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Scanning proton microprobe microanalysis for the assessment of homogeneity of IAEA urban dust reference materials*

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Abstract—In order to develop new reference materials for microanalytical nuclear techniques, scanning proton microprobe (SPM) technique was used to determine homogeneity level within 100×200 μm^2 micro-area on the small pieces of IAEA urban dust reference materials. The experimental methods were described in detail. The results show that IAEA-396A/M Vienna urban dust is homogeneous enough for small sample analysis of standard reference material (SRM).

Keywords: standard reference material (SRM); scanning proton microprobe; urban dust.

1 Introduction

Standard reference materials (SRM) are an indispensable element of quality assurance. They play a key role in demonstration of accuracy of analytical work. Up to now, the reference materials of various analytical techniques are mostly satisfactory, there is an increasing demand for micro qualitative information of nuclear analysis techniques. Most RMs are certified for minimum sample sizes larger than 100 mg in their certificates by producers. This is useless for methods, XRF, NAA, PIXE and other accelerator-based methods, RBS, NRA …… these commonly use and analyze samples in the mg mass range or even smaller samples. So much work still remains to be done to improve measurements capability for the determination of trace components present at the mg/kg to μg/kg levels in environmental and biological samples. Some specific natural matrix reference materials containing very low levels of trace elements and having high degree of homogeneity are developed for many micro-analytical procedures (Valkovic, 1992; Zeisler, 1995).

The CRP organized by IAEA specifically addresses the question of quality control materials for micro-analytical nuclear techniques. As a task we make efforts to do an improvement of required sample size of RMs by an order of magnitude at least, i.e. selected RMs should be certified for sample sizes of 10 mg or smaller. For this purpose, two samples of urban dust, IAEA-396A/S (particle size 6—30 μm) and IAEA-396A/M (particles size < 6 μm) were analyzed by Micro-PIXE for homogeneous determination at small scanning region (100×200 μm^2) for as many elements as feasible. The differences in elemental concentrations due to sample processing were also observed.

2 Experimental method

In order to assess distribution of trace elements and micro-homogeneity to smaller samples, some urban dust powder reference materials 396A/M and 396A/S were put into clean cups and dried at 85℃ for twenty four hours. Then 160 mg samples of both powder reference materials were

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weighed and φ13 mm diameter small pieces were prepared by pressing these samples in a 10 ton press.

Measurement is performed utilizing the scanning proton microprobe experimental set-up in our institute as shown in Fig. 1. It employs a NEC 4MV pelletron accelerator as an ion beam injector.

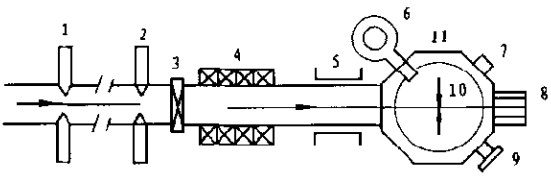

Fig. 1 A diagram of the scanning proton microprobe
1: object; 2: aperture; 3: vacuum valves; 4: quadrupole lenses; 5: deflect. coils; 6: Si(Li) detector; 7: window; 8: faraday cups; 9: vacuum pump; 10: sample target; 11: target chamber

The proton microprobe is Russian quadruplet constructed with four magnetic quadrupoles. The focal length of the microprobe line is greater than 40 cm and the overall length of the microprobe line is about 9m, in order to achieve a demagnification of 20 times. The beam size is around 2 μm and the current on the sample is about 10 PA. The vacuum target chamber is an octagonal construction. A retractable 28 mm^2 Ortec Si(Li) detector covered with a thin beryllium window is mounted at 135° to the beam direction. The scan size in this experiment is 100×200 μm^2 as shown in Fig. 2. A multiparameter multichannel analyzer ND-76 is used for event by event data collection and a Micro-VAX computer system is employed data treatment (Zhu, 1990; Zhang, 1996a; 1996b).

