

# Selective matrix removal and ICP-OES determination of trace uranium, rare earth elements and yttrium in zircon minerals

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**Abstract** In this paper an accurate and highly reproducible separation method for determination of trace amounts of uranium and rare earth elements (La–Lu and Y; abbreviated as REEs) in the refractory zircon mineral concentrates by inductively coupled plasma-optical emission spectrometer (ICP-OES) is described. The precipitation method used for separation of zirconium is simple, selective, rapid and environmental friendly. All the 16 geochemically important analytes were determined in a single solution with marginal improvement in detection limits (1.2–4.5 times) after separation. The method was validated by analyzing certified reference materials.

**Keywords** Zircon mineral · Separation · ICP-OES · Uranium · Rare earth elements

## Introduction

Zirconium, an industrially important metal with outstanding physical and chemical properties, used in nuclear applications (with low neutron cross section  $\sigma = 0.18$  barns) is obtained from the heavy zircon mineral available in the

beach sands [1, 2]. In nuclear industry,  $ZrO_2$  is used as a basic raw material for the fabrication of clad material such as zircalloys and also for the fabrication of the metallic fuel alloys such as U–Zr, U–Zr–Al, U–Pu–Zr etc. Zirconium when alloyed with niobium (zircaloy-2) is highly corrosion resistant and hence used in manufacturing components (nuclear fuel cladding material and core components) of a nuclear reactor mainly due to its properties; resistance to embrittlement and stability under elevated temperatures and excellent heat transfer characteristics [3]. Zircons are also geochemically important as it is an accessory mineral that crystallizes from compositionally diverse magmas and hydrothermal solutions. Zirconium is always associated with hafnium which is a neutron poison. In addition, zircon incorporates a few trace elements like uranium, thorium, barium, strontium, lead, REEs etc. in its matrix. They generally survive weathering and transport. This refractory nature of zircons allows preservation of age information through post crystallization geological events [4]. Some of these impurities such as Ce, Sm, Eu, Dy, Gd, Cd, B, Ag, Pb, V, Cr, Sn etc., have stringent specification limits in nuclear grade zirconium and careful control of these constituents at each stage of the fuel fabrication is essential from the neutronics point of view. Because the impurity contents greatly affect the properties of the metals and their alloys, the determination of these elements at trace and ultra-trace levels in the major zirconium matrix is very significant for the quality assurance [5].

REEs in zircons is determined and reported by many techniques like ICP-OES [6], ICP-MS [7], ETV-ICP-OES [8] etc. Since the mineral is refractory in nature, non-destructive analysis by ion microprobe, neutron activation [9], EDXRF [10, 11] etc. are preferred over the tedious chemical dissolution and analysis. However, destructive decomposition/dissolution of the refractory sample in

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aqueous media and analysis by ICP-OES has distinctive advantages over the non-destructive methods such as reduction/elimination of matrix effects on analytes and improved detection limits.

Many methods are reported for separation of REEs and U from the zirconium matrix like selective co-precipitation as their fluoride or oxalate, solvent extraction [12, 13], cation exchange chromatography [14] etc. However, it is known that during precipitation of fluoride and oxalate, zirconium is not completely separated. Hence, a rapid and effective method for complete removal of interfering zirconium matrix from the sample solutions prepared for determination of REEs and U in zircons by ICP-OES accurately has been developed.

In this reported work, zircon samples were decomposed and dissolved by high temperature fusion with a flux. The major matrix element, zirconium, was selectively precipitated as zirconyl phosphate and was removed completely. Uranium and REEs were determined in the filtrate by ICP-OES with better accuracy, precision and improved detection limits as compared to the results obtained by analysing solutions containing interfering matrix elements. The method was validated by analyzing CRMs and was applied to real zircon mineral concentrates.

## Experimental

### Chemicals and reagents

All the chemicals used such as  $\text{KHF}_2$ , NaF, were of GR Aldrich grade,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$  and ammonia solution were of Excelar grade procured from Fisher Scientific, India and for all dilutions Milli-Q (Millipore) water was used.

