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Method validation and uncertainty for the determination of rare earth elements, yttrium, thorium and phosphorus in monazite samples by ICP-OES

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ABSTRACT

A method is described for the inductively coupled plasma optical emission spectrometric (ICP-OES) determination of rare earth elements (REE), yttrium (Y), thorium (Th) and phosphorus (P) in monazite samples. Sample preparation was carried out by fuming with sulphuric acid followed by fluoride fusion of the remaining residue. The method was validated using the single laboratory approach by assessment of analytical performance characteristics like specificity, linearity, range, accuracy and precision. Spectral interferences were observed in the case of some heavy REE (Ho,Er,Tm) by light REE (Nd) and correction factors were deduced and applied. The limit of quantification, instrument linearity and the method range were evaluated. Relative standard deviation (RSD) values ranging from 2.6 to 10.2 % were obtained for repeatability studies and RSD values ranging from 1.7 to 11.1% for intra-lab reproducibility studies. Accuracy was established by application to a monazite certified reference material (CRM) and also through comparison of results obtained by present method with those obtained by an alternate method. The validation results were compliant with the acceptance criteria for the various parameters assessed. A simple procedure has been described for the estimation of associated measurement uncertainty using the GUM "bottom-up" modelling approach and results presented in this paper. The validated method was applied to the determination of REE, Y, Th and P in some monazite samples from India.

Capsule Summary: Rare Earth elements, yttrium, thorium and phosphorus in monazite samples were determined in monazite samples by ICP-OES using single sample preparation procedure after validation using a single laboratory approach and estimation of associated measurement uncertainty using GUM bottom-up approach. The method was applied to Indian monazite samples and good results were obtained.

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INTRODUCTION

Monazite is a radioactive phosphate mineral ((Ce, La, Nd, Th)PO_4) containing very high and variable concentrations of rare earth elements (REE) and thorium and constitutes an important resource for these elements (Voncken, 2016). The beach sand placer deposits found on the south-western and eastern coasts of India contain monazite along with other minerals such as ilmenite, rutile, zircon, sillimanite, and

Table 1: Instrumental parameters of ICP-OES

Mounting	Czerny-Turner
Focal length	1m
Grating	4320 grooves mm^{-1} 2400 grooves mm^{-1}
Order of measurement	1st
1st order resolution	0.005 nm
Type of generator	Solid state
Observation	Radial View
Frequency of generator	40.68 MHz
Power	1000W
Plasma gas flow rate	12 L min^{-1}
Sheath Gas flow rate	0.2 L min^{-1}
Nebulizer gas flow rate	0.8 L min^{-1}
Nebulizer type	Meinhard
Type of spray chamber	Cyclonic
Injector tube diameter	1.8 mm

garnet (Gupta and Krishnamurthy, 2003). Monazite in the beach sand is separated from other associated heavy minerals using gravity and electro-magnetic separation methods. There are many techniques capable of providing accurate quantitative analysis of REE minerals, broadly classified as micro analytical and bulk techniques. Although, in-situ micro analytical techniques like electron probe micro analyzer (EPMA), secondary ionization mass spectrometry (SIMS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), synchrotron x-ray fluorescence analysis (SXRF) have obviated the need for laborious mineral separations and wet chemical procedures, access to these techniques is limited owing to the small number of instruments available (Jones et al.,1995). Further, these in-situ micro analytical techniques are mainly used in geochronology and petrology to study the accessory mineral phases present in the different types of rocks. Monazite is an important chronometer and is frequently used to date igneous metamorphic, hydrothermal, and sedimentary rocks (Scherreret al., 2000). Though EPMA is well established for the quantitative analysis of monazite, the analyses are time consuming and require careful selection of sample preparation methods, standards and analytical settings. The widely employed bulk analytical techniques are ICP-OES and ICP-MS. These techniques are especially preferred in geochemical exploration programs where cost and time become important factors owing to the large number of samples that need to be analyzed for simultaneous multi-element determinations with concentrations ranging from parts per billion to percentage levels. In fact, use of both ICP-OES and ICP-MS provides the most comprehensive sample analysis for the greatest range of elements in exploration programs since the lack of sensitivity of ICP-OES makes it difficult to measure low concentrations of many trace elements, while the high sensitivity of ICP-MS makes it difficult to measure high concentrations of elements.

Since both ICP-OES and ICP-MS are solution based techniques, sample digestion using wet chemical procedures becomes imperative and unavoidable. Sample preparation of monazite samples for analyses by ICP-OES and ICP-MS is extremely difficult as vigorous conditions such as digestion with acids or fusion fluxes at elevated temperatures are required to bring about its complete decomposition. Conventionally, sulphuric acid is used to decompose monazite mineral by employing a simple fuming technique on a hot plate for 2–3 hours at 250–300 °C (Murty et al., 1990). But monazite samples often contain minor quantities of other associated heavy minerals (such as ilmenite, garnet, zircon, rutile, sillimanite etc.) which do not get decomposed completely during the sulphuric acid fuming step. Hence, fusion of the residue becomes necessary. Direct fusion of monazite samples with phosphate and fluoride salts for ICP spectrometry has also been reported (Padmasubashini and Satyanarayana, 2013; Radhamani et al., 2007). In ICP-OES analysis of monazites, heavy thorium matrix causes interferences. Further, the light REE to heavy REE concentration ratio is very high making it difficult to accurately determine very low concentrations of heavy REE (Eu-Lu) due to the spectral interferences. Hence, some authors have employed a solvent-extraction based method for the separation of heavy REE from light REE in monazite prior to their quantification by ICP-OES (Premdas and Khorge, 2006). In the present work, the authors have coupled the conventional sulphuric acid digestion step with a fluoride fusion for simultaneous determination of REE, thorium and phosphorus in monazite by ICP-OES and applied correction factors for inter REE spectral interferences.