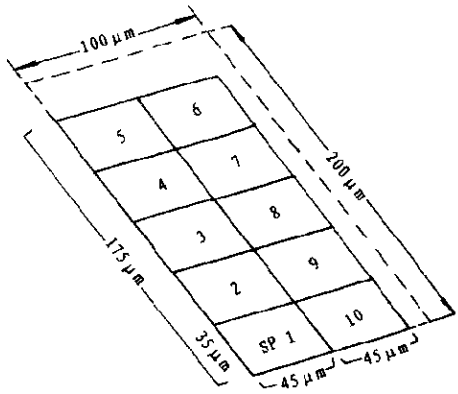

Fig. 2 A scanning region of Micro-PIXE

3 Results and discussion

Fig. 3 is a typical point PIXE spectrum of Vienna urban dust IAEA-396A/M. In order to evaluate the homogeneous level quantitatively in more micro area, we decide the scanning region 100×200 μm^2 into ten micro areas, each 35×45 μm^2, as shown in Fig. 2. The average results of ten micro PIXE intensity maps for each element are shown in Table 1. Also the same results are more directly displayed in two pictures of Fig. 4. The elements of As and Kr are under detective limit, so their data do not be included in Table 1. Among the two fractions of the Vienna urban dust IAEA-396 SRM, final fraction sample shows higher degree of homogeneity. From the X-ray intensity maps, very weak inhomogeneity is visible only for Cr and Ti. Coarse fraction has more signification inhomogeneity, visible for Al, Si, S, Cl, Ti and Cr. In the concentration data for the fine fraction sample just elements Ti and Cr have results scattered more than 25% and these are probably caused by insufficient statistics.

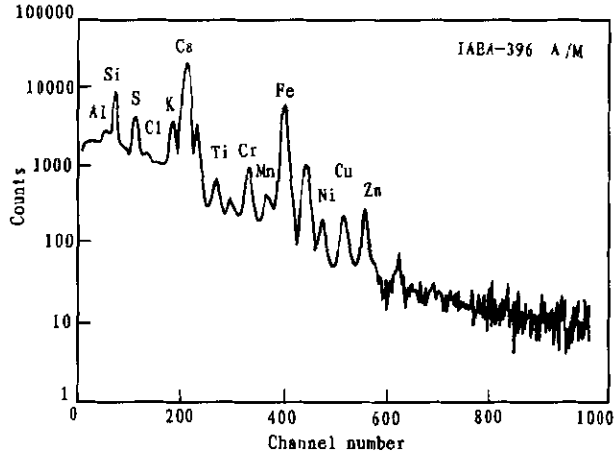

Fig. 3 A typical point PIXE spectrum of urban dust IAEA-396A/M

Table 1 Micro-PIXE results of IAEA-396A urban dust (net area)

Elements	IAEA-396A/M			IAEA-396 A/S		
	Average, X	Stan. dev., σ	Rel. dev., σ/X	Average, X	Stan. dev., σ	Rel. dev., σ/X
Al	591	88	15	860	297	35
Si	4392	443	10	4687	1523	32
S	1822	187	10	2461	664	27
Cl	251	52	25	314	185	59
K	2314	116	5	2586	256	10
Ca	13636	763	5	15882	1851	12
Ti	194	71	36	319	307	96
Cr	463	177	38	769	198	26
Fe	5083	183	3	6738	809	12
Ni	107	18	17	207	30	15
Cu	158	12	7	160	18	12
Zn	164	17	10	160	29	18

A sophisticated graphic program is built in to display elemental maps in the form of three dimensional isometric and two or three dimensional contour maps. It is interesting to see three dimensional distributions of elements in two kinds of Vienna urban dust in order to compare the particle size homogeneity. Fig. 5 shows three dimensional distributions of representative three elements within 100×200 μm^2 pressing pieces of 396A/M and 396A/S respectively. The contour maps are more favorable than other maps because from them one can get both qualitative information on distribution profile and quantitative information on elemental intensity and localization. From the pictures, it can be clearly seen that the homogeneous level in 396A/M is better than that in 396A/S. These results are also in accordance with Fig. 4.