Elemental Calibration standard solutions were prepared from high purity metals/oxides procured from Alfa Aesar, Johnson and Matthey, U.K. A stock solution with a concentration of 1 mg/mL was prepared and kept and subsequently diluted keeping 3 % (v/v) HCl for instrument calibration as and when required.

### Instrumentation

#### ICP-OES

All emission intensity measurements were made using the radial viewing ICP-OES model Ultima 2 (Horiba Jobin-Yvon, France) equipped with a crystal controlled RF generator of 40.68 MHz and a monochromator (focal length 1.0 m) employing ruled back to back grating of 4320 and 2400 grooves/mm. The sample introduction system had a concentric glass nebulizer and cyclonic spray chamber incorporated with a sheath gas device. Argon gas was

humidified before its introduction to the spray chamber. Back ground corrections were applied wherever necessary. The spectrometer was calibrated with mixed elemental standard solutions (0, 1 and 10  $\mu\text{g/mL}$ ).

#### Fluorimeter

An optical fluorimeter (Galvanek–Morrison type) model FL6224A, ECIL, India with 365 nm excitation source and was used for fluorescence intensity measurements during extraction fluorimetry. The instrument was equipped with filters for wavelength selection and PMT detector kept directly above the sample pellet. The fluorimeter was calibrated with pure uranium standards (as  $\text{U}_3\text{O}_8$ ; 0.02, 0.05 and 0.1  $\mu\text{g}$ ) added to platinum crucible (0.4 mL capacity) and fused with 0.4 g flux.

### Procedure

#### Dissolution of zircon minerals

0.500 g of the zircon sample (–200 mesh) was initially mixed with 2.5 g of  $\text{KHF}_2$ –NaF flux mixture (3:1) in a dry platinum crucible and fused on a low temperature flame till it is completely melted. The crucible was closed with the lid and returned to the flame for fusion. The mixture was swirled intermittently and mixed thoroughly for complete attack. After obtaining a clear melt, it was cooled and allowed to solidify. The fused mass was wetted with 2.0 mL concentrated  $\text{H}_2\text{SO}_4$  and heated till copious white fumes emerged and subsided, for complete removal of fluoride. The crucible and the contents were transferred to a beaker containing 5 mL, 12 M HCl and Milli-Q water for dissolution. Thus the final solution had 0.03 g/mL dissolved solids and acids. A set of ten zircon mineral samples was decomposed and dissolved in about 2 h.

#### Pellet fluorimetric determination of uranium (extraction fluorimetry) [15]

An aliquot of 3 mL was drawn from the above solution and dried on a water bath. The dried residue was treated with 2 mL (16 M) nitric acid and finally dissolved in 3 mL 1.6 M  $\text{HNO}_3$  and quantitatively transferred to a shaking vial. A saturated solution of aluminium nitrate, 15 mL containing 30 g, was added followed by 10 mL of ethyl acetate. The vial was closed tightly with a stopper and mixed thoroughly and agitated vigorously for 120 s. The layers were allowed to separate and using an eppendorf micropipette 100  $\mu\text{L}$  of the organic layer was transferred into a clean platinum dish containing a few drops of water for stripping. The dishes were kept under a IR lamp for drying and 0.4 g of NaF– $\text{Na}_2\text{CO}_3$  (1:4) flux was introduced using a pelletizer. The

dishes were heated to 850 °C for fusion of the flux and the dried residue of the sample inside a pre-heated muffle furnace. The fused melt in the platinum dish was taken out and allowed to cool to room temperature and introduced to the optical-reflection fluorimeter for measurement of the intensity of uranium fluorescence against calibration standards processed and prepared similarly.

#### Separation of zirconium

A 25 mL aliquot of the solution obtained by fusion with NaF–KHF<sub>2</sub> was treated with 10 mL ammonia to precipitate hydroxides of the analytes which was separated and dissolved in 75 mL 4 M HNO<sub>3</sub>. Further 5 mL of 10 % H<sub>3</sub>PO<sub>4</sub> solution was added and stirred thoroughly for 10–15 min for precipitation of zirconium and other phosphates. The solution was filtered and the filtrate was made-up to 25 mL volume after volume reduction by evaporation. The U and REEs were determined by ICP-OES at appropriate wavelengths as listed in Table 1.

