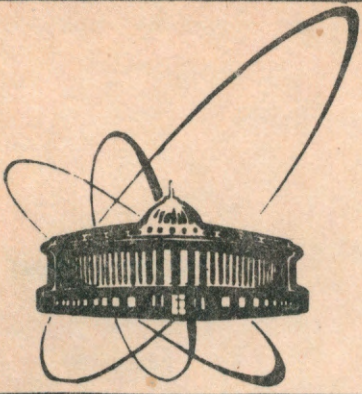

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FINE-POWDER Al_2O_3 AND SiO_2 FOR PREPARATION OF MULTIELEMENT STANDARDS FOR RARE-EARTH ELEMENTS ANALYSIS

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INTRODUCTION

Natural materials (granites, basalts, sediments, etc.) are often used in the activation analysis of geological and ecological samples as multielement standards (MES) as well as artificial MES [1] in the form of thin layered solid sorbents.

The use of natural standards is preferable due to the possibility of choosing the matrix composition and the geometry very similar to those of the samples under investigation. At the same time the presence in them of elements which disturb the analysis (Fe, Mn, Ba, Sc, etc.) significantly decreases the precision of the trace element determination.

This paper proposes to deal with fine powder Al_2O_3 and SiO_2, used in exchange chromatography, as artificial MES for REE. The sorption of REE (Tm, Sm, Yb, Eu, Tb) with required homogeneity has been conducted using the well-known analytical methods with the final drying of samples for two hours at 200° C. Powders are produced by the MERCK Company with the grain size of Al_2O_3 of 0.063 - 0.2 mm and of SiO_2 - 0.063 mm.

The homogeneity of the prepared standards was checked by means of neutron activation analysis at the nuclear reactor

IBR-2 of the JINR [2] and the reactor of the Imperial College [3]. Five groups of samples with the concentration of REE in ppm for the first group: Tb - 13, Sm - 15, Yb - 38, Eu - 350, Tm - 600 were used for this purpose. In each consequent group the concentration of all elements was three times greater than in the previous one.

In addition to the data on homogeneity, in the mentioned above, in the range of REEs' concentrations, the self-screening coefficients for resonance neutrons of spectrum close to 1/E were obtained.

RESULTS AND DISCUSSION

Homogeneity of two groups of samples of 0.5 and 0.1 grams in weight with rare-earth elements introduced, was determined using 6 samples irradiated in a well-homogenized field of resonance and thermal neutrons. Corrections for the neutron field inhomogeneity, did not exceed 3% in both cases.

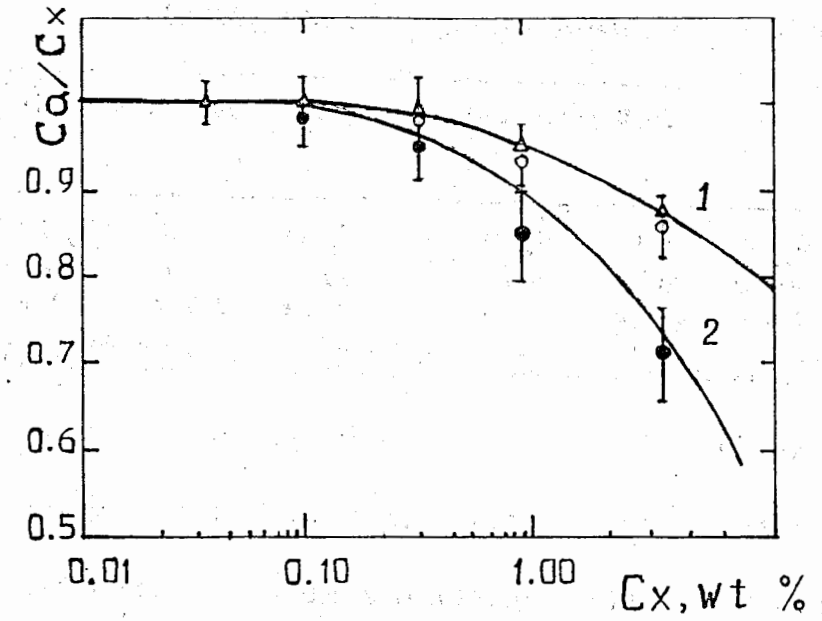
The SD homogeneity values obtained for the 1st and the 5th concentration groups at the drying temperatures of 90° and 200° C are presented in Table 1. The statistical SD values are given in brackets. As is seen from Table 1, the SD averaged over all elements for SiO_2 are more than twice as large as those for Al_2O_3, the fact being probably due to the agglomeration of the SiO_2 or its homogenization.

