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Role of Energy Dispersive XRF (ED-XRF) in Development of Rare Earth Element-2, International Certified Standard Reference Material: Ambiguities and Constraints

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ABSTRACT

The REE-2 is a carbonatite sample with rare earth elements provided from a Canadian mining company and distributed by Canadian Certified Reference Materials (CCRM), Canada. The reference material was provided to participate in the testing process (round-robin) and CSIR-NGRI, Hyderabad, state of the art analytical technique Energy Dispersive X-ray fluorescence (EDXRF) also contributed to the development of this (REE -2) reference material. In this paper, the efficacy of analytical protocol developed and comparing the results with twenty one industrial, commercial and government laboratories across globe in an inter-laboratory measurement program are presented. The CSIR-NGRI, EDXRF analytical facility contribution and steps to overcome during REE-2 development are briefly discussed. This contribution is to highlight the international analytical standards and protocols maintained at EDXRF laboratory vis-à-vis international laboratories.

INTRODUCTION

The Energy-Dispersive X-Ray Fluorescence (EDXRF), is a robust analytical tool for Rare Earth Element analyses (REE) and avoid the requirement of sample dissolution and minimise-the erratic and spurious results (Remya et al., 2015). The EDXRF laboratory of CSIR-NGRI participated in round robin league to compare results with international labs in terms of both the quality control (Accuracy and Precision) and development of the analytical procedures. Routinely, the CRM are used by several analytical labs to know the accuracy and precision levels irrespective of dissolution techniques (Thompson, 2012). In mineral exploration studies, especially for REE measurements limited number of CRMs are available. In the initial stages of exploration precision, sensitivity, and cost are the prime key factors in assessing a geochemical analytical method that would be adopted. Accuracy is not so important in these initial stages, but the instrumental technique sensitivity together with precision are very important as the method should have the ability to detect and reproduce the subtle anomalies above background or threshold levels. Five sub-samples from one bottle (100 grams) of REE-2 was provided to analyze elements that are routinely analyzed. One sub-sample from one bottle (30 grams) of REE-1 is to be analyzed as the control sample along with REE-2. Both REE-1 and REE-2 are supplied by CCRMP, Canada. The raw material was crushed, milled, sieved and blended, and has a particle size of less than 74 microns (200 mesh). REE-2 is packaged in glass bottles containing 100 grams each and distributed around the globe, twenty governments, industrial and few commercial laboratories participated in an inter laboratory measurement including the EDXRF facility (make Epsilon-5), at CSIR-NGRI, Hyderabad, India. In this paper, the results from EDXRF for the development of REE-2 along with steps, precautions and advantages of destructive vis-a vis non-destructive sample digestion techniques etc., are briefly addressed.

EXPERIMENTAL

The methods for the determination of the elements included digestion with both destructive and non-destructive methods. The various combinations of acids on a hot plate; and to maintain the sample homogeneity the fused beads were prepared (Fig 1) for measurements using Energy Dispersive X-ray fluorescence (EDXRF) (Arif and Sunder Raju, 2015). Other techniques like Instrumental neutron activation analysis(INAA), inductively coupled plasma– mass spectrometry (ICP-MS) and inductively coupled plasma–atomic emission spectroscopy(ICP-AES) were also carried out elsewhere. The carbon concentration was measured using combustion followed by IR (infrared) spectrometry. The concentration of sulphur was determined using combustion followed by infrared spectrometry; acid digestion using four acids or fusions followed by inductively coupled plasma–atomic emission spectroscopy, inductively coupled plasma – mass spectrometry or X-ray fluorescence. At CSIR-NGRI the ED-XRF (Epsilon 5; PANalytical B. V., Lelyweg, The Netherlands) used in the present study was equipped with a Sc/W anode X-ray tube with a Beryllium (Be) window and a high resolution Germanium (Ge) semi-conductor detector. The instrument has a setup of fifteen user selectable secondary targets to allow optimization of excitation source according to the element of interest. A three dimensional polarizing optics with Cartesian geometry improves detection limits by reducing spectral background to an order of magnitude lower than the traditional 2-D optics (Brouwer, 2010).

RESULTS

The final data obtained from 21 laboratories was subjected to statistical analysis at CCRMP, Canada using ANOVA to calculate the

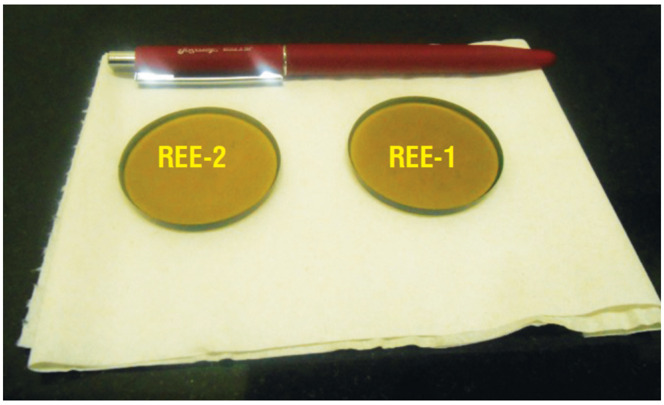

Fig.1. Fused Glass beads of REE-1 and REE-2.