Although, ICP-OES has become a routine analytical technique for metal determination in diverse samples and several papers have been published, information related to method validation is scarce (Mermet, 2005). There is a paucity of fully validated methods, especially for multi-element determination in mineral samples keeping in view that such validation and estimation of the associated measurement uncertainty is mandatory for laboratories seeking accreditation as per ISO/IEC: 17025 standard (ISO, 2005). In the present study, validation results using the single laboratory approach for multi-element determination in monazite samples by an ICP-OES method (IUPAC, 2002; Magnusson and Ornemark, 2014) have been presented. The publication in 1993 of the “Guide to the Expression of Uncertainty in Measurement” (the GUM) by ISO in collaboration with other organizations, formally established general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurements (ISO,1993). Several approaches for the evaluation of measurement uncertainty, based on the general principles of GUM, are known (ISO, 1993; Magnusson et al., 2013). The most popular approach is the modelling approach (also known as the bottom-up approach). A simple procedure has been described in this paper for estimation of the associated standard measurement uncertainty using the GUM “bottom-up” approach. Application of the validated method to the determination of REE,Y, Th and P in monazite samples originating from India has also been presented in this paper.

MATERIAL AND METHODS

Reagents and standards

All acids and reagents used were of analytical grade or better. All solutions were made using ultrapure (resistivity 18 MΩ cm) water. Traceable elemental standard stock solutions (1 mgmL^{-1}) were procured from Alfa Aeser for all elements determined. Mixed multi-element working standard solutions in the range 0.1-50 µg mL^{-1}were prepared from the above stock solutions by appropriate dilution, keeping 3% v/v of 12 M hydrochloric acid (HCl).

Instrumentation

An ICP-OES (Ultima-2, Jobin Yvon Ltd., France) was used for the determinations.

Analytical test procedure

Step 1-Sulphuric acid fuming: A sample portion in the range of 0.1-0.2 g was accurately weighed into a dry100-mL glass beaker, and 5 mL of 9M sulphuric acid (H_2SO_4) was added. The beaker was closed with a watch glass and placed on a hot plate (with frequent stirring) for digestion until the evolution of dense white fumes of sulphuric acid ceased and a moist residue was obtained. The fuming process was repeated with 5 mL of 9M H_2SO_4 until a moist residue was obtained.

The beaker was then removed from the hotplate and allowed for the digest to cool completely. 25 mL of ultra-pure water and 3 mL of 12 M HCl were added into the beaker and mixed to dissolve the residue. The solution obtained was filtered in to a 100 mL standard flask using a Whatman 540 filter paper. The beaker and filter paper were washed thoroughly with ultra-pure water and washings added to the filtrate. The filtrate was made up to 100 mL mark in the standard flask (solution-A). Residue was brought into solution using the fusion procedure described in step-2.

Step 2-Fusion of residue using fluoride salt mixture: The filter paper containing the residue, if any, after sulphuric acid fuming, was transferred into a clean dry platinum crucible, ashed at ~ 650 ^{0}C in a muffle furnace for one hour. The residue left behind was mixed with a flux mixture and fused as follows. A 0.5-1.0 g portion of a homogenous mixture of potassium biflouride (KHF_2) and sodium fluoride (NaF) flux (3:1 weight ratio) was added and mixed with the residue obtained. Then, the mixture was fused first at a low flame for 2 minutes and continued heating for 3-5 minutes until a clear red hot melt was obtained. The crucible was allowed to cool and 2-3 ml of 9M H_2SO_4 acid were added and heated on a burner till the evolution of white thick fumes of sulphuric acid ceased (for removal of residual fluoride). The crucible was removed from the flame, allowed to cool and immersed into a 250 mL glass beaker containing 3ml of 12 M HCl and 50 ml of ultra-pure water. The beaker was covered with a watch-glass and boiled on a burner till the fused mass dissolved fully and a clear solution was obtained. The crucible was removed from the solution, washed thoroughly with ultra-pure water and washings added to the solution. After cooling, the solution was transferred to a 100mL standard flask and made up to the mark (solution-B) with ultra-pure water.

Step 3-Determination of REE (La to Lu except Pm), Y, Th and P: Suitable aliquot of solutions A and B were taken in a 50 mL standard flask (solution C) and made up to the mark with ultra-pure water. Solution C was analyzed for REE, Y, Th and P by ICP-OES after a 3 point external calibration with standards in the range of 0.1 to 50 µgmL^{-1} and the concentration of elements in the solution was determined. From those results, the concentrations of the elements in the samples were calculated using the dilution factors and the sample weight taken.

