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Scanning proton microprobe microanalysis for the investigation of homogeneity of IAEA Urban Dust reference materials

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In order to develop new reference materials for microanalytical nuclear techniques, the Scanning Proton Microprobe (SPM) technique was used to determine homogeneity levels within 100×200 μm^2 micro-area on small pieces of IAEA Urban Dust reference materials. The experimental methods are described in detail. The results show that IAEA-396A/M Vienna Urban Dust is homogeneous enough for a SRM (≤10% for Si, S, K, Ca, Fe, Cu, Zn) for small sample analysis.

Introduction

Standard reference materials (SRM) are an indispensable element of quality assurance. Up to now, the reference materials have been mostly suitable for various analytical techniques, but there is an increasing demand for micro quantitative nuclear analysis. Most RMs are certified for minimum sample sizes larger than 100 mg by the producers. A minimum sample size, which is compatible with the respective analytical technique, however, is one of the most important requirements[1,2] for a suitable RM. Therefore RMs with such large sample sizes are useless for methods such as XRF, PIXE and other accelerator-based methods, which commonly use and analyze samples in the mg mass range or even smaller. 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.[3,4]

The co-ordinated research programme (CRP) organized by IAEA specifically addresses the question of quality control materials for micro-analytical nuclear techniques. The task is to improve the 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 (particle size < 6 μm) were analyzed by Micro-PIXE for the determination of homogeneity in a small scanning region (100×200 μm^2) for as many elements as feasible.

Experimental

In order to assess distribution of trace elements and micro-homogeneity of smaller samples, some Urban Dust powder reference materials 396A/M and 396A/S were put into clean cups and dried at 85 °C for twenty four hours. Then 160 mg samples of both powder reference materials were weighed and small pieces of 13 mm diameter 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 an NEC 4MV pelletron accelerator as an ion beam injector. The proton microprobe is a Russian quadruplet constructed of four magnetic quadruples. The focal length of the microprobe line is greater than 40 cm and the overall length of the microprobe line is about 9 m, 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 has 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 for data treatment.[5,6]

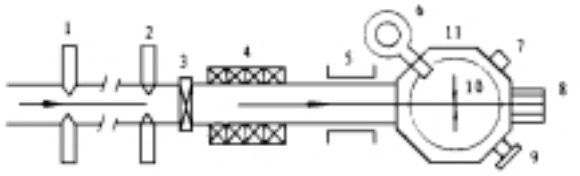

Fig. 1. A diagram of the scanning proton microprobe; 1 – object, 2 – aperture, 3 – vacuum valves, 4 – quadruple lenses, 5 – deflection coils, 6 – Si(Li) detector, 7 – window, 8 – faraday cups, 9 – vacuum pump, 10 – sample target, 11 – target chamber

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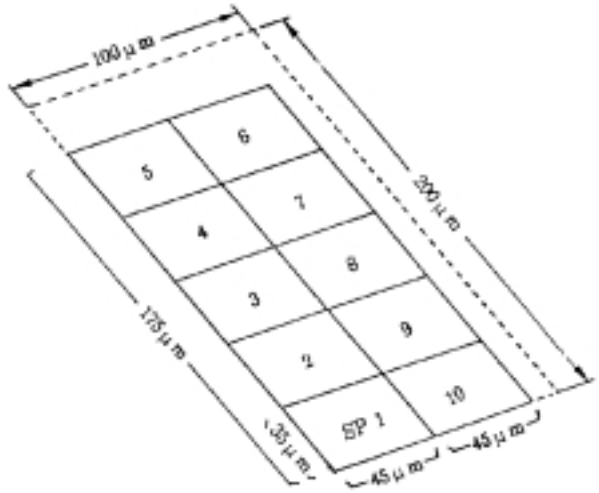

Fig. 2. A scanning region of micro-PIXE

Results and discussion

Figure 3 is a typical point PIXE spectrum of Vienna Urban Dust IAEA-396A/M. We performed the measurements of ten samples in succession for each scanning region 100×200 μm^2 for different independently prepared samples from the same material. In order to evaluate quantitatively the level of homogeneity in a small area, we divide the every scanning region of 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 of ten measurements for some elements are shown in Table 1. The results of Table 1 are also logarithmically displayed in two pictures of Fig. 4. Among the two fractions of the Vienna Urban dust IAEA-396 SRM, the final fraction sample shows a higher degree of homogeneity. The coarse fraction has more significant inhomogeneity, visible for Al, Si, S, Cl, Ti and Cr. In the elemental distribution data for the fine fraction sample (Table 1) only elements Ti and Cr have results scattered more than 25% and these are probably caused by insufficient counting statistics.

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. In Fig. 5 three dimensional distributions of representative three elements are shown 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 clearly be seen that the level of homogeneity in 396A/M is better than that in 396A/S. These results are also in accordance with Fig. 4.

Conclusions

Based on the total mass and the area of a 13 mm diameter small piece we can roughly estimate the sample mass in the scanning region of 35×45 μm^2. It is far less than the goal of analyzing samples in the mg mass range.