## Results and discussion

### Spectral interferences of Zr on analyte emission wavelengths

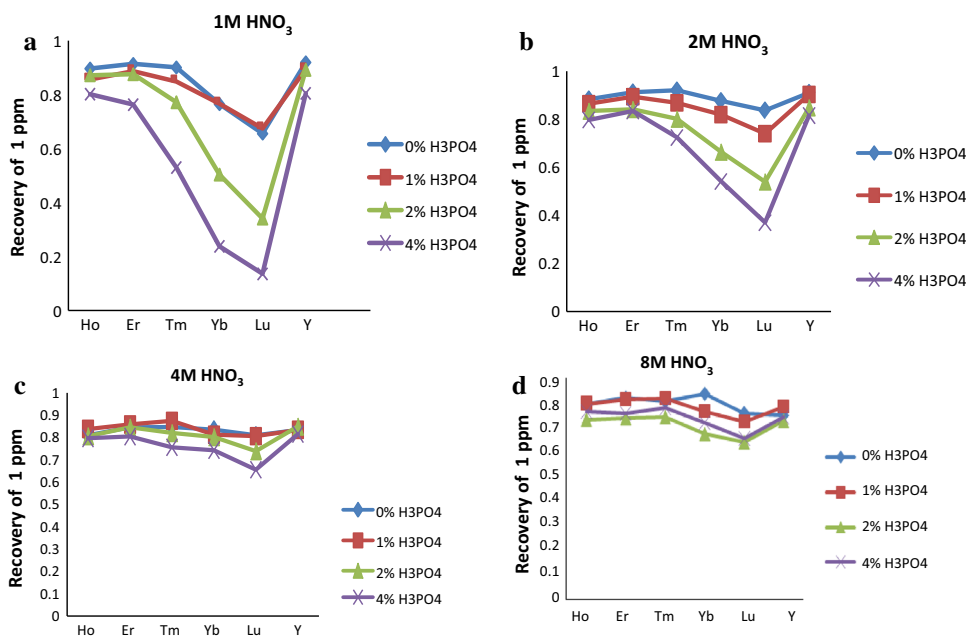
Zircon is a heavy, refractory mineral having trace quantities of U and REEs. When REEs and U were determined by ICP-OES without separation, spectral interference from the

major, emission line rich zirconium is inevitable. Although this affects each analyte emission wavelengths to a different extent, overall detection limits and precision were poorer. These interferences were evaluated by observing profiles of emission from each analyte. The major Zr gives emission line rich spectra and hence, causes spectral and physical interference during the analysis leading to erratic results. The dissolved solids increase the viscosity of the solution and alter the solution uptake rate of the concentric nebulizer and sample droplet size and their transportation rate to the plasma. The easily ionized elements (EIE) like Na, K etc. reduce the power available in the plasma and change its characteristics by reducing the electron density thereby the plasma is either extinguished or the emission from the analytes is greatly suppressed. This is evidenced by the reduction in the emission intensity of the analytes of interest (U and REEs) in the presence of synthetic zircon matrix and flux used to decompose the sample as given in Table 1. Recently [3, 16] studies were carried out and reported the spectral interference of zirconium on other analytes such as B, Cd, Sm, Dy, Gd, Na, Mg, Cr, Ca, V, Sn, Pb and Ag during ICP-OES analysis. They have categorized the interference into negligible, moderate and significant. In this study also an attempt was made to quantify the interference from the major zirconium on the most sensitive emission lines of uranium, REEs and Sc. It was found that Cerium emission line at 418.660 nm is highly interfered as the right hand background is highly elevated by Zr emission line. The left background of Ho at 345.600 nm was seen to be elevated. A direct on peak interference was observed on Tm