Determination of REE, Y and Th: A 0.2 g sample portion was accurately weighed and transferred into a clean and dry 75 mL capacity platinum crucible. A 4 g portion of a mixture of sodium di-hydrogen phosphate and di-sodium hydrogen phosphate salts (weight ratio 1:1) was added to the crucible and mixed thoroughly with the sample. The crucible was covered with a platinum lid and heated over a burner till a red hot melt was obtained. The melt was slowly swirled for proper mixing and continued heating for 5 more minutes with intermittent swirling. The crucible and its contents were allowed to cool and immersed in 70 mL of ultra-pure water taken in a 250 mL glass beaker. The beaker was heated on a boiling water bath for about 60 minutes till the contents of the crucible dissolved completely to give a clear solution. The crucible was removed from the beaker, washed with ultra-pure water and washings added into the beaker. The solution was transferred into a 100 mL standard flask and made up to the mark with ultra-pure water. The sample solution was analyzed for REE and Th after appropriate dilution by ICP-OES after a 3 point external calibration with standards in the range of 0.1 to 50 µgmL^{-1} and the concentration of elements in the solution was determined. From those results, the concentrations of the elements in the samples were calculated using the dilution factors and the sample weight taken.

Determination of P: A 0.2 g portion of monazite sample was accurately weighed and transferred into a clean and dry nickel crucible. A 1.0 g portion of Na_2O_2 flux was added to it and fused on a burner till a red hot melt was obtained. The crucible and its contents were cooled and placed in a 250 mL glass beaker and added 200 mL of ulta-pure water to it. The solution was kept aside for 10 hours to enable effective water leaching of the fused mass.

The solution was filtered through a Whatman 542 filter paper (15 cm) to a 250 mL standard flask. The beaker was washed thoroughly with ultra-pure water and washings added into the flask. Then, 10 mL of 12 M HCl was added for neutralization and made up to the mark with ultra-pure water. The solution was analyzed after appropriate dilution by ICP-OES for phosphorus.

RESULTS AND DISCUSSION

Optimization of instrumental parameters

Establishing ideal operating conditions is crucial to obtain reliable results. Critical instrumental parameters including RF power, nebulizer gas flow rate, and aspiration rate were optimized for achieving maximum sensitivity and precision. The optimum parameters employed in the study are given in Table 1.

Table 2: Correction factors for inter-REE interferences

Interference	Wavelength (nm)	Correction equation
Nd on Sm	359.262	[a]C_{Sm} (corrected)= $C_{Sm\ (obtained)}$ - 0.028 . C_{Nd}
Nd on Ho	345.600	[a]C_{Ho} (corrected)= $C_{Ho\ (obtained)}$ - 0.002 . C_{Nd}
Nd on Er	349.910	[a]C_{Er} (corrected)= $C_{Er\ (obtained)}$ - 0.002 . C_{Nd}

[a]C denotes the concentration in w/w %

Table 3: Analytical wavelength, limit of quantification (LOQ), instrumental linearity

Element	Wavelength (nm)	LOQ (μgmL^{-1})	b_1 [Slope of calibration line]	b_0 [y intercept]	R^2	RSS [Residual sum of squares]
Lanthanum (La)	333.749	0.050	16216.5	3615.9	0.99996	0.3318
Cerium (Ce)	418.660	0.050	12550.8	2077.35	0.99997	0.1955
Praseodymium (Pr)	422.293	0.100	7783.2	934.7	0.99999	0.0760
Neodymium (Nd)	430.357	0.050	15764.6	1847.2	0.99995	0.3750
Samarium (Sm)	359.262	0.050	14875.9	2004.6	0.99992	0.6247
Europium (Eu)	281.395	0.010	131720.5	20046.4	0.99995	0.3837
Gadolinium (Gd)	364.620	0.050	142642.3	18234.6	0.99996	0.2941
Terbium (Tb)	350.917	0.050	13313.6	2447.4	0.99994	0.4851
Dysprosium (Dy)	353.170	0.010	66544.0	1494.0	0.99993	0.0046
Holmium (Ho)	345.600	0.050	69451.3	1095.0	0.99993	0.0043
Erbium (Er)	349.910	0.050	79277.4	1547.0	0.99995	0.0032
Thulium (Tm)	346.221	0.010	65733.3	250.3	0.99999	0.0002
Ytterbium (Yb)	328.937	0.005	708545.5	3837.0	0.99996	0.0028
Lutetium (Lu)	261.542	0.005	663253.7	6656.5	0.99999	0.0011
Yttrium (Y)	371.029	0.010	730695.4	1480.3	0.99999	0.0005
Thorium(Th)	401.913	0.050	12947.4	472.2	0.99998	0.1729
Phosphorus (P)	213.618	0.100	1055.3	330.2	0.99995	0.3688

