A STUDY ON SAMPLING REPRESENTATIVENESS OF IAEA RM SD−M−2/TM MARINE SEDIMENT BY INAA

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ABSTRACT

The homogeneity of IAEA RM SD–M–2/TM Marine Sediment was tested by INAA. The sampling constants for 6 elements were determined.

Keywords: Sampling representativeness Standard reference material

1 INTRODUCTION

Homogeneity is one of the most important properties of Standard Reference Materials (SRM). Many workers have routinely used statistical tests (*e.g. F*–tests) and the degree of inhomogeneity (S_{inh})[1] for homogeneity testing of SRM. But these tests do not always give a true picture of sampling representativeness for a constituent, especially a trace element, in a given material.

Some modern trace analytical techniques (*e.g.* PIXE, LAMMA, *etc.*), require a sample size of mg or even less, as is limited by the instrument exploited or the technique itself. For some analytical objects (*e.g.* aerosols, monomineral grains, *etc.*), the amount of sample available is usually very small. In these cases, micro SRM samples are needed for quality control. However, information is not available for almost all the existing SRM on minimum sample size to ensure sampling representativeness for given elements.

Ingamells[2] proposed a sampling constant K_s for a well–mixed material. K_s can be determined from the relation

$$K_s = w R^2 \tag{1}$$

where R is the relative sampling uncertainty in percentage determined from analysing a set of subsamples of weight w.

INAA (instrumental neutron activation analysis) has recently been used for K_s determination of multielements in some materials[3,4,5]. However, no confirmation was given in any of the above studies as for whether the materials under investigation are "well–mixed", which is a prerequisite of the K_s theory.

Visman[6] developed a general theory of sampling that takes into account the effects of inhomogeneity to suit both well-mixed and segregated materials. According to Visman's theory, we developed the sampling constants a (homogeneity constant) and b (segregation constant) as below:

$$S(\%) = a/wn + b/n \qquad (2)$$

where S is the relative sampling variance in percentage, n the number of increments. The constants a and b can be obtained from the following equation:

$$a = n \cdot W_{sm} W_{lg} (S^2_{sm} - S^2_{lg})/(W_{lg} - W_{sm}) \qquad (3)$$

$$b = n\,(S^2_{sm} - a/W_{sm}) \qquad [\text{or } n\,(S^2_{lg} - a/W_{lg})] \qquad (4)$$

where S^2_{sm} and S^2_{lg} are the sampling variance for samll-subsamples and large-subsamples, W_{sm} and W_{lg} are the small-subsample weight and large-subsample weight, respectively.

In the present work, we have for the first time determined a and b for 6 elements in IAEA RM SD-M-2/TM marine sediment by INAA.

2 EXPERIMENTAL

2.1 *Preparation of samples and standards* For short time irradiations, seven 150-mg and fifteen 2-mg samples of SD-M-2/TM were packed in polyethylene (P.E.) bags. For long time irradiation fifteen each of the samples were wrapped in Al foils. Neutron flux variations were, as checked in advance, less than 1%. NBS SRM 1632a and 1633a and SRM GSD-12 were chosen as multielemental standards and/or assurance samples.

2.2 *Irradiation and counting* The irradiations were performed at HWRR of CIAE. Thermal neutron fluxes are $3\times 10^{13}\,ncm^{-2}s^{-1}$ for long irradiation and $1\times 10^{13}\,ncm^{-2}s^{-1}$ for short one. After irradiation the samples and standards were transfered into P.E. vials. The countings were carried out with a HPGe detector (26%, 1.9 keV), a Canberra S-40 MCA and a PDP-11/34A computer.

3 RESULTS AND DISCUSSION

The homogeneity evaluation is based on Youden's[7]. definition of the overall random error of an analysis.

$$S_o = (S^2_a + S^2_{inh})^{0.5} \qquad (5)$$

where S_o is the observed standard deviation, the S^2_a the variance due to random errors of the analysis, S^2_{inh} a variance due to sample inhomogeneity. Thus, S_{inh} can be calculated as

$$S_{inh} = (S^2_o - S^2_a)^{0.5} \qquad (6)$$

In INAA, the S_a value can be approximated by

$$S_a = (S_g^2 + S_i^2 + S_c^2 + S_w^2)^{0.5} \qquad (7)$$

where S_g is the random error due to variations in counting geometry, S_i is the random error due to difference in the effective neutron flux, S_c is the counting statistical error, S_w is the weighing error.

