

# Source Identification of Lead Pollution in the Atmosphere of Shanghai City by Analyzing Single Aerosol Particles (SAP)

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A new method combining the pattern recognition (PR) technique with micro-PIXE spectrum was used for direct assessment of lead pollution in the atmosphere of Shanghai City. Single aerosol particles (SAP) of PM<sub>10</sub> (<10 μm) were analyzed using the nuclear microprobe. Every particle is characterized with its micro-PIXE spectrum, which can be considered its fingerprint. The PR technique was applied to trace a lead contaminated aerosol particle back to its source. The discrimination of different pollutant sources was enhanced with investigating the individual aerosol particles. The results showed that the lead contamination from automobile exhaust should not be neglected. The lead concentration with low level was detected in most unleaded gasoline particles; however, the highest lead level of 1500 ppm was found in one of them. Furthermore, four other main pollutant sources contributing to the lead contamination in the Shanghai atmosphere were clearly identified by this method. They are the cement industry, the coal combustion, the oil combustion, and the metallurgic industry. Some other unidentified particles suggested that some more lead emitters might also exist in Shanghai.

## Introduction

The lead pollution in atmospheric environment has been emphasized since the 1960s because of its potential adversity to health effects (1). Recent research of lead toxicity shows that lead, even at a trace level, can affect children growth and intelligence (2). Lead pollution has been widespread in some industrialized areas. Shanghai is a big commercialized and industrialized city in China. It has a population of 13 millions and has been developing rapidly in recent years. Atmospheric quality has been paid much attention in coordinated with the industrial activities. The high lead level in the local atmosphere turned to be a crucial environmental problem since the early 1990s (3). It has been improved after the local government phased out of the leaded gasoline in 1997. Even with this improvement, recent environment

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survey shows that the lead pollution still widely exists in the atmosphere of Shanghai. Anthropogenic lead pollution in the air is mostly derived from the industrial activity (4). To find ways to reduce its quantity and impacts, it requires a good understanding of the lead emitter sources.

There have been many reports on the source identification of lead contamination in the field of environmental science (5–7). The majority of them relied on bulk elemental analysis of filters loaded with the sampled particles, which were called by total suspended particles (TSP). Enrichment factors, chemical mass balance, relative lead concentration and isotopic ratios were the main methods used for the data procession (7–11). The principle for these methods was that for each measurement they could give out the relative contribution of the lead sources to the local environment. Because they measured many different particles as a whole, the ambiguities of lead pollution source identification might happen, and some minor lead sources would be lost even if a large amount of sample measurements and a time-consuming statistic data handling were used (12, 13).

The limitation of the bulk analytical method can be avoided by the method of single aerosol particle (SAP) analysis (14). Applying this method, the size, shape, and color of the analyzed particles, which are important in aerosol studies, can be selected. Some individual particles may have their characteristic elements at concentrations lower than the detection limits of bulk analysis. However, these elements can be easily determined by single particle analysis. Although the electron microprobe can measure individual aerosol particles very efficiently, its relatively low sensitivity restricted its applications because some important trace element features in individual particles may be lost (15).

The development of the nuclear microprobe offers a new possibility for SAP studies. It is suitable to the individual particle analysis because it has a reasonable spatial resolution (1 μm), high sensitivity, and versatile analytical techniques (16, 17). These advantages give micro-PIXE analysis a unique role in determining low levels of trace elements, such as lead in a SAP (18). The PIXE spectrum pattern was considered the fingerprint of the particle. A method of pattern recognition (PR) was developed for the identification of the spectrum pattern. The strategy for the fingerprint classification and identification was used to identify each measured aerosol particle.

There are two steps for the identification of lead contaminated particles in the atmosphere. At first, a set of particles PM<sub>10</sub> (<10 μm) was collected from the probable lead emitter sources in Shanghai City. Micro-PIXE analysis was performed on these single particles one by one. Their spectra were recorded into a database as a fingerprint library of the local lead pollution sources. Then, another set of SAP (also PM<sub>10</sub>) was collected from the center of the city. These environmental monitor samples were analyzed by the same way, and the PR method was used to compare their spectra with those in the library and to identify the origins of these lead contaminated particles.

## Materials and Methods

**Sample Collection and Preparation.** The TSP source samples were collected from 20 industrial trails, such as ferrous and nonferrous smelters, iron and steel plants, oil and coal combustors, cement factories, building construction sites, and automobile exhaust gases, etc. These sources were thought to contribute most of the aerosol particles floating in the atmosphere over the Shanghai City. The environmental monitor samples were collected in the atmosphere 2 m above

the ground at the city center. Hence, they represented the most harmful particles of risk to the urban residents.

A cascade impact sampler (model HY-1) was used, and single particles were collected on polystyrene fibrillate filters. Ninety-seven percent of the particles were smaller than 10  $\mu\text{m}$ , and 70% of them were smaller than 3  $\mu\text{m}$ . Several methods for SAP sample preparation had been reported in our earlier works (19). However, none of them could separate small particles ( $<3 \mu\text{m}$ ) clearly, and only groups of SAP had been measured (20). To measure the single particles one by one, it was essentially important 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 requests in mind, a new method for SAP sample preparation was developed.