Table 4: Results for method range

Element	b_1 [Slope]	b_0 [y intercept]	R^2	RSD (%)	Range (%, w/w)
La	1.001	0.049	0.999	0.7-1.9	0.01-20.0
Ce	0.992	0.398	0.997	1.7-3.0	0.01-40.0
Pr	0.994	0.038	0.999	1.12-3.7	0.02-10.0
Nd	0.998	0.011	0.999	0.3-2.0	0.01-20.0
Sm	1.005	0.051	0.999	0.2-2.8	0.01-10.0
Eu	0.957	0.002	0.999	0.6-7.8	0.001-1.0
Gd	1.003	0.018	0.999	0.7-2.1	0.01-5.0
Tb	1.002	0.014	0.999	0.1-2.2	0.01-5.0
Dy	1.002	0.002	0.999	0.8-2.3	0.01-5.0
Ho	1.003	0.002	0.999	0.4-3.2	0.001-2.0
Er	1.003	0.001	0.999	0.2-2.0	0.001-2.0
Tm	1.002	0.002	0.999	0.3-2.5	0.001-1.0
Yb	1.000	0.000	0.999	1.3-3.6	0.001-1.0
Lu	1.000	0.000	0.999	1.1-4.5	0.001-1.0
Y	0.977	0.001	0.990	0.6-2.5	0.01-10.0
Th	0.999	0.019	0.999	0.2-3.0	0.01-20.0
P	1.008	0.170	0.996	0.7-2.5	0.01-40.0

Table 5: Results for accuracy of CRM IGS-36

Elements	Unit	Accepted Value*(AV)	Present Value (PV)	R.S.D (%)
La	%	10.17	9.96	1.3
Ce	%	20.28	21.34	1.5
Pr	%	2.31	2.21	1.3
Nd	%	9.01	9.14	1.4
Sm	%	1.33	1.31	1.5
Eu	ppm	302	349	4.4
Gd	%	0.67	0.74	2.9
Tb	%	0.094	0.106	2.3
Dy	%	0.27	0.32	3.6
Ho	ppm	347	352	5.4
Er	ppm	535	576	4.3
Tm	ppm	57	50	5.7
Yb	ppm	259	313	1.5
Lu	ppm	51	47	12.9
Y	%	0.88	0.94	4.1
Th	%	5.38	5.42	1.4
P	%	Not available	11.36	1.3

*Lister (1981)

Method validation

Systematic method validation involves evaluation of several analytical performance characteristics and ascertaining whether they fulfill the acceptance criteria. In the present work a single-laboratory approach was adopted. The 'Performance characteristics' that need to be demonstrated in case of assay methods are specificity/selectivity, trueness/accuracy, precision (repeatability and intermediate precision) and working range including linearity (IUPAC, 2002). The data pertaining to performance characteristics were assimilated, evaluated and checked whether acceptance criteria were fulfilled. Following fulfillment of acceptance criteria, the method was deemed to be validated.

Assessment of specificity (selectivity)

Loss of specificity can be due to interferences and matrix effects. The specificity of the present method was investigated by recording the emission profile at the selected analyte emission wavelengths of: i) process blank spiked with appropriate amount of analyte and ii) process

Table 6: Results for accuracy of sample (AMD-MZ-11) by test method and alternate method

Element	Unit	By present method (n=3)	By alternate method* (n=3)	Recovery (%)
La	%	13.20	12.70	96
Ce	%	27.05	25.24	93
Pr	%	2.44	2.30	94
Nd	%	11.68	10.91	93
Sm	%	1.85	1.68	91
Eu	%	0.008	0.008	100
Gd	%	0.78	0.73	94
Tb	%	0.11	0.11	100
Dy	%	0.21	0.21	100
Ho	%	0.004	0.004	100
Er	%	0.046	0.046	100
Tm	%	0.007	0.007	100
Yb	%	0.003	0.003	100
Lu	%	0.001	0.001	100
Y	%	0.46	0.47	102
Th	%	8.01	7.82	98
P	%	12.42	11.92	96

*Radhamani et al. (2007)

Table 7: Results for repeatability (n=10) of sample "AMD-MZ-12"

Element	Mean	unit	RSD_R%	Horwitz $PRSD_R$ %	HorRat (r)	Acceptable (Range: 0.3-1.3)
La	7.15	%	1.5	3	0.5	Yes
Ce	15.16	%	1.8	2.7	0.7	Yes
Pr	1.42	%	1.4	3.8	0.4	Yes
Nd	5.62	%	1.2	3.1	0.4	Yes
Sm	1.77	%	1.6	3.7	0.4	Yes
Eu	0.003	%	12.5	9.6	1.3	Yes
Gd	0.95	%	1.3	4	0.3	Yes
Tb	0.17	%	1.5	5.2	0.3	Yes
Dy	0.39	%	1.7	4.6	0.4	Yes
Ho	0.037	%	3.8	6.5	0.6	Yes
Er	0.052	%	3.6	6.2	0.6	Yes
Tm	0.007	%	8.1	8.5	1	Yes
Yb	0.024	%	2.8	7	0.4	Yes
Lu	0.002	%	8.1	10.2	0.8	Yes
Y	0.94	%	1.5	4	0.4	Yes
Th	13.36	%	1.3	2.7	0.5	Yes
P	9.35	%	1.6	2.9	0.6	Yes

blank spiked with analyte and the concomitant elements (suspected interferents) and iii) process blank spiked with concomitant elements only. All elements were spiked in appropriate amounts representative of a typical sample composition. The emission spectra for analyte in absence and presence of concomitant elements were visually compared. Different wavelengths were studied for various elements and wavelengths with optimum sensitivity which were free from spectral interferences were selected. In ICP-OES determination of REE, especially in concentrated samples like monazites, increased background intensities are found with increasing REE and thorium concentrations. Because many REE have multiple-line spectra in ICP-OES, a possibility of mutual spectral interferences among REE exists (Premdas and Khorge, 2006). Especially, in monazite samples, light REE (La, Ce, Pr, Nd, Sm) occur in much higher concentration compared to heavy REE (Eu-Lu) and this leads to interferences of light REE on some heavy REE. Measurements were carried out at alternate wavelengths wherever feasible. In absence of suitable alternate wavelengths as with the case of Sm, Er and Ho, appropriate correction factors were deduced and applied. The interferences observed and the correction factors deduced are shown in Table 2.