Relevant parameters for S_{inh} calculations using Eqs (6 and 7) are summarized in Table 1 and 2. The standard deviations due to variations in irradiation and counting geometry $(S_i^2+S_g^2)^{0.5}$ were estimated to be close to 1%. The weighing errors are negligible for the large subsamples and are about 1% for the small subsamples. With these estimations, the degree of inhomogeneity S_{inh} could be calculated as long as $S_o >$ S_a. And the sampling constants a and b can be calculated from Eqs (3 and 4).

Table 1

Evaluation of the degree of inhomogeneity for large—subsamples of SD—M—2/TM (μ g/g)

Element	$X \pm S$*	S_o (%)	S_c (%)	$S_i^2+S_g^2$ (%)	S_a^2 (%)	S_{inh}^2(%)	n**
Cr	96.1±1.7	1.8	0.4	1.0	1.16	2.08	15
La	27.9±0.7	2.6	0.6	1.0	1.36	2.25	15
Sm	4.66±0.12	2.6	2.0	1.0	5.00	1.76	11
Eu	0.933±0.013	1.4	0.5	1.0	1.25	0.71	15
Lu	0.272±0.013	4.9	3.0	1.0	10.0	14.01	15
Th	8.64±0.16	1.9	0.6	1.0	1.36	2.25	15

In Table 1 and 2, * Data given here are tentative and uncertainties are in 68% confidence level ** Number of subsamples

Table 2

Evaluation of the degree of inhomogeneity for small—subsample of SD—M—2/TM (μ g/g)

Element	$X \pm S$*	S_o (%)	S_c (%)	$S_i^2+S_g^2$ (%)	S_w^2 (%)	S_a^2 (%)	S_{inh}^2(%)	n**
Cr	98.5±3.9	3.9	1.6	1.0	1.0	3.69	11.52	15
La	28.2±1.6	5.8	2.6	1.0	1.0	8.76	24.88	15
Sm	4.63±0.36	7.7	2.9	1.0	1.0	10.4	48.88	15
Eu	0.781±0.0056	7.2	3.8	1.0	1.0	16.4	35.4	15
Lu	0.297±0.078	26.0	17.0	1.0	1.0	291.0	385.0	15
Th	8.68±0.49	5.6	1.7	1.0	1.0	4.89	26.47	15

Table 3

Results of the sampling constants for SD—M—2/TM

Element	a (mg)	b
Cr	23.3	1.93
La	48.1	5.09
Sm	116.4	0.99
Eu	85.7	0.13
Lu	916.4	7.88
Th	59.8	1.86

In evaluation of the sampling constants, we considered that (A) the sampling constants (a and b) are meaningful only when the sampling variance is discernible in the overall variance (say, $S_{inh}/S_o > 50\%$), (B) if $S^2_{lg} W_{lg} > S^2_{sm} W_{sm}$ and $S^2_{sm} > S^2_{lg}$, the sample is considered to be segregated and S_{sm} and S_{lg} can then be used to estimate the values of *a* and *b*. The results of *a* and *b* for Cr, La, Sm, Eu, Lu and Th are listed in Table 3.

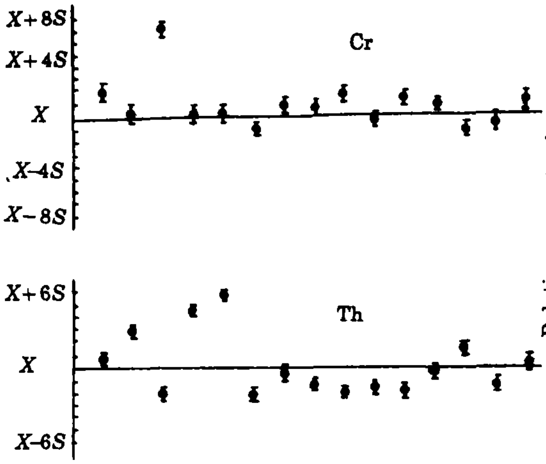

Fig.1 Variation of data for Cr and Th in SD−M−2/TM (sample size=2 mg)

