not reported by Pandey et al.

The method detection limits (LOD) for the nine elements were studied under optimum experimental conditions (56-57). A blank solution comprised of all the reagents used for dissolution of 100 mg of zircaloy-2 (1 g in case of Cd) was subjected to the separation procedures and made up to a final volume of 25 mL in 1% (v/v) nitric acid. This solution was used for the determination of the detection limit. The detection limits, based on three times the standard deviation of the blank (N=10), and the

TABLE VI
Results of Recovery Study of Trace Metallic Impurities in CRM NIST 360b Zircaloy After Matrix Separation (N=30)

Elements	Expected Value ($\mu\text{g g}^{-1}$)	Experimental ICP-MS Value ($\mu\text{g g}^{-1}$)
V	<30 ^a	26.44±1.31
Cr	1000±100	999±66
Mn	10±5	9.55±0.52
Fe	2100±100	2114±20.36
Ni	25±10	30.31±2.42
Cu	20±10	20.5±1.6
Cd	<1	0.39±0.3
Pb	<30 ^a	3.94±0.27
U	2 ^a	1.9±0.1

^a These are not certified, but given as additional information on the composition.

instrumental detection limits (3σ) for these elements (determined by taking 1% Suprapur® nitric acid) are listed in Table VII.

The reproducibility of the method was evaluated for 10 measurements of a 25-mL solution containing 1 μg of V, Mn, Cu, Pb and U, 10 μg of Cr, Ni in 100 mg of zircaloy-2 and 0.5 μg of Cd in 1 g of zircaloy-2. The percentage relative standard deviation (%RSD) of these determinations are given in Table VIII.

TABLE VII
Results of Method Detection Limit (N=10) and Instrumental Detection Limit (N=10)

Elements	MDL ^a ($\mu\text{g Kg}^{-1}$)	IDL ^b ($\mu\text{g L}^{-1}$)
V	1.93	0.19
Cr	1.81	0.22
Mn	1.98	0.26
Fe	3.15	0.41
Ni	2.06	0.28
Cu	1.76	0.18
Cd	1.13	0.13
Pb	0.86	0.08
U	0.77	0.06

^a MDL = Method Detection Limit.

^b IDL = Instrumental Detection Limit.

TABLE VIII
Results of (%) Relative Standard Deviation

Elements	(%) RSD
V	6.0
Cr	9.0
Mn	8.0
Fe	10.0
Ni	7.0
Cu	8.0
Cd	7.0
Pb	4.0
U	6.0

CONCLUSION

The method proposed effectively separates the elements V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U from the zirconium matrix and quantitatively measures these nine elements by inductively coupled plasma mass spectrometry (ICP-MS). Use of synergistic solvent extraction by HTTA and TBPO in 1,2-dichloroethane reduces the matrix concentration to tolerable limits of $<10 \text{ mg L}^{-1}$. Using this analytical methodology, it is now possible to assign concentration of the elements V, Pb, and U in NIST 360b zircaloy as 26.44 ± 1.31 , 3.94 ± 0.27 , and $1.9 \pm 0.1 \text{ } \mu\text{g g}^{-1}$. The limits of quantification (10σ) of the present method for the nine elements (V, Cr, Mn, Fe, Ni, Cu, Cd, Pb, and U) are 6.4, 5.9, 6.5, 10.4, 6.8, 5.8, 3.7, 2.8, and $2.5 \text{ } \mu\text{g Kg}^{-1}$ of zirconium, respectively.

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