Limit of quantification (LOQ)

The limit of quantification for elements at respective wavelengths used was calculated by multiplying Background Equivalent Concentrations "BEC" (obtained using 1μgmL^{-1} standard of each of the elements doped with the process blank solution)by ten times of RSD of the blank. LOQ= BEC. 10 . $\mathrm{RSD_{BL}}$ (Equation 1). The wavelengths used and LOQ values for different elements are presented in Table 3. LOQ values ranged from 0.005 to 0.1 μgmL^{-1}.

Table 8: Results for within lab reproducibility (n=10) of sample "AMD-MZ-13"

Element	Mean	unit	$\mathrm{RSD_R}$%	Horwitz $\mathrm{PRSD_R}$ %	HorRat(r)	Acceptable (Range:0.5-2.0)
La	10.93	%	1.7	2.8	0.6	Yes
Ce	23.07	%	2.3	2.5	0.9	Yes
Pr	2.01	%	3.3	3.6	0.9	Yes
Nd	8.76	%	3.1	2.9	1.1	Yes
Sm	1.46	%	1.9	3.8	0.5	Yes
Eu	0.026	%	7.6	6.9	1.1	Yes
Gd	0.66	%	4.1	4.2	1	Yes
Tb	0.084	%	7.7	5.8	1.3	Yes
Dy	0.17	%	3.5	5.2	0.7	Yes
Ho	0.032	%	8.6	6.7	1.3	Yes
Er	0.04	%	3.9	6.5	0.6	Yes
Tm	0.006	%	11.1	8.6	1.3	Yes
Yb	0.007	%	8.1	8.5	1	Yes
Lu	0.001	%	10.8	10.9	1	Yes
Y	0.4	%	1.8	4.6	0.4	Yes
Th	6.95	%	2.5	3	0.8	Yes
P	11.66	%	2.7	2.8	1	Yes

Table 9: Uncertainty Budget

Source of uncertainty	Input /output	Notation in model equation	Estimate	Standard Uncertainty	Probability distribution - Type A or B
X_1	Mass of sample in g	M_x	Input, x_1	$u(x_1)$	Normal, Type B
X_2	Volume of sample solution in mL	V_x	Input, x_2	$u(x_2)$	Normal, Type B
X_3	Dilution factor of sample solution	D.F	Input, x_3	$u(x_3)$	Normal, Type B
X_4	Concentration of element in solution in µg/mL	$C_{x\text{-anal}}$	Input, x_4	$u(x_4)$	Normal, Type B
X_5	Repeatability - Analyst 1 in % g/g		Input, x_5	$u(x_5)$	Normal, Type A
X_6	Repeatability- Analyst 2 in % g/g		Input, x_6	$u(x_6)$	Normal, Type A
X_7	Recovery uncertainty (CRM study)	R_x	Input, x_7	$u(x_7)$	Normal, Type A
Y	Concentration in element "X" in sample in % g/g	$C_{x\text{-sample}}$	Output, y	$u_c(y)$	

Linearity (instrument working range)

In order to assess the instrument working range and confirm its fitness for purpose, a series of six calibration standards were prepared, emission intensities from ICP-OES were recorded using the calibration function available in the software. The relationship between concentration and instrument response was plotted using regression equation (linear fit: $Y=b_0+ b_1 X$ where “Y” corresponds to emission intensities and “X” concentration of standards, b_0 and b_1 are the y-intercept and slope respectively). The results are presented in Table 4. The ICP-OES response for all elements is linear in 0-150% of the target concentration range as is evident from the linear calibration curve with $R^2 \geq 0.999$ and also from the random distribution of residuals around zero concentration, thus satisfying acceptance criteria.

Assessment of method range

The ‘method working range’ is the interval over which the method provides results with an acceptable uncertainty. In order to assess the method working range, samples with known concentrations preferably covering the whole range of interest should be available. Since real samples covering entire range were not available, spiked materials were used. IGS-36 is a monazite CRM supplied by British Geological Survey/Institute of Geological Sciences, U.K. For preparing synthetic samples in the range of 0.01-0.5% of various elements, appropriate portions of specpure silicon dioxide powder (obtained from Alfa Aeser) was mixed with appropriate weight portions of the above CRM. For preparing synthetic samples containing analytes in the range 1-20%, the following procedure was used. Appropriate aliquots of standard solutions were taken in a crucible and dried. Accurately weighed portions of specpure silicon dioxide powder were added to obtain spiked materials with the range of elements from 1.0% to 20%. Solutions of spiked materials were prepared and analyzed as per test procedure. Each measurement was replicated 3 times and an average was used for calculation of the result. The obtained concentration values of elements were compared to the actual concentration values taken. The measured concentrations versus actual concentrations for all spiked/synthetic materials taken were plotted applying the regression equation (linear fit: $Y=b_0+ b_1 X$ where “Y” corresponds to obtained concentration, “X” corresponds to actual concentration, b_0 and b_1 are y-intercept and slope respectively). The results obtained are presented in Table 4. Random distribution of residuals about zero was obtained confirming absence of systematic error. The RSD values obtained were within 10% for the entire concentration range and the coefficient of determination was also greater than 0.99, thus indicating good accuracy and precision over the tested range for all elements.

