research papers

Source identification of PM$_{10}$, collected at a heavy-traffic roadside, by analyzing individual particles using synchrotron radiation

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Synchrotron radiation microbeam X-ray fluorescence (micro-SXRF) was used to analyze individual aerosol particles collected at a height of 2 m above a heavy-traffic roadside in a heavy-industrial area of Shanghai. A pattern recognition technique, which took micro-SXRF spectra of single aerosol particles as its fingerprint, was used to identify the origins of the particles. The particles collected from the environmental monitoring site are mainly from metallurgic industry (26%), unleaded gasoline automobile exhaust (15%), coal combustion (10%), cement dust (10%) and motorcycle exhaust (8%).

1. Introduction

In urban areas, air particle pollution is of particular concern because of the relevance of possible delayed health effects associated with the continuous exposure of a high-density population (Dokery *et al.*, 1993). PM$_{10}$ (particulate matter with an aerodynamic diameter of less than 10 µm) is considered to be a health hazard since it can reach the lower respiratory tract, where it is phagocytized by alveolar macrophages (Zheng *et al.*, 2004). In order to achieve the abatement of PM$_{10}$ pollution, it is necessity to identify sources of PM$_{10}$ pollution for which control measures can be taken. Conventional methods of source apportionment usually involve applying different statistical methods to the results of aerosol bulk analysis. These methods have some limitations. Ambiguities of pollution source identification may occur in the bulk analysis because many different particles are measured as a whole. Some individual particles may have their own characteristic elements at concentrations lower than the detection limits of bulk analysis; these elements can be easily determined by single-particle analysis. Therefore, the limitations of bulk analysis can be avoided by the use of individual-particle analysis (Grime, 1998). So far, most individual-aerosol-particle analysis has been carried out using scanning electron microscopy (SEM), laser microanalysis (LAMMA) and scanning proton microprobe (SPM) techniques (Osipowicz *et al.*, 1995). The present paper describes an area of environmental research in which synchrotron radiation microbeam X-ray fluorescence (micro-SXRF) can be used effectively. Micro-SXRF measurements can be carried out in air, can be used for non-conductive sample analysis and are non-destructive compared with charged-particle excitation methods. By means of a microbeam X-ray, micro-SXRF is a good tool for the analysis of individual particles with diameters of several micrometers. A particular advantage of micro-SXRF over conventional X-ray source and particle excitation methods is the extremely high brilliance achieved with synchrotron radiation sources. Therefore, it is possible to analyze a large number of particles, as a spectrum of a single aerosol particle can be obtained in a very short time. Camerani and co-workers (Camerani *et al.*, 2001; Camerani Piniani *et al.*, 2002) have recently proved that micro-SXRF is an excellent method for characterization of individual aerosol particles. These authors determined the elemental composition and the distribution of some elements in the particles. Because of the geometrical and morphological variety of single particles, it is very difficult to quantify accurately the element concentration in a single particle. However, in the source apportionment of individual particles, one is mostly interested in whether a given particle has the same relative intensity of chemical composition as a particle of known source rather than the quantitative intensities of that particle. From this point of view, we propose the application of pattern recognition methods to the identification of individual particles by using their micro-SXRF spectra.

In the present work, individual particles collected from known pollution sources were analyzed by micro-SXRF, and the micro-SXRF spectra were used to establish a fingerprint database of pollution sources. Individual aerosol particles collected from an environmental monitoring site were analyzed with the same facilities. The origins of these environmental monitoring particles were identified by comparing their micro-SXRF spectral patterns with those in the fingerprint database using a pattern recognition technique.

