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Identification of air pollution sources by single aerosol particle fingerprints – micro-PIXE spectra

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Abstract

A new method for direct assessment of air pollution is developed by using nuclear microprobe techniques to analyse single aerosol particles (SAP). Every particle is characterized by its PIXE spectrum which can be considered to be its fingerprint. The strategy for fingerprint classification and identification is used to trace a measured aerosol particle to its original source. Most of the particles have a size of up to 3 μm. The particles are separately attached to a clean thin foil. The Leipzig Nanoprobe, LIPSION, is used for this study. There are two steps in the new method. First, collect samples from different sources, measure them and compile their characteristic spectra into a library. Then, assess the environmental samples by comparing their spectra with those in the library. An artificial neural network (ANN) package is used for spectrum comparison.

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1. Introduction

Atmospheric environmental pollution is a global problem because aerosol particles can be transported over long distances and they have impacts on the global climate [1]. One of the major goals of environmental pollution monitoring and controlling is to identify the pollution sources and find ways to reduce their impacts. There have been many reports on the IBA applications to air pollution assessment, the PIXE technique in particular has been used widely and routinely for this purpose. Most of them used the bulk analysis of the total suspended particles (TSP) loaded on filters. Because many different particles are measured as a whole, ambiguities of pollution source identification occurred even if a large amount of sample measurements and a time consuming statistical data handling were used [2,3].

The limitation of the bulk analytical method can be avoided by the method of single aerosol particle (SAP) analysis. Applying this method, the size, shape and colour of the analysed particles,

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which are important in aerosol studies, can be selected. The characteristic elements of some individual particles may be at concentrations lower than the detectable limits of bulk analysis. However, these elements can be easily determined by single particle analysis. Although the electron microprobe can measure SAP very efficiently [4], its relatively low sensitivity restricted its applications, because some important trace element features in SAP may be lost.

A nuclear microprobe is suitable for SAP analysis, because it offers a reasonable spatial resolution (1 μm), high sensitivity and versatile analytical techniques [5,6]. It has been proved that the PIXE results of single particle analysis agree with those of bulk analysis to a tolerance of 10–20% [7,8]. Because of the geometrical and morphological factors of individual particles, the traditional quantitative PIXE analysis programs cannot be used with good accuracy [9]. Some calculation methods which try to reduce these effects have been discussed [10]. However, we can recognize each particle directly by its spectrum instead of its chemical composition. The spectrum pattern can be considered to be each particle's fingerprint. The strategy for the fingerprint classification and identification can be used to identify each measured aerosol particle. Based on the artificial neural network (ANN) technique, a pattern recognition procedure is developed for the identification. There are two steps in the procedure. First, a set of particles collected from different pollution sources is analysed by the nuclear microprobe. Their single particle PIXE spectra are recorded in a database as a fingerprint library of the pollution sources. Then, the environmental particles are measured with the same facilities. Their identification is performed by the ANN program when it reads the spectra of the particles.

2. SAP measurement

2.1. SAP sample preparation

The pollution source samples were collected from industrial excrements, such as ferrous or nonferrous smelters, iron and steel plants, oil or coal combustors, cement factories, building construction sites, vehicle exhausted gas and soil dusts. They contribute most of the aerosol particles floating in the atmosphere over Shanghai city. The environmental monitor samples were collected at the city centre.

A cascade impact sampler (model HY-1) is used and SAPs are collected on polystyrene fibre filters. 97% of the particles are smaller than 10 μm and 70% of them are smaller than 3 μm. Several methods for SAP sample preparation have been reported in our earlier work [11]. However, none of them could separate small particles (<3 μm) clearly and only groups of SAP had been measured [12]. In order to measure single particles one by one, it is essential to isolate the particles from each other on a thin foil. The isolated particles should be close enough to be found easily during a beam scanning. Keeping these requirements in mind, a new method for SAP sample preparation was developed.

A solution of nylon powder in iso-butyl alcohol was prepared at a temperature of 80°C. A droplet of the solution was dropped onto a rotary beaker of deionized water at room temperature. The droplet spread out and a very thin (0.2 μm) nylon foil was formed on the water surface. Just after the formation of the foil (in a few seconds), the collected single particles were dropped dispersively from the filter onto the sticky foil by a small shaker. After five minutes solidification, the foil attached to a stainless steel frame was taken out of the water. The single particles were separately embedded in the thin, clean and taut nylon foil. After 24 h baking at a temperature of 60°C, the SAP sample was ready for single particle analysis by the nuclear microprobe.