Assessment of accuracy

Very few CRMs are available for monazite. Even with those available, certified or even probable values are not available for most constituent elements. IGS-36 is the only monazite CRM for which certified values are available for most constituent elements and hence it has been widely analyzed. In this study, CRM“IGS-36” was analyzed by the test method in ten replicates and values obtained were

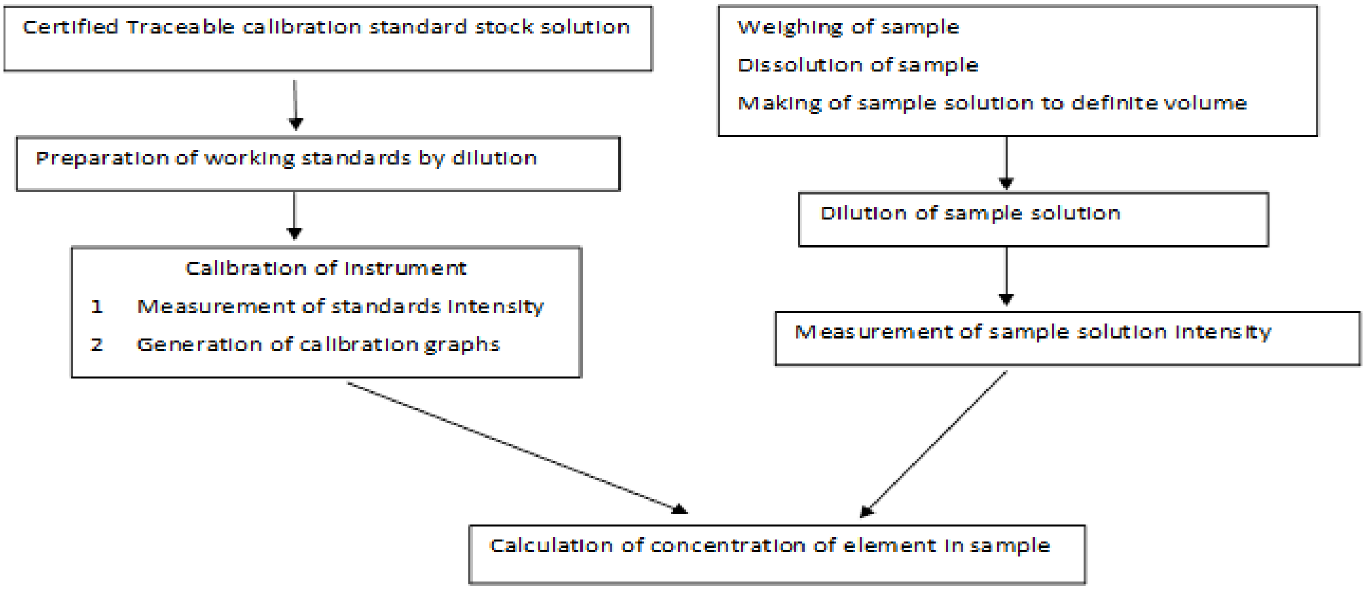

Fig. 1: Flow diagram of ICP-OES method

checked against the accepted values (Lister, 1978; Lister, 1981). The results presented in Table 5 are within acceptable uncertainty limits of the certified/accepted values for the CRM, thereby confirming the accuracy of the method. Phosphorus value in IGS-36 has not been reported so far in literature. The value reported in the present paper can serve as usable value for the above CRM.

Since no other CRMs were available, further assessment of accuracy was carried out by analyzing a monazite sample by an alternate method which involved sample solution preparation by mixed phosphate fusion followed by ICP-OES determination of REE, Th and sample solution by peroxide fusion-water leach followed by ICP-OES determination of P (Radhamani et al., 2007). Results obtained by the two methods were compared and the percentage recovery (R %) of the elements in the samples was calculated using the following Eq. 2.

$$\mathrm{R\%} = \frac{\text{Value obtained by alternate method}}{\text{Value obtained by test method}} \cdot 100 \qquad (2)$$

The recoveries are presented in Table 6. The values obtained by both methods were in good agreement with recovery ratios ranging from 91-102%. On the basis of the results obtained, the present method was deemed to be accurate.

Repeatability (short term precision)

Repeatability measurements were carried out with a natural monazite sample. Ten replicate measurements were made on the same sample in the same laboratory using the same equipment by the same analyst. The mean and relative standard deviation "RSD_R" of the results was evaluated. Horwitz ratio was employed as acceptance criteria (Horwitz and Albert, 2006; Rivera and Rodriguez, 2014). Horwitz Ratio (HorRat) is the ratio of RSD_R calculated from the data of laboratory, to the RSD predicted from the Horwitz equation ($PRSD_R$). The average concentration of 10 analyses obtained for every element were used for calculating $PRSD_R$ (%) = $2C^{-0.15,}$ where C is expressed in dimensionless mass fraction. For single-laboratory validation studies, under repeatability conditions, acceptable values for HorRat(r) are between 0.3 and 1.3. The results are presented in Table 7. The HorRat(r) ratio of all the elements were well within the range of 0.3 to 1.3 for their respective mass concentration ranges and hence acceptable.