2. Experimental

2.1. Sample collection and preparation

Individual aerosol particles of source samples were collected from 14 pollution sources, including iron and steel smelters, oil and coal combustion, cement and soil dust, and vehicle and motorcycle exhaust emissions. These sources are thought to contribute most of the aerosol particles to the atmosphere of Shanghai city. Environmental monitoring samples were collected at a busy roadside in the heavy-industrial area Baoshan, which is located north of Shanghai city center. Sampling was carried out in September 2003. A medium-volume air sampler (ZW-100, manufactured by Qingdao Laoshan Applicable Technology Institute, China) was used to collect PM$_{10}$. The sampler was operated at a height of 2 m above ground level. Since the heights of adults are mostly in the range 1.5–2 m, particles at a height of 2 m are considered to be most harmful to urban residents (Wang *et al.*, 2000).

The samples of individual particles used for the micro-SXRF measurements were prepared as follows. A solution of nylon powder in isobutyl alcohol was prepared at a temperature of 353 K, and a droplet of the solution was dropped onto the surface of deionized water at room temperature. The droplet stretched and a very thin nylon foil (~0.2 µm) was formed on the water surface. Just after the formation of the foil, collected single particles were dropped onto the foil. After a 15 min solidification, the foil was removed from the water using an aluminium frame. The single particles were separately embedded in the thin and flat nylon foil. After 24 h in a dryer, the sample was ready for analysis by micro-SXRF.

2.2. Individual-aerosol-particle measurement

The micro-SXRF measurements for the individual particles were carried out at the X-ray fluorescence station of beamline 4W1B of the Beijing Synchrotron Radiation facility (BSRF). The electron energy and maximum ring current of the BSRF storage ring were 2.2 GeV and 110 mA, respectively. A white beam with an energy of 3.5–30 keV produced by the bending magnet was used for the excitation of

DOI: 10.1107/S0909049504017236

characteristic X-rays from single aerosol particles. The beam size, restricted by vertical and horizontal slits, was about 20×10 µm. A computer-controlled three-dimensional sample stage was used, and an Si(Li) detector with an energy resolution of 133 eV (5.9 keV) was placed at $90°$ to the incident-beam direction. The sample was measured in air, and the distance between the sample and the detector was 1.5 cm. A schematic diagram of the BSRF 4W1B XRF facility is shown in Fig. 1.

280 single aerosol particles of pollution sources and more than 200 particles of samples collected at the monitoring site were analyzed.

3. Principle of source identification of individual aerosol particle

Previous studies have revealed that particles from different pollution sources have different chemical compositions (Cohen *et al.*, 1996). The micro-SXRF technique has a high sensitivity (the minimum detection limitation is at the p.p.m. level). The elemental composition of a single aerosol particle is represented by its micro-SXRF spectrum. The shape of the spectrum (referred to as the spectrum pattern) will be different if the particles are from different pollution sources. Therefore, the micro-SXRF spectrum pattern can be considered as a fingerprint of a single aerosol particle. In the source apportionment, we do not attempt to quantify the particle elemental composition on the basis of the micro-SXRF spectrum because of the geometrical and morphological influence of a single particle. However, we can recognize each particle directly by its spectrum pattern instead of its elemental composition. This method allows the possibility of source apportionment of individual aerosol particles. In the process of source identification, a pattern recognition technique was used.

The principle of the pattern recognition technique of the micro-SXRF spectrum is as follows. A micro-SXRF spectrum can be treated as an n-component column vector in Euclidean space. The vectors $\mathbf{X} = (x_1, x_2, \cdots, x_n)^T$ and $\mathbf{Y} = (y_1, y_2, \ldots, y_n)^T$ are the representations of two different micro-SXRF spectra. For pattern recognition, two spectrum vectors are considered similar if the Euclidean angle, θ, between the two vectors is small enough. The discriminative function of two spectrum vectors is defined as

$$\cos \theta = \mathbf{X}^T \cdot \mathbf{Y}/[(\mathbf{X}^T \cdot \mathbf{X})(\mathbf{Y}^T \cdot \mathbf{Y})]^{1/2}.$$