2.2. SAP measurement by the nuclear microprobe

Because most of the particles are smaller than 3 μm, both high spatial resolution and high beam current are needed. The Leipzig nuclear microprobe, LIPSION, satisfied the experimental requirements. A detailed description of LIPSION can be found in another contribution to this conference [13]. A 100 μm object diaphragm and a 100 μm aperture diaphragm were used to

produce a focused beam spot with 1 μm size and 80 pA current. A 50 nC integrated beam charge was required for each particle measurement.

Much experimental time was spent on searching for isolated small particles. A proper searching procedure was important for high experimental efficiency. At first, a large scan was needed to survey the sample in order to find areas where the isolated small particles were accumulated. Fig. 1 shows a PIXE image in a large scanning area (28×28 μm^2), in which several isolated small particles were closely situated. The coordinates of each small particle in the large scanning area were digitized and recorded for further small scans. A small scanning area (6–10 μm) was set up and one or more isolated particles were moved into the area. Fig. 2 shows nine examples of PIXE images in the small scan area. The high stability of the beam and the high precision of the sample positioning made the SAP measurements very efficient. In average, a total of 15 min was needed to search for and to measure each of the single particles. It is economically acceptable for an enlarged investigation.

The characteristic PIXE spectrum of each particle was extracted from raw data according to the particle shape. Fig. 3 shows a PIXE spectrum extracted from a particle excreted by a vehicle burning leaded petrol. A rough assessment of chemical composition in a single particle could be achieved simply by visual inspection of its spectral features. Hence, one could estimate the possible source of a particle from its spectrum provided that the spectral features of particles from all sources had been learnt beforehand. In order to do this, an ANN program called PATTERN was used.

3. Spectrum identification with ANN technique

The ANN attempts to simulate the function of the human brain for qualitative assessment. It has been applied successfully to the interpretation of various spectra in the fields of infrared [14,15],

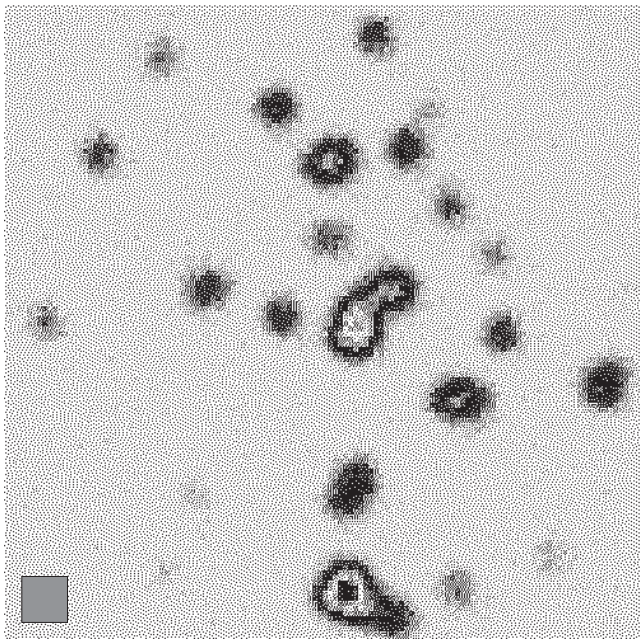

Fig. 1. PIXE image in a medium-sized (28×28 μm^2) scanning area, in which several isolated small aerosol particles are closely situated. A 2 μm square mark is presented at the bottom left of the area.

