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Homogeneity Study of Bauxite Reference Materials

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Abstract

Laboratories involved in chemical analysis are becoming more aware of the need to implement some kind of quality system. In order to ensure that correct level of accuracy is achieved, it is imperative that quality policies must be based on use of Certified Reference materials. Homogeneity and stability are two crucial characteristics of any Certified Reference materials (CRM). Utmost care must be taken during preparation of materials as homogeneous and stable possible. However, careful preparation by itself is not enough. Positive demonstration of homogeneity is essential from the perspective of implementing uncertainty calculation. In many cases, homogeneity studies fail to give sufficient quantitative information, mainly because of a lack of measurement repeatability and insufficient number of replicates. In this work a systematic approach has been followed for preparation of Bauxite Certified Reference Materials.

INTRODUCTION

Characterization of materials plays a vital role in chemical and metallurgical industries. The suitability of material / products are entirely based on the measurement and in order to increase the acceptability of products / materials, it is imperative that measurements must be accurate and reliable, which can be achieved by the use of certified reference materials (CRMs). Their use in calibration of analytical equipments and validation of test methods ensures high quality in measurements and it provides traceability to the measurement data with national / international measurement systems (SI unit) also. In the present scenario of globalization of economy, use of certified reference materials (CRMs) in measurements is essential for global acceptance of products and test reports. There use are mandatory requirement for compliance of quality systems (ISO 9000, ISO/IEC standard 17025) and laboratory accreditation. International manufacturers of CRMs are meeting most of the requirement of CRMs of the country. To meet the demand of CRMs indigenously, JNARDDC, Nagpur has taken up programme on preparation of certified reference materials for selected ores.

HOMOGENEITY OF CRM

Homogeneity testing is a well-known phenomenon in the preparation and certification of reference materials. It also finds its application in the preparation and checking of proficiency testing material. The design of the homogeneity study is the same for both between bottle and within-bottle testing. Within bottle homogeneity, dictates the minimum sample intake and between bottle homogeneity, which deals with bottle to bottle variation.

Certified reference materials undergo a batch certification, which implies that a small number of sample is taken from a batch, characterized, and these results are then assumed to be representative of all remaining samples. An important aspect in this design is the translation of the characterization data to a single sample, as usually the laboratory will be using only one sample of the batch. This form of homogeneity is very important and can be influenced to a certain extent by well-designed sample preparation procedures. Another sub sampling problem associated with many reference materials is

that only a small test portion is drawn from the sample to carry out the measurement. Obviously, this test portion must be representative of the sample, otherwise the certified value is still not applicable. Both kinds of homogeneity tests have been examined and evaluated in the paper.

PREPARATION OF BAUXITE CERTIFIED REFERENCE MATERIAL

Under this work, 20.0 kg of each of bauxite ore were collected from Panchpatmali (JNA / Bx / 1) and Mainpat deposit (JNA / Bx / 4). Preparation of material was carried out in way to minimize the heterogeneity. Colleted bauxite were crushed and grinded and finally it was sieved through a 200-mm sieve in order to eliminate possible impurities and big particles. After sieving the powder, it was homogenized by passing it through a sample divider and mixing it back several times. Finally the material was bottled in glass bottles, which had been previously washed in 10% HNO3 and rinsed with distilled water, with tight screw cap. As the preparation of the bauxite do not require any change in the matrix, the representativeness was not affected.

HOMOGENEITY TESTS

Both kind of homogeneity was evaluated in accordance to ASTM standard E – 826. Ten bottles for each material were used in the homogeneity tests. Five independent measurements were carried out for each bottle, so a total of 50 concentration values were obtained for each analyte of concern (Al_2O_3, Fe_2O_3 & SiO_2).