Based on the total mass and the area of a ϕ13 mm diameter small piece we can roughly estimate the mass of scanning region 35×45 μm^2 as 2 μg. It is far less than analysis samples in the mg mass

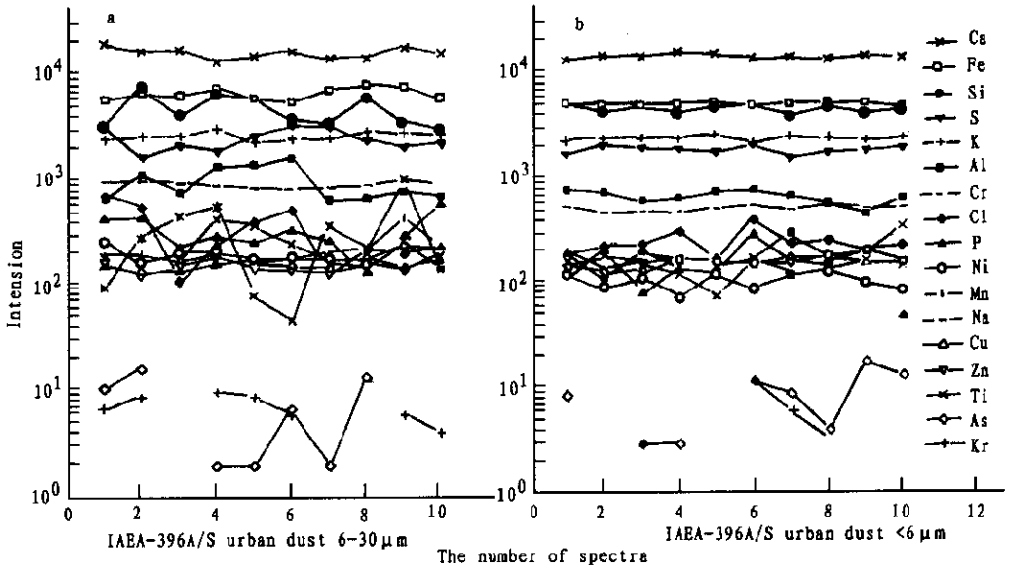

Fig. 4 Results in ten spectrum of IAEA urban dust

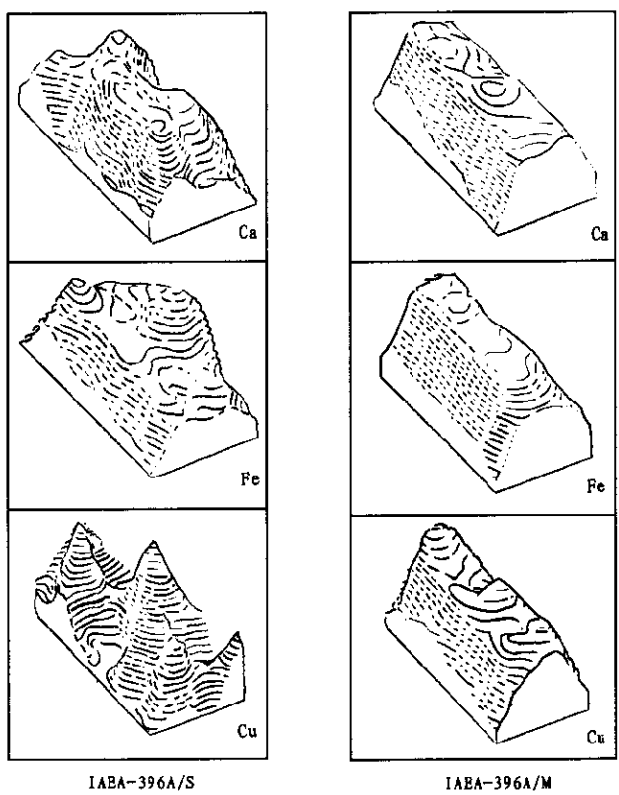

Fig. 5 Distribution maps of elements in the scanning region $100 \times 200\ \mu m^2$ of Vienna urban dust IAEA-396A/M and IAEA-396A/S

range goal. We can see that IAEA-396A/M has very good homogeneity level at such low scale and is suitable for possible certification at the 1 mg level. To sum up, by the development of focused proton or X-ray beams, the quantitative analysis of elemental distribution in the micro masses (go down to μg or even ng level) can be obtained. Also the advantage of the SPM PIXE technique is possibility of monitoring homogeneity of all elements in the sample by means of the X-ray intensity maps across the scanned region.

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