$\mathbf{X}^T$ and $\mathbf{Y}^T$ are the transposes of $\mathbf{X}$ and $\mathbf{Y}$, respectively. The numerator is the dot product of the two vectors, and the denominator is the product of their magnitudes. The value of $\cos \theta$ will be close to 1 if the two micro-SXRF spectra are very similar. A program for identifying a micro-SXRF spectrum of an individual aerosol particle has been developed.
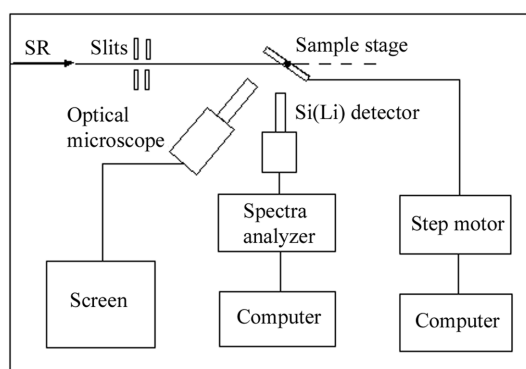
The identification of the atmospheric particles was carried out in two steps. Firstly, the spectra of the 280 single particles of PM_{10} collected from known pollution sources were recorded in a database to create a fingerprint library of pollution sources. The pattern recognition program was then used to compare the spectra of the single aerosol particles collected from the environmental monitoring site with those in the fingerprint library of pollution sources, and the origins of the particles were identified.

4. Results and discussion

4.1. Fingerprint of pollution sources

Fig. 2 shows micro-SXRF spectra of several pollution source particles. Each source has a typical fingerprint. The main feature of the spectrum of vehicle exhaust emission was found to be high peak counts of K, Ca, Ti, Fe, Cu, Zn, Pb and Br. Besides an abundance of K, Ca and Fe, the rare earth element Rb was found in the micro-SXRF spectrum of soil dust. From the micro-SXRF spectra of single aerosol particles, even different subclasses can be discriminated. For example, iron smelters, sintering plants and steel smelters all belong to the class of metallurgic industry, but they are discriminated clearly by the micro-SXRF spectra of their individual particles. It was found that the peak counts of K and Ti are higher than the counts of other elements in the iron-smelter spectrum but not in the steel-smelter and sintering-plant spectra. On the other hand, the intensity of Zn in the steel-smelter spectrum is stronger than that in the iron-smelter and sintering-plant spectra. Lead was found in all of the spectra except soil dust, which indicates that metallurgic industry emission (steel smelter, iron smelter and sintering plant), coal combustion and vehicle exhaust are contributors to the lead pollution in the air of this area. In summary, the discrimination of different pollution sources is enhanced by the measurement of individual particles.

The spectra of single particles from 14 pollution sources were recorded in the database of pollution sources.

4.2. Source apportionment of individual particles

The micro-SXRF spectra of the ~200 individual aerosol particles collected at the environmental monitoring site were compared with the spectra of the pollution source particles in the database using the pattern recognition program. Fig. 3 shows a pair of spectra for comparison. One is an unknown spectrum from the environmental monitoring site, and the other is a typical spectrum from a pollution source (iron smelter). By visual inspection, it is obvious that the two spectra have similar features, which implies similar composition; $\cos \theta$ between the two spectra is 0.99. It can thus be deduced that the unknown particle is derived from iron smelters. Source identification of the particles from the environmental monitoring site shows that the sources of these particles can be classified into seven known categories, *viz.* the metallurgic industry, vehicle exhaust, soil dust, motorcycle exhaust, coal combustion, cement dust and diesel exhaust, and some unidentified sources (Fig. 4).