**Table 1** Wavelengths used in ICP-OES and extent of interference of 1 mg/mL Zr on the analytes

Elements	ICP-OES wavelengths (nm)	Contribution of 1 mg/mL Zr alone (µg/mL)	% Recovery of 1 µg/mL analytes doped in solution of 1 mg/mL Zr	% RSD
La	333.749	−0.032	90	2.4
Ce	418.660	0.690	157	13.5
Ce	413.765	0.002	100	2.3
Pr	422.293	−0.098	93	1.5
Nd	430.357	−0.260	73	1.9
Sm	442.434	0.001	93	1.8
Eu	381.965	0.002	95	2.2
Gd	364.620	−0.002	94	6.8
Tb	350.917	0.028	100	0.7
Dy	353.170	−0.010	96	0.7
Ho	345.600	−0.023	94	3.8
Er	349.910	−0.008	95	2.2
Tm	346.221	0.000	98	2.2
Yb	328.937	0.003	93	1.5
Lu	261.542	−0.025	95	2.2
Y	371.029	−0.009	96	2.2
U	409.014	−0.014	61	1.2

**Fig. 1 a–d** Effect of nitric acid and phosphoric acid on recovery of 1 ppm analytes



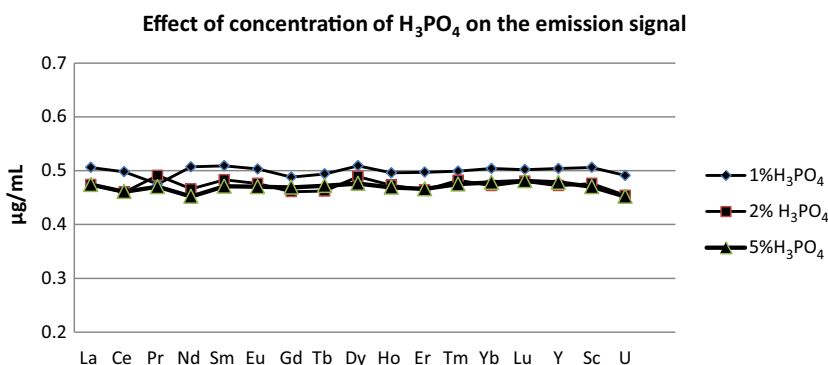
and Y. As illustrated in the Table 1, a recovery 60 % for uranium was only observed for 1 μg/mL level in presence of 1 mg/mL zirconium. The right background of the 409.014 nm emission line of uranium was elevated deteriorating the detection limits.

Therefore, for the accurate analysis of trace elements in zircon mineral matrix, separation of the major matrix component i.e., zirconium is mandatory. The routinely used separation method for Th and REEs is the co-precipitation of their fluorides along with calcium. Zirconium fluorides remain soluble in the solution. It is very tedious and slow as it involves digestion of the sample with HF for at least 12–15 h in a Teflon or platinum dish and subsequent filtration, ignition of the filter paper to recover the precipitate quantitatively and further dissolution of the residue with acid treatment. Moreover, the separation is not complete. The solubility product values reported [17] shows that as the atomic number increases REE-fluorides have increased solubility. Hence, a simpler and environmental friendly separation method was standardized as described below.

**Selective separation of zirconium with phosphoric acid**

All phosphates of titanium group precipitate in strongly acidic solutions which is important in the separation of Zr from other matrix elements. Hence, solutions containing zirconium could be decontaminated by precipitating it as phosphate by adding dilute phosphoric acid or sodium hydrogen phosphate. However, the major concern during this precipitation process is the loss of analytes by co-precipitation or exchange of ions with zirconium phosphate, an effective inorganic ion-exchanger [18] that possesses high stability at extreme temperature and ionizing radiation doses. Solubility product values reported by Firsching et al. [19] for trivalent REE-phosphates shows that their solubility in water is very low whereas in presence of 0.5 % (v/v) HClO<sub>4</sub> they are soluble even at 0.005 M concentration. Solubility of uranium in phosphoric acid solutions is well known and accepted. Hence, determination of U and REEs after precipitative separation of zirconium as its phosphate