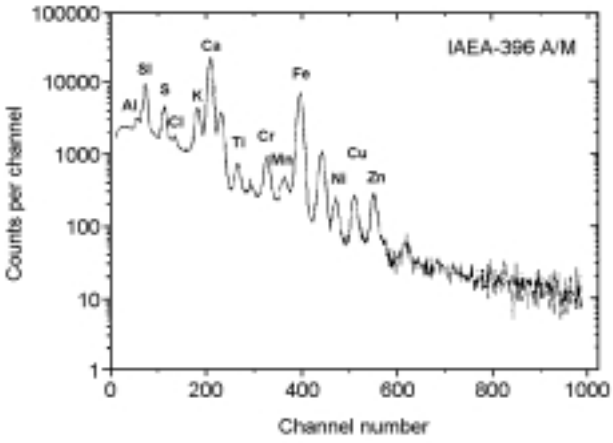

Fig. 3. A typical point PIXE spectrum of Urban Dust IAEA-396A/M

Table 1. Micro-PIXE results of IAEA-396A Urban Dust

Element	IAEA-396A/M Average	St. Dev.	Rel. Dev.	IAEA-396A/S Average	St. Dev.	Rel. Dev.
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

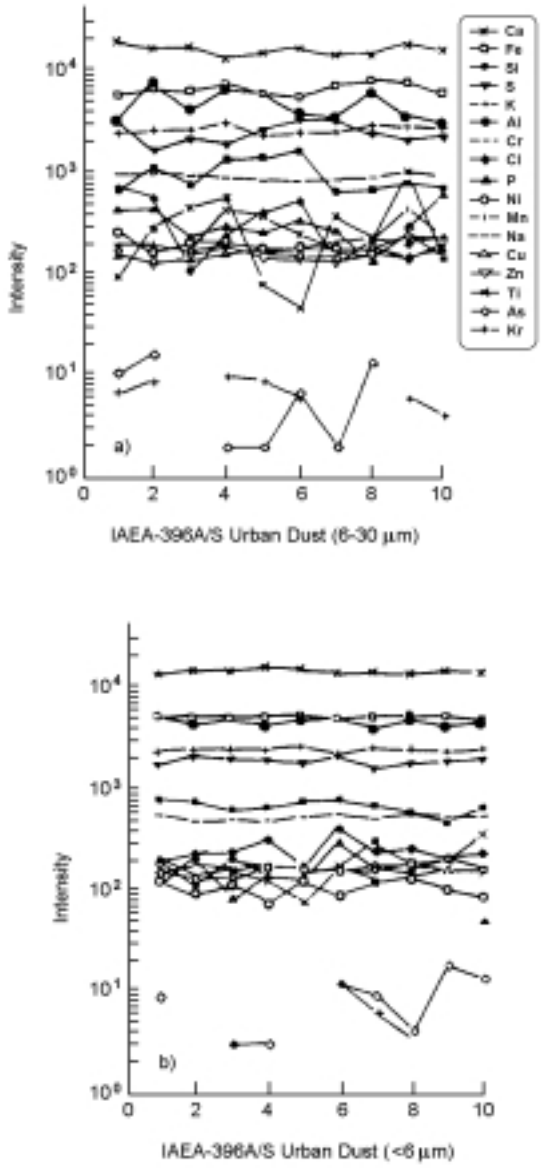

Fig. 4. Results in ten spectrum of IAEA Urban Dust

We can see that IAEA-396A/M has a very good homogeneity level at such low scale and is suitable for possible certification at the 1 mg level.

Using focused proton beams, the analysis of elemental distributions in the micro mass range (down to μg or even ng level) can be obtained. The quantitative analysis is not shown in this paper, but the method of relative mass distribution is also recognized as a valid approach for the homogeneity evaluation. An advantage of the SPM PIXE technique is the possibility of monitoring the homogeneity of all elements in the sample by means of the X-ray intensity maps across the scanned region.

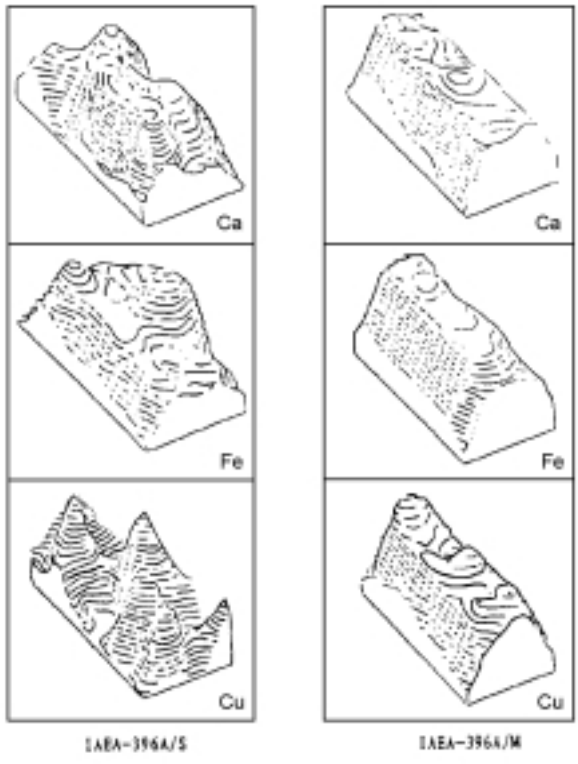

Fig. 5. Distribution maps of elements in the scanning region 100×200 μm^2 of Vienna Urban Dust IAEA-396A/M and IAEA-396A/S

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