About 26% of measured particles were derived from metallurgic industry (the sum of iron smelters, steel smelters, coke ovens and sintering plants), indicating that metallurgic industry contributes most of the PM_{10} sample analyzed. This conclusion is not surprising, because the sampling site is located in the heavy-industry zone of Shanghai. The Baosteel Group, one of the most important metallurgic enterprises of China, is located in this area, and some other metallurgic activities, such as the Shanghai No. 1 steel plant, are near the sampling site. In the investigation, 12% and 8% of analyzed particles were found to derive from iron smelting and sintering plants, respectively; fewer particles were found to derive from steel smelting
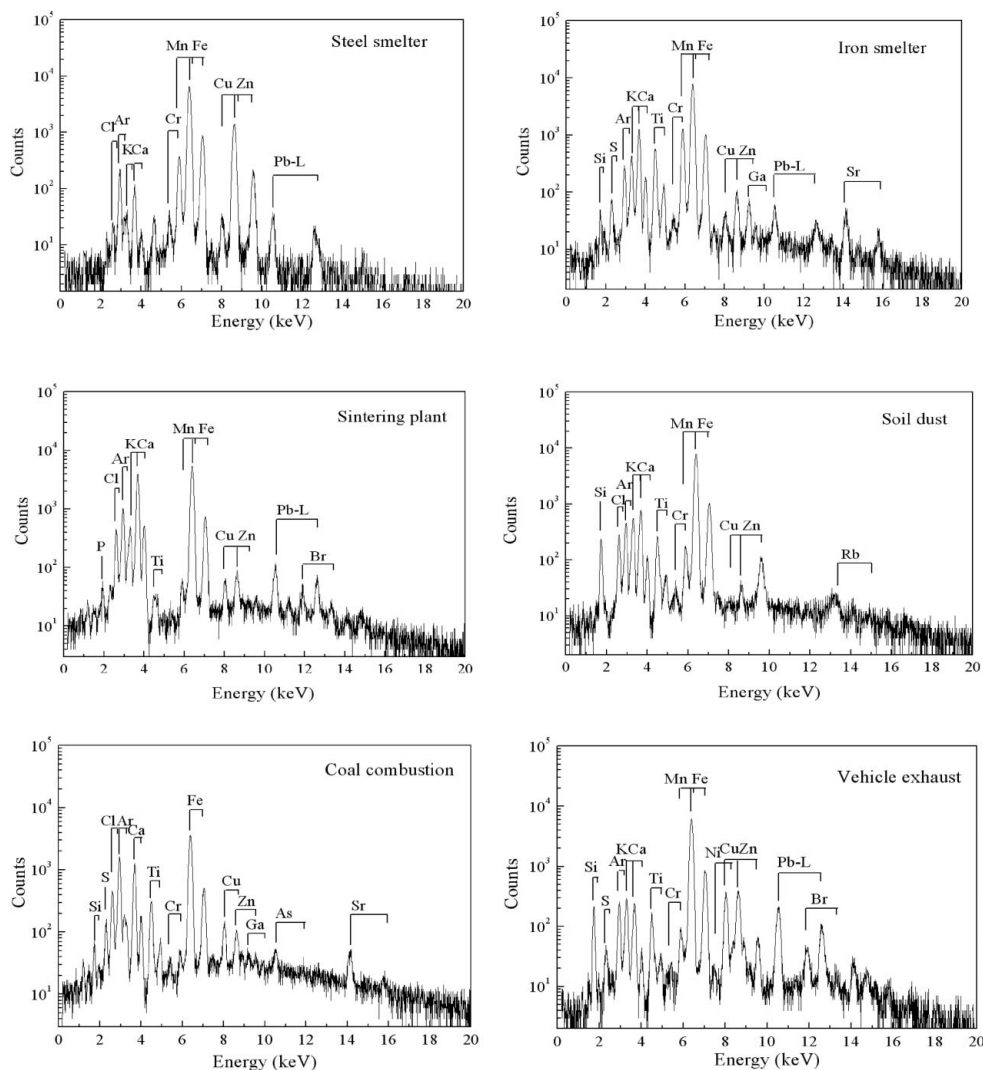

Figure 1
A schematic diagram of the BSRF XRF.