**Fig. 2** Effect of concentration of H<sub>3</sub>PO<sub>4</sub> (1–5 %) on the emission signal of the REEs at 0.5 μg/mL



is being thought of. As the refractory zircon mineral concentrate samples were prepared by fusion with 2.5 g flux and sulfuric acid fuming and subsequent dissolution in dilute HCl, the solution contains high total dissolved solids. As the concentration of elements of interest was very low, dilution was not suitable for minimization of the effect of dissolved salts before the analysis. Hence, a hydroxide precipitation was performed prior to precipitation of zirconium to remove all matrix elements. During hydroxide precipitation (R<sub>2</sub>O<sub>3</sub>), the monovalent and divalent cations remain soluble whereas cations with higher valency are precipitated as their hydroxides. Though the R<sub>2</sub>O<sub>3</sub> precipitation is not selective, it is highly quantitative. The hydroxides were dissolved in 4 M HNO<sub>3</sub>. In order to optimize the concentration of HNO<sub>3</sub> during precipitation, it was varied from 1 to 8 M. The best recoveries were obtained from 2 M onwards for uranium and all REEs except Er, Tm, Yb and Lu. However, from 4 M HNO<sub>3</sub> onwards all elements gave more than 97 % recoveries. Hence, that was fixed for further studies.

A study as regards the extent of decontamination of zirconium from the solution and co-precipitation of the analytes was also conducted. It was found that at 1 % (v/v) H<sub>3</sub>PO<sub>4</sub> itself, the decontamination of Zr was complete (>99.99 %). Moreover, the recoveries of heavier REEs (Ho–Lu) were declining with the increase in the phosphoric acid content with same amount of HNO<sub>3</sub>. The results are given in the graphical form in the Fig. 1a–d. Elements from La to Dy did not show much variation in the recoveries at different acid conditions. Hence, results obtained for Ho–Lu and Y are only depicted in the figures. In all the figures, one line (0 % H<sub>3</sub>PO<sub>4</sub>) was also included for showing the effect of the presence of the zirconium on the emission intensity measurements with ICP-OES. Hence, optimum conditions for precipitation and accurate analysis by ICP-OES would be 1 % H<sub>3</sub>PO<sub>4</sub> in 4 M HNO<sub>3</sub>. At lower nitric acid concentration, on increasing the concentration of phosphate ions, the recovery of Dy, Ho, Er, Tm, Yb and Lu is decreasing. Larger the concentration of phosphate ions, lesser is the solubility of these elements. However, at higher concentration of nitric acid the solubility of these phosphates are better and thus the recovery is satisfactory. Th<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> and ScPO<sub>4</sub> etc. are insoluble and hence were found to get precipitated along with the zirconium phosphate and could not be determined.

**Effect of H<sub>3</sub>PO<sub>4</sub> during the ICP-OES emission intensity measurements**

To assess the effect of concentration of H<sub>3</sub>PO<sub>4</sub> on the emission intensity of the analytes at the stipulated wavelengths, concentration ranging from 1 to 5 % H<sub>3</sub>PO<sub>4</sub> solutions were prepared and doped with 0.5 µg/mL of

**Table 2** Repeatability measurements for a zircon sample using the proposed method

Sample	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	Y (µg/g)	U <sub>3</sub> O <sub>8</sub> (µg/g)
Expt-1	398	960	92	469	133	25	147	25	208	50	214	42	334	69	1629	655
Expt-2	390	940	89	447	130	24	145	24	201	50	201	41	326	65	1560	640
Expt-3	385	930	90	440	132	24	145	25	198	47	203	40	322	66	1582	645
Average	391 ± 6	943 ± 15	90 ± 1	452 ± 15	132 ± 1	24 ± 1	145 ± 1	25 ± 1	202 ± 5	49 ± 2	206 ± 7	41 ± 1	327 ± 6	67 ± 2	1590 ± 35	647 ± 8
% RSD	1.7	1.6	1.4	3.4	1.2	2.1	0.8	2.0	2.6	3.9	3.3	2.6	1.8	2.7	2.2	1.2