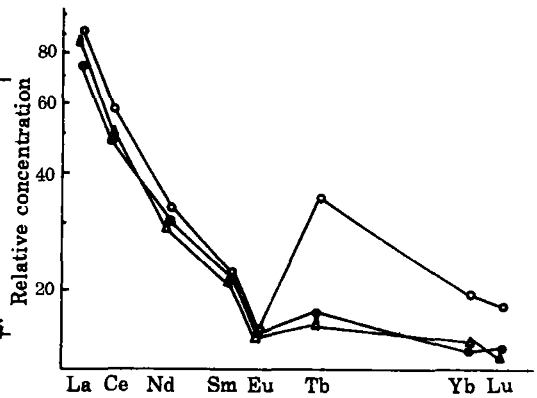

Fig.2 Chondrite−normalized REE distribution in SD−M−2/TM (sample size=2 mg)

The chondrite values are from Wakita[8]

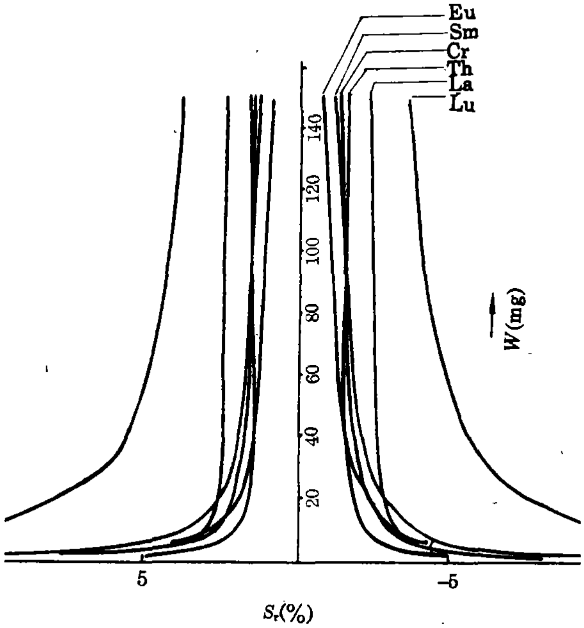

Fig.3 Relative sampling variance of REE with subsample weight *W*

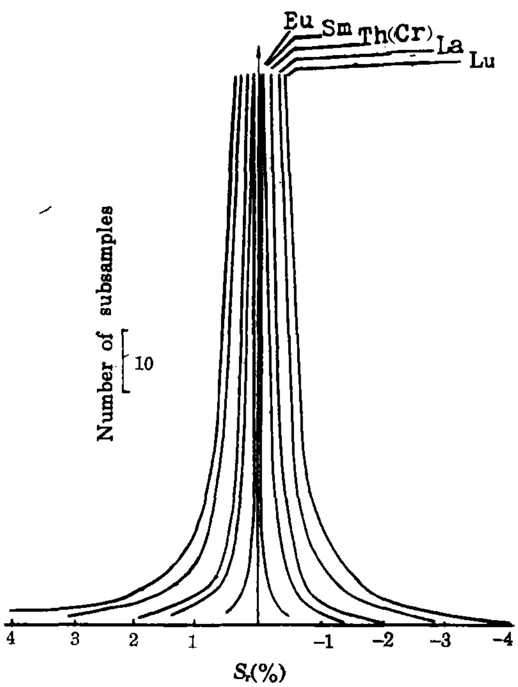

Fig.4 Effect of *n* on sampling uncertainty

The following conclusions for marine sediment SD–M–2/TM can be drawn: (a) Elements such as Na, Sc, Fe are found to be homogeneous at sample size of 2 mg. And the results of these elements demonstrate that the analytical method is in a state of statistical control. (b) The sampling constant a and b vary greatly with elements. (c) Some elements such as Cr, Th and REE are found to be segregated obviously. Fig. 1 shows the data for Cr and Th in SD–M–2/TM of a 2 mg sample size. The error bars are statistical counting errors. x and s used in this figure are mean values and corresponding errors for Cr and Th. The segregation of the REE is clearly reflected in the plot of chondrite–normalized REE distribution in Fig.2. The obvious differences in REE patterns of different subsamples, especially for Tb, Yb and Lu, show the serious inhomogeneity and segregation of these elements. (d) The relative sampling variance for a given element in a material can be estimated for any subsample size w from the Eq. (2) when values of a and b are known for this element.

As shown in Fig.3, sampling errors change rapidly for the small size samples. From a certain sample size (depending on element) the curves are leveled off. This indicates that further increase in sample size will not improve the sampling variance. This is because the term b/n in Eq. (2) dominates the sampling variance. In this case, sampling variance will continue to decrease as the number of subsamples increases, as shown in Fig.4.

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