Figure 2
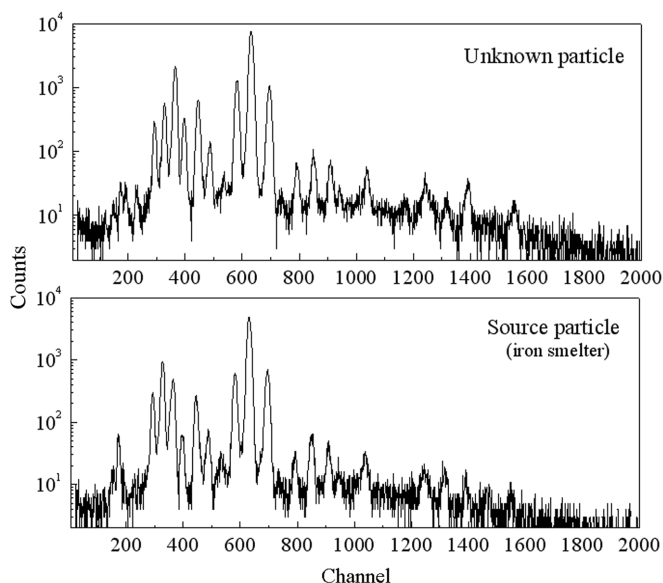Single-particle micro-SXRF spectra of different pollution sources.

Figure 3
Micro-SXRF spectra of the particles from an unknown individual particle (top) and a pollution source (bottom).

and coke ovens. Thus, if the emissions of sintering plants and iron smelters are controlled, the air quality in this area may be further improved.

15% of the particles derived from unleaded gasoline vehicle exhaust emissions, and 2% of the particles were from leaded gasoline vehicle exhaust emissions; vehicle exhaust emissions are thus still an important pollution source of PM_{10}, which should not be ignored. The contribution of vehicle exhaust emissions to PM_{10} pollution in the Baoshan area is higher than that in the central area of Shanghai (Qiu *et al.*, 2001). We deduce that this difference arises because our sampling site is located in the heavy-industry area and the sampling was carried out at a height of 2 m above ground level. There is heavy traffic every day in this region, and therefore the contribution of vehicle exhaust emissions to air pollution is more than that reported by Qiu *et al.* (2001). It is notable that 2% of the particles were found to be derived from vehicle exhaust emissions from leaded gasoline, although Shanghai city phased out the use of leaded gasoline in 1997. Possible reasons for the presence of lead are as follows. Firstly, Shanghai city is a busy metropolis; a lot of vehicles pass through the city from other areas, where leaded gasoline might still be used. Secondly, the illegal supply of leaded gasoline might be continuing. Finally, the sediment of former leaded gasoline particles may be blown up by the heavy traffic.

About 10% of the particles collected are from coal combustion; this finding is consistent with the result of Chen *et al.* (1997). The
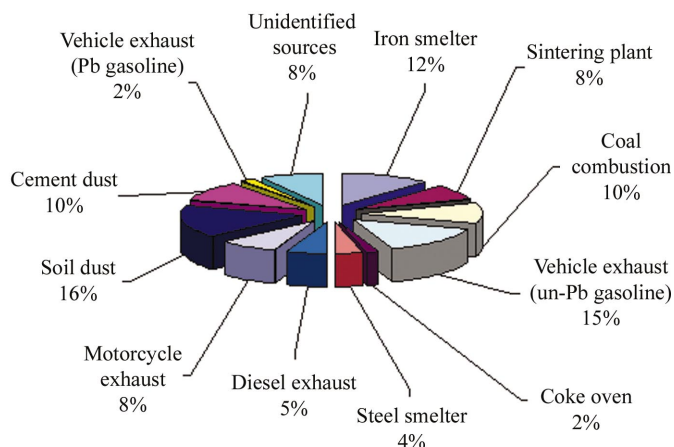

Figure 4
Origins of analyzed single PM_{10} particles collected at a heavy-traffic roadside

primary reason for the high proportion of coal pollution present is that coal is still used as a main fuel in Shanghai; in the heavy-industry area, coal is used by many uncontrolled ovens and smelters. Furthermore, a coal-fired power plant is located near the sampling site.