**Table 3** Comparison of Detection limits for analytes by ICP-OES before and after separation

Element	ICP-OES wavelengths (nm)	Before separation ( $\mu\text{g/mL}$ )		After separation ( $\mu\text{g/mL}$ )		Enhancement in DL
		BEC	DL	BEC	DL	
La	333.749	0.092	0.0028	0.032	0.0009	3.1
Ce	418.660	0.134	0.0048	0.131	0.0039	1.2
Pr	422.293	0.490	0.0147	0.378	0.0113	1.3
Nd	430.357	0.515	0.0155	0.114	0.0034	4.5
Sm	442.434	0.063	0.0019	0.047	0.0014	1.4
Eu	381.965	0.023	0.0007	0.020	0.0006	1.2
Gd	364.620	0.050	0.0015	0.030	0.0009	1.7
Tb	350.917	0.135	0.0040	0.076	0.0023	1.8
Dy	353.170	0.021	0.0006	0.016	0.0005	1.3
Ho	345.600	0.118	0.0035	0.049	0.0015	2.4
Er	349.910	0.096	0.0029	0.028	0.0009	3.2
Tm	346.221	0.042	0.0013	0.017	0.0005	2.5
Yb	328.937	0.026	0.0008	0.009	0.0003	2.6
Lu	261.542	0.047	0.0014	0.012	0.0004	3.6
Y	371.029	0.013	0.0004	0.009	0.0003	1.3
U	409.014	0.733	0.0220	0.414	0.0124	1.8
U	367.007	0.644	0.0193	0.416	0.0125	1.5

individual REEs and U. The emission intensities from these solutions were measured and corresponding concentrations were determined. It was found that at 1 %  $\text{H}_3\text{PO}_4$ , the recovery of analytes was more than 97 %. However, at higher concentrations of phosphoric acid the emission intensity of analytes were slightly reduced up to 90 %. This was attributed to the background elevation effects of phosphoric acid on the trace concentration of the analytes. The results are depicted in the Fig. 2 given below. Sc also was recovered satisfactorily.

### Analytical figures of merit

#### Reproducibility of the method

To establish the reproducibility of the proposed method of matrix removal of zirconium and determination of the analytes of interest in the filtrate by ICP-OES, one zircon sample was analyzed repeatedly ( $n = 3$ , each being part of a different fusion and separation run) and the variation in the results obtained were tabulated. The solutions were analysed against a blank and a standard which was matrix matched. It was found that an RSD varied from 0.8 to 3.9 % at sub-ppm level. The results alongwith the calculations are being presented in the Table 2.

**Detection limits** In order to compare the instrumental detection limits for the analytes before and after separation of the major matrix zirconium, two solutions were prepared

both containing 1  $\mu\text{g/mL}$  analytes and 1  $\text{mg/mL}$  of Zirconium. One solution was analyzed without separation and the other one was processed through the proposed separation procedure. An enhancement of maximum 4.5 was observed for Nd at 430.357 nm after the separation. A minimum enhancement of 1.2 was observed for Ce 418.660 nm as the presence of Zr enhanced the emission peak intensity as well as background intensity used for calculation of background equivalent concentration (BEC) and detection limit (DL) using Eqs. (1), (2) and (3).

$$\text{BEC} = \frac{\text{Concentration } (\mu\text{g/mL}) \times \text{Background intensity}}{(\text{Peak Intensity} - \text{Background Intensity})} \quad (1)$$

$$\text{Detection limit (DL)} = \text{BEC} \times 0.03 \quad (2)$$

$$\text{Enhancement in DL} = \frac{\text{DL before separation}}{\text{DL after separation}} \quad (3)$$

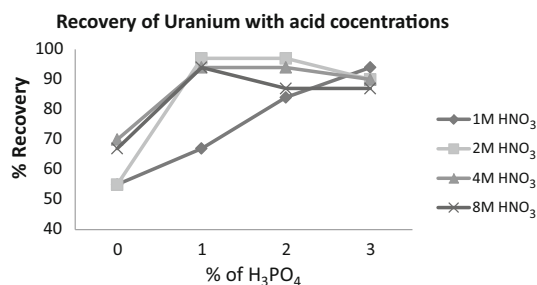
**Validation of the method** To check the accuracy of the proposed method two zircon standard reference materials BCS IGS-35 (British Geological Survey-Institute of Geological Sciences, U. K.) and CERAM 2CAS15 (obtained from Bureau of Analysed Samples Ltd., U.K.) were analysed and tabulated in Table 5. The values obtained were compared with those reported by Perkins et al. [20] for BGS IGS 35 by solution ICP-MS method and those reported by Singh et al. [7] for CERAM 2CAS15 after  $\text{KHF}_2$ -NaF fusion analysis by ICP-MS without separation.