Within lab reproducibility (Intermediate precision)

For assessing intermediate precision, ten replicate measurements were made on the same sample in the same laboratory using the same equipment by different analysts on different days. For validation studies, under reproducibility conditions, acceptable values for HorRat(r) are between 0.5 and 2.0. The HorRat(r) of all 15 REE (La to Lu), Th, P for sample measurements are presented in Table 8. The HorRat(r) ratio of all the elements were within the range of 0.5 to 2.0 for their respective mass concentration ranges and hence acceptable.

Estimation of uncertainty

The measurement uncertainty is estimated by the top-down or bottom-up approaches. The GUM modeling approach is known as the "bottom-up approach", where all conceivable sources of uncertainty are systematically evaluated using a model equation and are combined into total uncertainty using the law of propagation of uncertainty. In the "top-down" approach the methodology is considered as a whole and the uncertainty is evaluated based on inter-laboratory ILCE/PT data. The latter approach has the advantage that usually it is easier to implement in routine laboratories which sometimes do not have the time or the resources to develop a strict GUM estimation. In the present work, measurement uncertainty was estimated using GUM "bottom-up" approach as per the following procedure.

In the first step, the test method was summarized in step-wise operations to identify sources of uncertainty as shown in Fig 1. In the second step, a mathematical model equation for arriving at the test results as per test method was set up as shown in Eq. 3.

$$C_{x-sample} = \frac{C_{x-anal} * D.F * V_x * 10^{-4}}{M_x * R_x} \qquad (3)$$

Where, M_x is mass of the sample taken in grams , V_x is the volume of the made-up sample solution in mL, D.F is the dilution factor of sample solution (i.e 5,10 etc.), R_x is the recovery factor of element "X" from sample into solution (maximum of 1), $C_{x\text{-anal}}$ is the concentration of element "X" in the solution in $\mu g mL^{-1}$ obtained from calibration graph and intensity of solution, $C_{x\text{-sample}}$ is the concentration of element "X" in sample in wt %.

In the third step, the different sources of all possible uncertainties associated with the inputs in the model equation were identified. The cause-effect (fish-bone) diagram depicting the various significant sources of uncertainty is shown in fig 2.Only sources of uncertainty considered significant were evaluated. Sample was taken as representative and homogenous. Uncertainty in mass of the sample (X_1) due to balance calibration was included. Uncertainty in sample solution volume (X_2) associated with volumetric glassware calibration was also included.
Uncertainty associated with the dilution factor (X_3) of sample solution was evaluated from uncertainty associated with the volumetric glassware calibration. Calibration uncertainty (X_4) emanating from uncertainty with concentration of calibration stock standard solution and volumetric glassware calibration was included. The contribution of repeatability to different sources of measurement uncertainty were combined into one contribution and obtained by repeatability studies by two

analysts. In the fourth step, the evaluation of uncertainties associated with inputs was carried out. The input and output estimates evaluated are listed in the Table 9. The uncertainty estimates were categorized into “Type A” or “Type B” and were evaluated accordingly. The standard uncertainties associated with gravimetric, volumetric operations and certified standard stock solutions are “Type B” estimates and were evaluated from the calibration certificates. The uncertainty associated with concentration of element in sample was evaluated from repeatability data which is a “Type A” estimate. A sample was analyzed replicates by two analysts independently for repeatability as per test method and outputs in the model equation are evaluated using the input values. The results were compiled to get the repeatability uncertainty (X_5 and X_6).A monazite CRM (IGS-36) was analyzed under repeatability condition and repeatability data was to evaluate recovery uncertainty (X_7) as “Type A” estimate. In the next step, output estimate was calculated by substituting the input estimates in the model equation. In the final step, evaluation of combined total standard uncertainty in output estimate *i.e* test result was carried out using the relative uncertainties associated with the input estimates using shown below ($u_c(y)$).

$$u_c(y) = y \cdot \sqrt{\left(\frac{u(x_1)}{x_1}\right)^2 + \left(\frac{u(x_2)}{x_2}\right)^2 + \left(\frac{u(x_3)}{x_3}\right)^2 + \left(\frac{u(x_4)}{x_4}\right)^2 + \left(\frac{u(x_5)}{x_5}\right)^2 + \left(\frac{u(x_6)}{x_6}\right)^2 + \left(\frac{u(x_7)}{x_7}\right)^2}$$

An expanded uncertainty in measurement (U) is obtained by multiplying the standard uncertainty $u_c(y)$ of the output estimate “y” by a coverage factor k, $U = k\, u_c(y)$. Since, a normal (Gaussian) distribution can be attributed to the measurand and the standard uncertainty associated with the output estimate has sufficient reliability, the standard coverage factor $k = 2$ was used. The measurement uncertainty values for a monazite sample are in S1 data. It was observed that maximum contribution to total measurement uncertainty was from repeatability uncertainty and recovery uncertainty.