Table 1: Homogeneity of Al_2O_3 and SiO_2 MES Samples

Element	Al_2O_3 SD,% (st. SD%)			SiO_2 SD,% (st. SD%)		
	C_I gr 90 C 0.5 g	C_V gr 90 C 0.5 g	C_V gr 200 C 0.1 g	C_I gr 90 C 0.5 g	C_V gr 90 C 0.5 g	C_V gr 200 C 0.1 g
Tb	1.23(2)	0.0(3)	0.46(0.5)	0.0(1.6)	4.0(3.3)	1.9(1)
Sm	0.5(0.8)	-	-	3.0(0.4)	-	-
Yb	1.1(2)	0.0(3)	1.3(2.5)	2.8(1.6)	3.4(3.2)	2.4(3.4)
Eu	0.54(1.0)	1.55(0.6)	0.76(0.5)	2.3(0.4)	3.0(0.6)	1.2(1.0)
Tm	1.0(0.6)	2.15(0.4)	1.65(0.3)	1.8(0.2)	3.5(0.7)	2.3(0.4)
Averaged over all elements	0.87	0.93	1.04	2.0	3.5	1.95

For all of the concentrations practically no difference in SD was obtained at sample weights of 0.5 and 0.1 g. This permits the use of Al_2O_3 and SiO_2 matrices of less than 0.1 g weight as MES.

The figure shows the dependence of the resonance neutrons self-screening $C_a/C_x = f(C_x)$ at equal concentrations of Eu and Tb introduced into matrices of Al_2O_3 and dried at temperatures of 90°, 200° and 400° C for Eu, and at 200°, 400° C for Tb. Here C_x is the concentration of elements



introduced into Al_2O_3 ; and C_a, the concentration of elements obtained by the neutron activation analysis.

For Tb (curve 1) experimental points are obtained at temperatures of drying of 200° and 400° C. For Eu (curve 2) the experimental errors correspond to SD for four measurements at 200°C, one at 90°, and one at 400° C.

The experimental values for C_a/C_x obtained in the cadmium channel of the IBR-2 reactor are satisfactorily described by the expression

$$C_a / C_x = (1 - \exp(- \sum_I \Delta x))/ \sum_I \Delta x$$

obtained for a monodirectional neutron beam. Here

$$\sum_I \Delta x = (0.6\ I\ C\ \rho\ )/A$$

for a sample area of S= 1 cm^2, where I is the resonance integral in barns; C, the concentration of the introduced elements in g/g; ρ, the matrix density; and A, the atomic weight of the introduced element.

The dependence of $C_a/C_x = f(C_x)$ on Eu and Tb, was obtained at values of resonance integrals equal to 1400 and 630 barn, respectively. One may see from them that C_a/C_x decreases only by 1.5% at concentrations up to 10^{-3} g/g for Eu and 3.3 10^{-3} g/g for Tb. From these dependencies it also follows that even at long-time drying of the samples at 400°C, no loss of Eu or Tb takes place.

Of course, both Al_2O_3 and SiO_2 are not superpure materials and so before using them as MES, one should have the data on their impurity elements' content.

This content for the sorbents used was determined by means of the activation analysis in the cadmium channel of the reactor IBR-2. The elements were determined using isotopes with half-lives of more than 14 hours. The results obtained for the REE are given in Table 2; and for other elements, in Table 3. These tables contain, for comparison, the data on the impurities of two natural standards SL-1 (sediments) and SGA-AS-1 (apatites). As is seen from Table 1, compared to SL-1, the content of the REE (besides Tb) is below 0.5% in an Al_2O_3 matrix. Tm is an exception for SiO_2 (10% if compared to SL - 1).