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consensus values and other statistical parameters from the data from interlaboratory measurement program. The values are deemed to be certified if derived from 10 or more sets of data that meet Canadian certified reference material program (CCRMP) statistical criterion regarding the agreement of the results. Thirty-three analytes were certified, apart from that uncertified values for twenty-four provisional values were derived from 8 or 9 sets of data that fulfil the CCRMP statistical criterion regarding agreement; or 10 or more sets of data, that do not fulfil the CCRMP statistical criteria required for certification; or 6 or 7 sets of data for which the statistical analysis of the data warranted provisional status. This latter group includes beryllium; and both copper and nickel, specifically by acid digestion. Indicative values for 12 analytes, were derived from the means of a minimum of 3 sets of data.

SAMPLE PREPARATION

The data is based on samples of 0.8 to 2 grams ignited for 0.5 to 4 hours at 650 to 1050°C, the data generally includes sets by combustion followed by infrared spectroscopy and various fusions The loss of ignition was carefully determined using one gram of sample at 1000°C for four hours. The data-sets generated usually includes by digestion using four acids (hydrochloric, nitric, hydrofluoric and perchloric) and various fusions techniques; and for some elements, fused pellet, fusion or pressed powder pellet followed by x-ray fluorescence and instrumental neutron activation analysis (INAA) was used. Hence, there is a minimal variation with certain elements as shown in Table 1. The Spectra of REE suite with Kα lines is shown in Figs. 2a and b.

Table 1. Reported and certified values of elements reported by EDXRF

Element	Unit	Preparation	EDXRF Reported	Certified values
Al	%	Fused pellet	0.35	0.76
Ba	%	Fused pellet	3.90	5.02
Ca	%	Fused pellet	15.74	13.68
Er	µg/g	Fused pellet	186.32	14.00
Eu	µg/g	Fused pellet	81.50	96.6
Gd	µg/g	Fused pellet	299.51	219
Ho	µg/g	Fused pellet	92.74	7.87
K	%	Fused pellet	0.26	0.012
La	µg/g	Fused pellet	2996.15	5130
Na	%	Fused pellet	0.22	0.21
Nb	µg/g	Fused pellet	1033.15	1060
Nd	µg/g	Fused pellet	4721.99	3660
Ni	µg/g	Fused pellet	3.29	8.99
Pr	µg/g	Fused pellet	1833.58	1075
Rb	µg/g	Fused pellet	17.15	1.22
Sc	µg/g	Fused pellet	9.27	57.5
Si	%	Fused pellet	2.50	1.37
Sm	µg/g	Fused pellet	442.51	410
Sr	µg/g	Fused pellet	2128.57	2300
Tb	µg/g	Fused pellet	57.92	20.3
Th	µg/g	Fused pellet	770.28	737
Ti	%	Fused pellet	0.27	0.26
U	µg/g	Fused pellet	5.35	3.73
Y	µg/g	Fused pellet	263.81	176
Zr	µg/g	Fused pellet	1826.42	1830