**Table 4** Results obtained by the proposed method in comparison to the well established methods [7] and reported values [20]

Element	BCS IGS-35			CERAM 2CAS-15		
	Reported value [20] ( $\mu\text{g/g}$ )	Proposed method (mean $\pm$ SD) <sup>a</sup> ( $\mu\text{g/g}$ )	ICP-MS ( $\mu\text{g/g}$ )	Reported value [7] ( $\mu\text{g/g}$ )	Proposed method (mean $\pm$ SD) <sup>a</sup> ( $\mu\text{g/g}$ )	ICP-MS ( $\mu\text{g/g}$ )
La	82.8 $\pm$ 4.9	91 $\pm$ 2	89	41.6	40 $\pm$ 2	39
Ce	183 $\pm$ 4.6	181 $\pm$ 2	190	103.2	106 $\pm$ 3	110
Pr	19.8 $\pm$ 8.8	21 $\pm$ 1	22	10.8	13 $\pm$ 1	14
Nd	77.2 $\pm$ 5.4	83 $\pm$ 2	77	41.7	42 $\pm$ 2	39
Sm	19.4 $\pm$ 8.0	21 $\pm$ 1	20	13.2	15 $\pm$ 1	12
Eu	2.84 $\pm$ 8.4	2.4 $\pm$ 0.1	2	2.3	2.1 $\pm$ 0.1	2
Gd	33.1 $\pm$ 4.2	36 $\pm$ 1	34	25.7	27 $\pm$ 1	28
Tb	10.0 $\pm$ 4.2	7 $\pm$ 1	8	8.2	8 $\pm$ 1	10
Dy	103.4 $\pm$ 4.1	86 $\pm$ 2	88	85.9	77 $\pm$ 2	84
Ho	33.6 $\pm$ 4.7	29 $\pm$ 1	26	27.5	20 $\pm$ 2	26
Er	141.8 $\pm$ 3.0	123 $\pm$ 2	111	117.3	99 $\pm$ 3	118
Tm	28.9 $\pm$ 3.8	21 $\pm$ 1	18	24.5	22 $\pm$ 2	25
Yb	283.3 $\pm$ 7.0	229.5 $\pm$ 1.3	240	200	193.8 $\pm$ 2.2	200
Lu	51.0 $\pm$ 4.0	48.3 $\pm$ 0.6	50	41.0	35.5 $\pm$ 1.8	34
Y	1005 $\pm$ 1.7	1050 $\pm$ 7.5	1056	987	840 $\pm$ 5	900
U	272 $\pm$ 7.8	289 $\pm$ 3	264	240	264 $\pm$ 3	255

<sup>a</sup> Average of three independent replicates ( $n = 3$ )

**Fig. 3** Effect acids on the recovery of U<sub>3</sub>O<sub>8</sub>

Almost all the elements of interest were recovered quantitatively and the variations were within the experimental error allowed. The experimental precision obtained by the present method is better than those reported except for Y in BGS IGS 35. The method was further confirmed by analyzing the separated sample solutions by ICP-MS at specified mass numbers reported.

**Uranium determination** The routinely applied pellet fluorimetry for uranium determination in zircon sample require solvent extractive separation using ethyl acetate in presence of a salting out agent. The organic layer is stripped with water and dried in a platinum crucible. The dry residue is fused with NaF–Na<sub>2</sub>CO<sub>3</sub> flux at 850 °C and the fluorescence intensities are measured using an optical fluorimeter pre-

calibrated using the pure standard pellets fused and prepared side by side. This procedure though well established, is labour intensive involving solvent extraction, stripping, drying, fusion with a flux in a platinum crucible and require highly skillful personnel. Moreover, co-extracted elements like Th, Zr, Fe, Mn etc. act as fluorescence quenchers. Cuttita et al. [15] have studied and reported that during extraction fluorimetry of uranium, zirconium quenches the fluorescence drastically by 70–80 %. They have proposed the removal of zirconium with phosphate and subsequent solvent extraction of uranium which improved the results considerably.