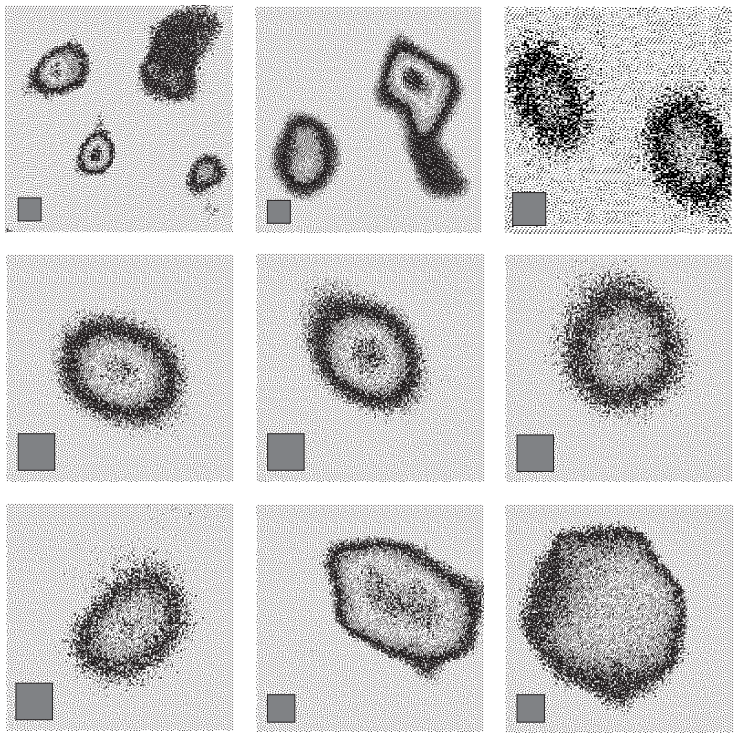

Fig. 2. Nine examples of PIXE images in small scan areas (6–10 μm), in which one or more isolated small aerosol particles are covered. A 1 μm square mark is presented in each area showing the size of the particles.

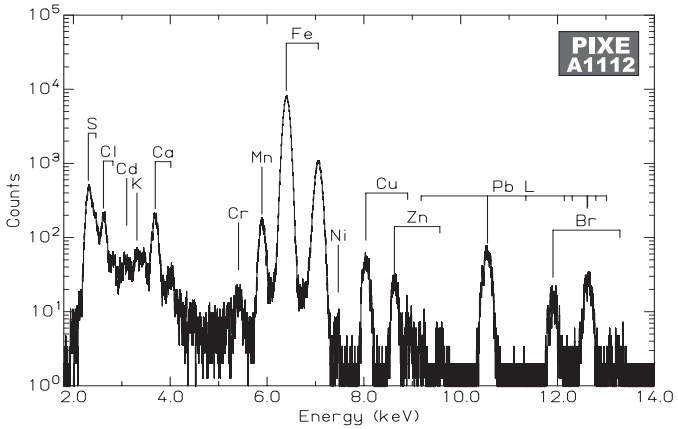

Fig. 3. PIXE spectrum extracted from a single aerosol particle excreted by a vehicle burning leaded petrol. Harmful elements Pb, Br and Cd can be seen in the spectrum.

ultraviolet [16], gamma-ray [17], and X-ray [18,19] spectroscopy. An extensive description of ANN by McClelland and Rumelhart is available [20].

An artificial neuron receives signals from external sources or from other neurons and produces one output value that can be used as an input to

other neurons or an output result of the network. The topology of an ANN depends on the complexity of application. A three-layer architecture (input, middle and output) is used in this work. The input layer contains 1024 neurons corresponding to 1024 channels of a spectrum. The output layer contains N neurons corresponding to the number of reference patterns (pollution sources). Each of the neurons in the output layer produces an output value 1 or 0 (>0.7 or <0.3).

Like a real brain, an ANN has to take a training course before doing any identification jobs. The purpose of the network training is to find the right combination of all parameters in a network which can produce a desired output code for every reference pattern. While the network reads a reference pattern, the modifications of the parameters take place in the backward direction, that is from the output layer to the input layer. After several periods of modification and regressions, the final total error for all of the input patterns reaches a low criterion. The training course is then finished and all the "knowledge" learned in the course is stored in a matrix. The neural network is now able to perform a reliable identification job for any unknown input pattern. Only when an unknown spectrum fits one of the reference patterns well enough, does its corresponding neuron give out a value of 1. All others give an output of 0.

4. Results and discussion

74 SAPs from pollution sources were measured. Their PIXE spectra were classified according to the corresponding sources. 12 reference spectrum patterns characteristic of their sources were recognized and used for the ANN training. 309 environmental monitoring particles were collected at the city centre of Shanghai. The environmental samples were measured with the same facilities. Their PIXE spectra were read by the network and their origins were then identified.

The apportionment of the air pollution sources in Shanghai resulting from the network identification is presented in Fig. 4. The cement industry contributes one-third of the aerosol particles in the region. It is true that municipal construction has been the largest business in the city recently. Due to the heavy traffic in the city, the gas exhausted by vehicles is the second largest contributor to the local air pollution. Surprisingly, it was discovered that the solid particles excreted by the vehicles contained obviously high levels of the harmful elements lead, cadmium and bromine (Fig. 3). Most vehicles in Shanghai are still burning leaded petrol.

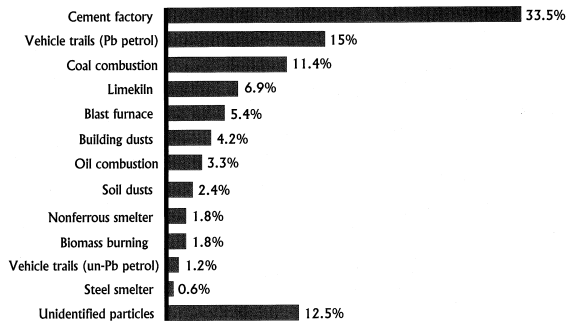

Fig. 4. Apportionment of single aerosol particles in Shanghai according to their origins.