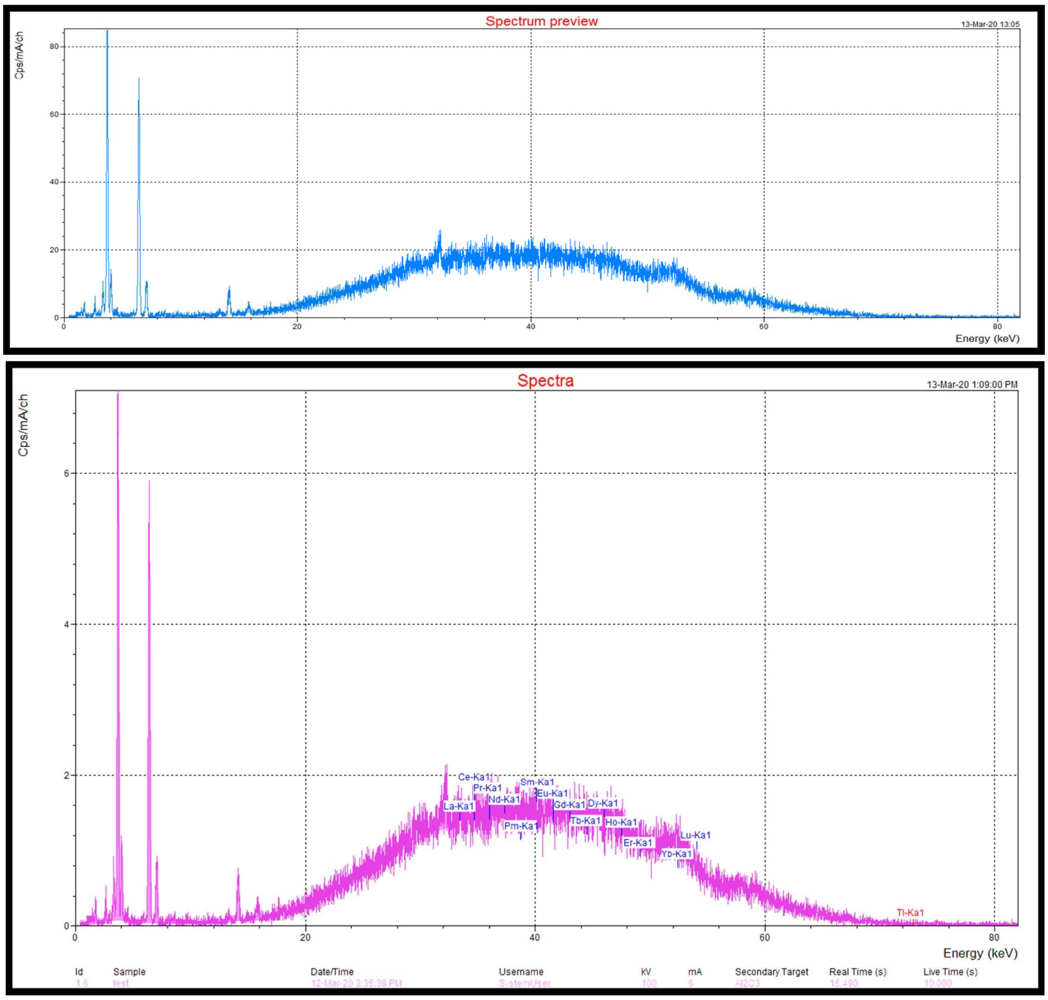

Fig.2. **(a)** Spectrum preview during analyses. **(b)** Spectra of REE with K alpha lines.

Table 2. Comparison of destructive vs non-destructive techniques

Sl. No.	Destructive techniques	Non destructive
1	Sample contamination	Nil
2	Contamination due to acids and dilution	Absent
3	Especially ICP techniques on selection of isotopic mas abundances	X Ray source and selections of secondary targets or dedicated spectrometers
4	More Inter-element effects	Line overlaps for transition elements
5	More time consuming	Quick with good precision and accuracy
6	Limited Availability of Certified to Standard Reference material to matrix	Avoid cross contamination to use directly the certified standard reference material

CONCLUSIONS

For certain elements like Al, Er, Ho, K, La the reported (Table 1) concentrations data appear to be one half or 2 times higher concentrations than the certified values. The possible reasons could be (a) due to interelement interference's, (b) peak overlaps arising from multiple elements in the sample and (c) limited detection, (d) two x-ray peaks arriving at detector at same time i.e sum of the peaks or peaks from x-ray sources i.e. Rayleigh peaks from x-ray source target, i.e., $Ag\ L_{\alpha}, L_{\beta}$ and Compton peaks from x-ray source target, i.e., typically at energies *less than* $Ag\ L_{\alpha}, L_{\beta}$, (e) other artificats like x-ray cup, contaminants on x-ray window (De Boer, 1990). To overcome this artefact problem, blank samples by batch were run. Whereas few elements like La, Ho, and Er lack strong first order x-ray i.e. $K\alpha$ lines or interfere with other second order lines etc. The EDXRF generated data corroborates to certified values (Table 1). The advantage of EDXRF is to use of 100 KeV X-Ray tube excitation potential to excite x-ray lines REE (LREE and HREE) effectively. The ED-XRF has become the instrument of choice with several advantages: (a) high spectral resolution; (b) low detection limit; (c) non-destructive and less time consuming analytical techniques for wide range elements (Na to U) in comparison with other *in situ* based techniques. The use of Compton normalization partially corrects for self-absorption and varying sample density (i.e., x-ray tube source backscatter from sample) (Markowicz, 2011). However, the data generated by EDXRF corroborates with destructive techniques irrespective of acid dissolution or the method adopted for deriving REE-2 data sets. The maximum standard deviation within labs is 4 for Gd and between labs is 21 for Pb and confidence interval of mean is 4.3 for Pb (as Gd and Pb) are heavy elements and used as secondary targets in EDXRF.

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