During the determination of uranium by ICP-OES in those solutions containing higher concentration of zirconium, the background emission intensity at the analytical wavelengths used (409.014 and 367.007 nm) was enhanced. This in turn deteriorated the detection limits as illustrated in Table 3. The proposed method of zirconium removal as phosphate and further determination with ICP-OES is rather simple and rapid alternate for analysis of uranium in zircon samples (Table 4). The close agreement of the values obtained and that obtained through well established methods validated the results. Figure 3 shows the optimized acid concentrations for near complete recovery at 1 % phosphoric acid and 2 M HNO<sub>3</sub>.

#### Application to zircon mineral concentrates

The proposed method was applied to a few zircon mineral concentrate samples obtained from different beach sands of

**Table 5** Major elemental composition (%) of zircon concentrate samples analysed

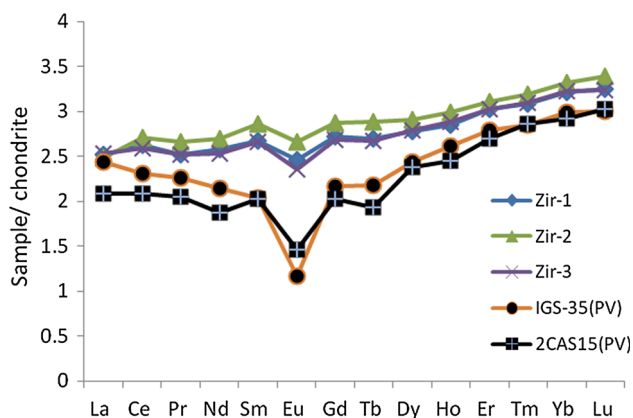
Sample code no.	ZrO <sub>2</sub>	HfO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	P <sub>2</sub> O <sub>5</sub>
Zir-1	60.85	1.23	32.56	0.26	0.21	0.81	<0.01	<0.02	0.38	0.20
Zir-2	59.56	1.13	31.41	3.27	0.94	0.38	<0.01	<0.02	2.70	0.62
Zir-3	59.35	1.15	33.38	0.65	0.45	0.86	<0.01	<0.02	0.88	0.31

**Table 6** Results (µg/g) obtained for zircon concentrate samples from beach sands of South India

Element	Zir-1		Zir-2		Zir-3	
	Proposed method (ICP-OES)	Reported method (ICP-MS)	Proposed method (ICP-OES)	Reported method (ICP-MS)	Proposed method (ICP-OES)	Reported method (ICP-MS)
La	113	98	105	108	40	38
Ce	342	317	365	369	259	247
Pr	37	36	36	37	19	24
Nd	203	206	213	228	173	149
Sm	62	58	86	86	81	69
Eu	7	6	20	8	20	6
Gd	122	135	117	129	115	218
Tb	22	20	20	24	21	40
Dy	195	183	196	190	188	177
Ho	53	48	49	50	49	45
Er	214	230	206	213	201	172
Tm	38	37	37	36	35	23
Yb	332	307	313	325	326	321
Lu	59	63	62	61	66	58
Y	1772	1824	1538	1631	1580	1590

Element/oxide	Zir-1		Zir-2		Zir-3	
	Proposed method (ICP-OES)	Extraction fluorimetry	Proposed method (ICP-OES)	Extraction fluorimetry	Proposed method (ICP-OES)	Extraction fluorimetry
U <sub>3</sub> O <sub>8</sub>	484	467	568	510	513	498

**Fig. 4** Chondrite normalized plot of the REEs in zircon samples after separation

eastern and western coasts of India. The major elemental composition data is presented in the Table 5 below. The values obtained for the REEs and U were in close agreement with those obtained by following the established reported procedures. The comparison of the results is given in the Table 6. The values were normalised with chondritic values reported by Masuda et al. [21] and is illustrated in the Fig. 4 showing negative europium anomaly.

## Conclusion

The proposed method of selective precipitative separation of the interfering major zirconium component as its phosphate and determination of uranium and REEs accurately



and precisely by ICP-OES was rapid and effective. Complete decontamination of zirconium was possible at very low concentration of phosphoric acid and reasonable quantity of nitric acid. All the 16 elements were analyzed in a single solution. As it did not involve any organic solvent for separation, the method was environmental friendly. The method standardized could be used for routine analysis of uranium and REEs in refractory zircons minerals using ICP-OES with high sample throughput.

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