In this investigation, 12.5% aerosol particles could not be identified. It was suggested that they might come from pollution sources other than those considered. By means of the pattern recognition in the ANN program, the unidentified particles could be clustered into nine species, which was useful for seeking new pollution sources.

5. Conclusion

From the point of view of environmental monitoring, 12 pollution sources and a few hundred particle samples are not enough for an accurate investigation in a large industrial city like Shanghai. This work is the beginning of a project dealing with ecological research and environmental conservation. It provides a new method for air pollution source identification and apportionment by direct SAP analysis and ANN assessment. A nuclear microprobe with micrometre spatial resolution, a bright and stable ion beam and precise sample placement is able to perform the single particle analysis efficiently enough for an enlarged investigation.

The result of the preliminary trial of this method with aerosol samples from Shanghai showed that more than one-third of the particles floating in the city atmosphere originated from the cement industry. 15% of the solid particles contained high levels of the harmful elements lead, cadmium and bromine. These particles have been excreted by traffic.

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References

[1] R.J. Charlson, J. Langner, H. Rodhe, C.B. Leovy, S.G. Garren, Tellus AB 43 (1991) 152.
[2] D.D. Cohen, G.M. Bailey, R. Kondepudi, Nucl. Instr. and Meth. B 109/110 (1996) 218.
[3] G.M.B. Marcazzan, X-Ray Spectrum 27 (4) (1998) 247.
[4] R.V. Grieken, S. Hoornaert, K. Gysels, J. Osan, A. Worobjec, in: Proceedings of the Sixth International Conference on Nuclear Microprobe Technology and Applications, Spier Estate, South Africa, 11–16 October 1998.
[5] D.D. Hickmott, J.M. Herrin, R. Abell, M. George, J. Stimac, E.R. Gauerke, R.F. Denniston, Nucl. Instr. and Meth. B 130 (1997) 564.
[6] I. Orlic, T. Osipowicz, F. Watt, S.M. Tang, Nucl. Instr. and Meth. B 104 (1995) 630.
[7] W. Maenhaut, R. Salomonovic, J. Ptasinski, G.W. Grime, Nucl. Instr. and Meth. B 130 (1997) 576.
[8] F. Gerab, P. Artaxo, E. Swietlicki, J. Pallon, Nucl. Instr. and Meth. B 136/138 (1998) 318.
[9] M. Jaksic, I. Bogdanovic, E. Gereda, S. Fazinic, V. Valkovic, Nucl. Instr. and Meth. B 77 (1993) 505.
[10] S. Zhou, I. Orlic, J.L. Sanchez, C.L. Lee, F. Watt, in: Proceedings of the Sixth International Conference on Nuclear Microprobe Technology and Applications, Spier Estate, South Africa, 11–16 October 1998.
[11] Y. Sha, Y. Gu, G. Liu, A. Wang, P. Zhang, J. Zhu, J. Shi, S. Yang, P. Liu, X. Li, Nucl. Instr. and Meth. B 109/110 (1996) 79.
[12] Y. Sha, J. Shi, Y. Gu, J. Zhu, X. Li, Nucl. Sci. Techniques 7 (1) (1996) 61.
[13] T. Butz, R.-H. Flagmeyer, J. Heitmann, D.N. Jamieson, G.J.F. Legge, D. Lehmann, U. Reibetanz, T. Reinert, A. Saint, D. Spemann, R. Szymanski, W. Tröger, J. Vogt, J. Zhu, Nucl. Instr. and Meth. B 161–163 (2000) 323.
[14] K. Tanabe, T. Tamura, H. Uesaka, Appl. Spectroscopy 16 (5) (1992) 807.
[15] M. Meyer, T. Weigelt, Anal. Chim. Acta 265 (2) (1992) 183.
[16] C.R. Mittermayr, A.C.J.H. Drouen, M. Otto, Anal. Chim. Acta 294 (2) (1994) 227.
[17] Z. Cheng, M. Li, S. Xu, Nucl. Tech. (in Chinese) 19 (8) (1996) 449.
[18] A.L. Allanic, J.Y. Jezequel, J.C. Andre, Anal. Chem. 64 (21) (1992) 2618.
[19] M. Bos, H.T. Weber, Anal. Chim. Acta 247 (1) (1991) 97.
[20] J.L. McClelland, D.E. Rumelhart, Parallel Distributed Processing, vol. 1, MIT Bradfort Press, Cambridge, 1986.