Traditionally, the pollution caused by motorcycle exhaust emissions is not identified because it is difficult to distinguish motorcycle exhaust from vehicle exhaust emissions by the methods of bulk analysis. Therefore, the contribution of motorcycle exhaust to air pollution is usually underestimated. However, particles from motorcycle exhaust emissions can be discriminated from vehicle emissions by the method of single-particle analysis. In this work, we find that 8% of the analyzed particles are from motorcycle exhaust emissions, indicating that the contribution of motorcycle exhaust emissions to air pollution should not be ignored. Because of its convenience and economy, the motorcycle has been widely used recently. It was reported that there were about 370 000 motorcycles in Shanghai in 2001 (Wu & Jiang, 2001). Pollution caused by motorcycles is therefore a major problem for air pollution.

We were unable to identify about 8% of the particles used in this work. It is suggested that they might come from other pollution sources, which are not yet included in our pollution source library. It will therefore be necessary to identify these additional pollution sources, in order to enable the more accurate and more comprehensive determination of the origin of airborne particles.

5. Conclusion

Micro-SXRF was used successfully to study the origins of single aerosol particles. The discrimination of different pollutant sources was enhanced by single-aerosol-particle analysis. A method based on the analysis of individual aerosol particles combined with a pattern recognition technique was developed in order to identify pollution sources of PM_{10} collected at a heavy-traffic roadside. The results show that (i) metallurgic industry contributes most of the PM_{10} pollution to the air at a height of 2 m in Baoshan, (ii) efforts should be made to control the emission of iron smelters and sintering plants so that air pollution can be further controlled, (iii) the pollution caused by vehicle exhaust is still notable and some aerosol particles derive from leaded gasoline automobile exhaust, and (iv) the pollution caused by motorcycle exhaust should not be ignored.

References

Camerani, M. C., Somogyi, A., Drakopoulos, M. & Steenari, B. (2001). *Spectrochim. Acta Part B*, **56**, 1355–1365.

Camerani Piniani, M. C., Somogyi, A., Simonivici, A. S., Ansell, S., Steenari, B. & Lindqvist, L. (2002). *Environ. Sci. Technol.* **36**, 3165–3169.

Chen, M. H., Chen, J. S. & Li, D. (1997). *Shanghai Environ. Sci.* **169**, 15–17. (In Chinese with English abstract.)

Cohen, D. D., Bailey, G. M. & Kondepudi, R. (1996). *Nucl. Instrum. Methods Phys. Res. B*, **109–110**, 218–231.

Dokery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G. & Speizer, F. E. (1993). *N. Engl. J. Med.* **329**, 1753–1759.

Grime, G. W. (1998). *X-ray Spectrom.* **27**, 221–231.

Osipowicz, I. O., Watt, T. F. & Tang, S. M. (1995). *Nucl. Instrum. Methods Phys. Res. B*, **104**, 630–637.

Qiu, Z., Guo, P., Wang, J., Lu, R., Qiu, H., Li, X. & Zhu, J. (2001). *Environ. Sci.* **22**, 51–54. (In Chinese with English abstract.)

Wang, J., Guo, P., Li, X., Zhu, J., Heitmann, T. J., Spemann, D., Vogt, J., Flagmeyer, R. H. & Butz, T. (2000). *Environ. Sci. Technol.* **34**, 1900–1905.

Wu, W. & Jiang, J. (2001). http://auto.sina.com.cn/news/2001-12-20/17602.shtml.

Zheng, J., Tan, M., Shibata, Y., Tanaka, A., Li, Y., Zhang, G., Zhang, Y. & Shan, Z. (2004). *Atmos. Environ.* **38**, 1191–1200.