CHARACTERIZATION OF BAUXITE

Different amount of bauxite samples (0.5, 1.0 and 2.0 gms) were taken from same bottle, in order to work out the minimum sample in take, which can ensure the repeatability and reproducibility of measurements and found that 1 gm of sample in take is sufficient to ensure the reproducibility. Samples were analysed following IS - 2000. Standard deviation were estimated for within bottle and between bottle variability and given in the table below:

Table 1: Standard Deviation Variability of Bauxite Reference Materials

Sample & analyte	Within bottle	between bottle
JNA / Bx / 1		
▪ Al2O3	0.30	0.38
▪ Fe2O3	0.38	0.42
▪ SiO2	0.11	0.15
JNA / Bx / 4		
▪ Al2O3	0.41	0.47
▪ Fe2O3	0.31	0.36
▪ SiO2	0.19	0.24

RESULTS AND DISCUSSION

Analysis of variance of the results was carried out for each or the element measured. The results for each of the elements of bauxite follow a normal distribution. Variance analysis shows that there is no significant difference in the variability of concentrations within bottles and among bottles of all the analytes of bauxite. As results, materials proved to be homogeneous. The variability of results for each element is estimated, using the following equation and complied in table 2.

$$S_{bb} = \sqrt{\frac{MS_{bb} - MS_{wb}}{N}}$$

Where MS_{bb} is between bottles mean square and is the between bottle and n is number of independent measurements.

Table 2: Variability of Elements Concentration Measurements

Average concentrations, standard deviations and among bottle variability				
Material	**Element**	**Average Concentration %**	**Standard deviation**	**Variability**
JNA / Bx / 1	Al_2O_3	41.21	0.38	0.21
	SiO_2	1.38	0.42	0.18
	Fe_2O_3	31.46	0.15	0.10
JNA / Bx / 4	Al_2O_3	49.45	0.47	0.32
	SiO_2	3.21	0.36	0.28
	Fe_2O_3	17.24	0.24	0.19

STABILITY TEST

The stability test were carried out using IRMM protocol. In order to check the stability of each component, three bottles of each material were kept at different temperature for different time. The reference temperature was 18 – 20° C and other temperature was room temperature 30 – 35° C. Concentrations of each element were measured after 1 & 3 months, and the ratio (R_ts) of the concentration of the elements in the sample at selected temperature were calculated and given in the table 3

Table 3: Results of Stability Test

Material	**Element**	**One Month**			**Three Month**		
		Conc at 18 – 20° C	**Conc at 30 – 35° C**	**(R_ts)**	**Conc at 18 – 20° C**	**Conc at 30 – 35° C**	**(R_ts)**
JNA/Bx/1	Al_2O_3	41.13	42.08	1.02	40.78	41.03	0.99
	SiO_2	1.35	1.32	0.98	1.31	1.38	0.94
	Fe_2O_3	31.02	32.26	1.04	31.00	31.65	0.97
JNA/Bx/4	Al_2O_3	49.35	48.87	1.04	49.45	49.85	0.99
	SiO_2	3.15	3.31	1.15	3.18	3.02	1.05
	Fe_2O_3	17.34	17.02	1.02	17.67	17.38	1.01

ESTIMATION OF MEASUREMENT UNCERTAINTY

Uncertainty of measurement for each analyte was estimated following the protocol of Eurochem guide. All the contributing factors were taken into consideration. Individual uncertainty of measurement for each analyte is given in table 4:

Table 4: Uncertainty Estimate

Material	**Element**	**MOU %**
JNA / Bx / 1	Al_2O_3	± 0.52
	SiO_2	± 0. 13
	Fe_2O_3	± 0. 24
JNA / Bx / 4	Al_2O_3	± 0. 47
	SiO_2	± 0. 18
	Fe_2O_3	± 0. 31

CONCLUSIONS

According to the results obtained, both materials are homogeneous and stable, so they can be considered suitable reference materials for inter-laboratory comparison. However, the values of the

concentrations obtained are only informative values in absence of inter laboratory comparison data and cannot be used to check the accuracy of the analytical procedures. The main point of the homogeneity and stability tests is that it is not really necessary to use an accurate procedure as long as it is reproducible. It is important to bear in mind that the analytical procedure used to prove the homogeneity of the material must be reproducible or, at least, more reproducible than the analytical procedure to be checked afterwards with this material.

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