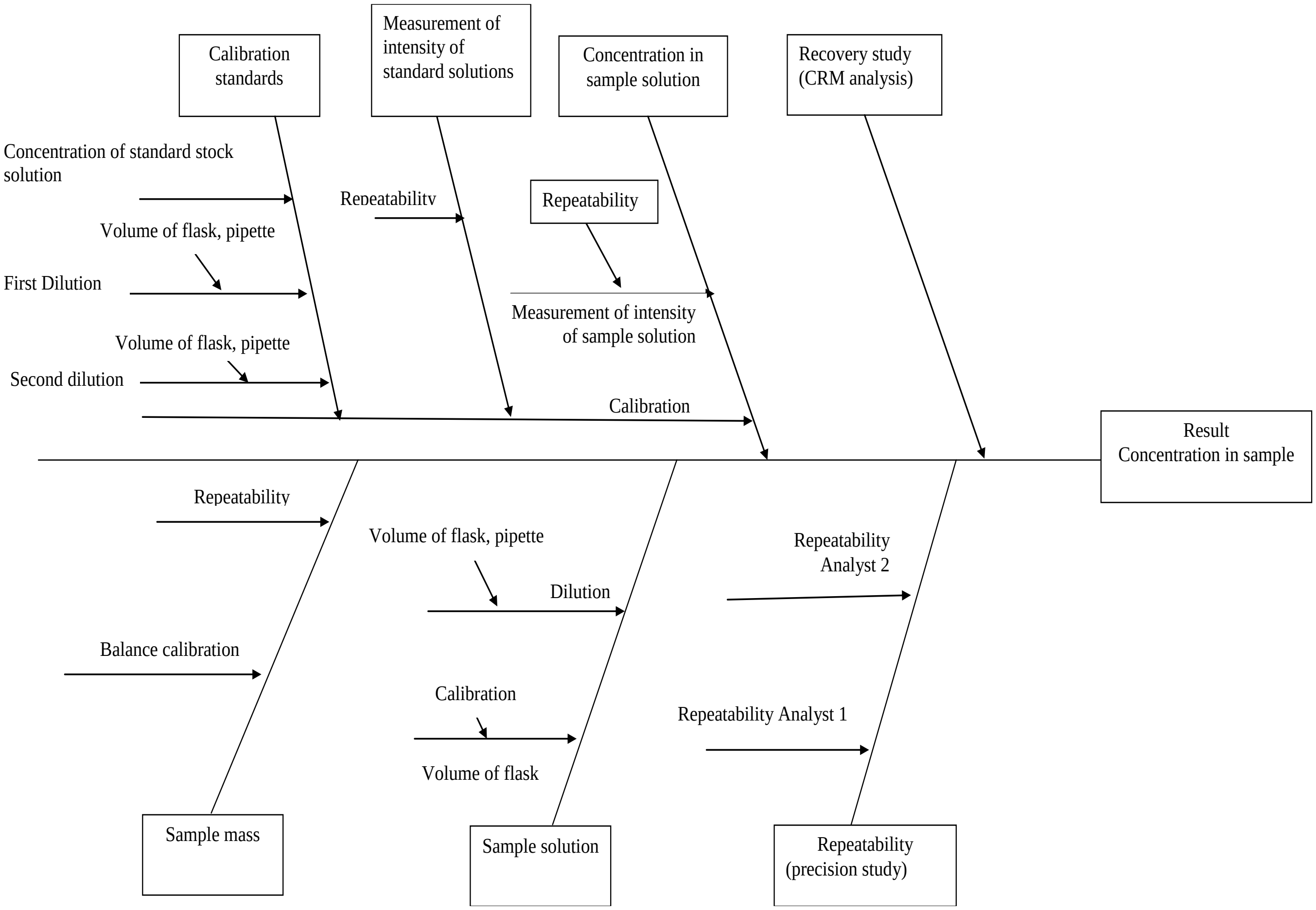

Fig. 2: Cause & Effect diagram depicting sources of uncertainty

Application of developed method

The solution preparation in the present method involves a sulphuric acid fuming step and fusion with a fluoride salt mixture of residue remaining after the fuming step. Some corrections were necessary due interferences of light REE on some heavy REE elements. The method shows good accuracy and precision over the entire method range. Further, the sample solution showed good stability and could be used for determination of several other major, minor and trace constituents by ICP-OES as well. The present method was applied for REE, Y, Th and P determination in monazite samples originating from India. The % RSD for all of the estimated elements varied from 1 to 5% at the mg g^{-1} level and from 5 to 15% at the µg g^{-1} levels of concentration (S2).

CONCLUSIONS

Validation of a method using the single laboratory approach for accurate quantification of REE, Y, Th and P in monazite samples by ICP-OES is presented. The validation data were found to fulfill acceptance criteria for various analytical performance characteristics. A simple procedure for estimation of total standard measurement uncertainty by GUM “bottom-up” approach has been also been described. The proposed method is fast and enables quantification of all the key constituent elements in monazite sample with a single sample digestion procedure and therefore will be of immense use in geochemical exploration programs wherein large numbers of samples need to be analyzed with time and economic constraints.

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