Therefore if, in the given Al_2O_3 and SiO_2 matrices, 10,

Table 2: REE Content Determined by INAA

Element	Concentration, ppm			
	SiO_2	Al_2O_3	SL-1	SGA-AS-1
La	0.49±0.033	0.0029±0.0003	52.6±3.1	2176±94
Ce	0.48±0.045	<0.01	117±17	-
Nd	0.35±0.052	<0.1	43.8±2.8	1087±124
Sm	0.032±0.0016	0.013±0.0008	9.25±0.51	162±24
Eu	0.007±0.0008	<0.006	1.6	46.7±1.3
Tb	0.0037±0.0003	0.39±0.06	1.4	13.9±1.5
Tm	0.083±0.004	<0.009	0.66	-
Yb	0.037±0.004	<0.01	3.42±0.64	11.4±2

100 times higher concentrations of Tm for SiO_2 and Tb for Al_2O_3, respectively, are introduced; the increment contribution of these elements into their final concentration would not exceed 1%. As is seen from Table 3, the concentrations of some other impurity elements in Al_2O_3 and SiO_2 matrices are less by more than 100 times than, for example, in SL-1.

The analysis of the content of impurity elements in these matrices has proved their ratio (especially in SiO_2) to be more convenient for use in multielement neutron activation analysis compared to such natural standards as SL-1, or SGA-AS-1. For this reason natural SiO_2 fine powders can be used as a material for MES in the multielement activation analysis of superpure materials with impurity concentrations at a level of ppb and lower, when the weights of samples for the needs of sensitivity should not exceed 10 - 15 g. These materials should first

Table 3: Elemental Composition of Al_2O_3 and SiO_2 MES Standards

Element	Concentration, ppm			
	SiO_2	Al_2O_3	SL-1	SGA-AS-1
As	0.038±0.03	0.05±0.004	2.75±2.9	-
Au	<0.015 ppb	0.045±0.006 ppb	10	-
Ba	19.0±2	0.21±0.025	639±53	767±9
Br	0.14±0.017	0.02±0.0003	6.82±1.73	-
Cr	3.4 ±0.22	<0.3	104±9	13
Cu	14.9±1.0	<3.0	30±5.6	54±4.5
Cs	0.008±0.0005	<0.001	7.01±0.88	-
Fe	28.6±2.1	126 ±9.0	6.74±0.17wt	0.5 wt%
Ga	<0.2	26±2.6	24	-
Ge	166±43	<50	25	-
Hf	0.7±0.02	0.37 ±0.04	4.16±0.58	1.13±0.17
K	71.8±20	<30	1.5 wt%	2088
Mo	3.88±0.96	0.55 ±0.14	1.3	-
Na	538±84	-	0.172±0.012wt%	3841±564
Ni	1.12±0.12	0.12 ±0.008	44.9±8.0	9.0
Ru	1.5±0.32	<0.3	0.13	-
Sb	0.097±0.008	0.019±0.0015	1.31±0.12	-
Se	0.019±0.025	0.014±0.0018	2.9	-
Sc	0.053±0.008	0.079±0.01	17.3±1.1	0.244±0.035
Sr	4.74±0.8	0.77 ±0.2	80	2 wt%
Sn	<6	12.9±4.1	4.0	-
Ta	0.019±0.0007	0.001±0.00005	1.6	2.65±0.23
Te	<0.1	0.15±0.034	2.0	-
Th	0.1±0.0032	0.015±0.0005	14±1.0	21.8±2.1
Ti	16.8 ±3	<4.5	0.517±0.037wt%	2927±554
U	0.014±0.0005	0.015±0.00023	4.02±0.32	4.4±0.9
W	<0.02	0.059±0.006	6.0	-
Zn	2.35±0.1	10.2±0.4	223±10	38.0±7.6

be certified, of course.

The materials proposed here for use as MES standards, both in natural form and with additionally introduced elements, are planned to be used in the LNPh of the JINR as standards in the activation analysis of heavy metals (Cu, Zn, Cd, As, HG et al.) and REE in ecologically-pure grain

crops, i.e., when for analysis, one needs samples of weights up to 10 g to obtain sufficient sensitivity.

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