A solution of nylon powder in isobutyl 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 stretched, and a very thin (0.2  $\mu\text{m}$ ) nylon foil was formed on the water surface. Just after the formation of the foil (in a few seconds), the collected single particles were dispersively dropped from the filter onto the sticky foil by a small shaker. After 5 min of solidification, the foil attached on a stainless steel frame was taken out of the water. The single particles were separately embedded in the thin, taut, and flat nylon foil. After 24 h baking at a temperature of 60 °C, the SAP sample was ready for individual particle analysis by the nuclear microprobe.

**Single Aerosol Particles (SAP) Measurement by the Nuclear Microprobe.** A reliable and efficient experiment for SAP analysis demanded good performances of the nuclear microprobe. Because most of the particles were smaller than 3  $\mu\text{m}$ , both high spatial resolution and high beam current were needed. The Leipzig nuclear microprobe, LIPSION satisfied the experimental requirements. A detailed description of LIPSION could be found elsewhere (21). A 100  $\mu\text{m}$  object diaphragm and a 100  $\mu\text{m}$  aperture diaphragm were used to produce a focused beam spot with 1  $\mu\text{m}$  size and 80 pA beam current. Random beam scanning and two stations list mode were used for the PIXE and RBS data acquisition (22). The micro-PIXE spectrum provided the major information for PR identification. The RBS spectrum was used for judgment of some ambiguous results coming from PIXE alone. The particles were so small that this analysis could be considered thin target measurements. The beam charge was collected with a downstream Faraday cup. There were no conductive coating on the sample surface and no data correction for the effects of the particle matrix and shapes. A 20 nC integrated beam charge was required for each particle measurement. Each single particle measurement took about 15 min. The accelerator and the microprobe of LIPSION performed in a very stable working condition. Both the high stability of the beam and the high precision of the sample displacement made the SAP measurements very efficient.

Figure 1 shows a micro-PIXE spectrum of an individual particle coming from leaded gasoline. A rough assessment of the chemical composition in a single particle could be achieved simply by visual inspection of its spectrum feature. In the source identification of SAP, one is mostly interested in whether a given particle has the same composition as a known source particle, rather than the quantitative chemical composition of the particle. From this point of view, we propose the application of pattern recognition to the identification of individual aerosol particles by directly using their micro-PIXE spectra.

**Spectrum Identification with Pattern Recognition (PR).** The principle of the pattern recognition technique has been described in detail elsewhere (23, 24). Here, a brief description of the method and its application to PIXE spectrum was presented as followings.

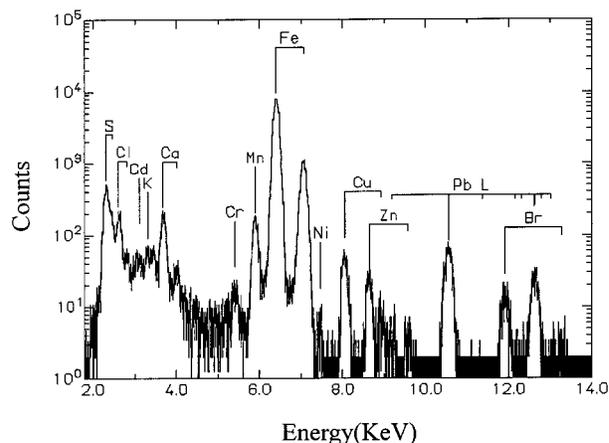


FIGURE 1. A PIXE spectrum of an individual aerosol particle coming from leaded gasoline.

A PIXE spectrum can be treated as an  $n$ -component column vector in an  $n$ -dimensional Euclidean space. In pattern recognition, two PIXE spectra are considered similar if the Euclidean angle between the two spectrum vectors in the  $n$ -dimensional Euclidean space is close to zero. The discriminative function is defined as below:

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

Here  $\bar{X}$  and  $\bar{Y}$  are the transposes of  $\bar{X}$  and  $\bar{Y}$ , respectively. The numerator is the dot product of the two vectors, and the denominator is the product of their magnitude. The  $\cos \theta$  means the degree of similarity for the two spectra. Its value will be close to 1 if the two PIXE spectra have similar features. The value of  $\cos \theta$  is independent of the intensities of the spectra.

The PR program for the SAP identification was developed on a personal computer. The flowchart of the program was shown in Figure 2. All the PIXE spectra of the particles from the lead emitter sources were stored as a database of reference spectra patterns. Any unknown spectrum could be identified with the program in 0.1 s. The PR program ran with graphic user interface (GUI). It was easy to operate even for inexperienced persons.

## Results and Discussion

**Fingerprints of Emitter Source.** The discrimination of different pollutant sources was enhanced by investigating single aerosol particles (SAP). Two hundred SAPs from emitter sources were analyzed. About 60 particles had detectable lead. Their micro-PIXE spectra were classified according to the corresponding pollutant sources. Each source had its typical fingerprint and some subfingerprints with different characterization of PIXE spectra. These lead contaminated particles could be classified into six categories. They were the cement industry, the automobile exhaust using both leaded and unleaded gasoline, the oil combustion, the coal combustion, and the metallurgic industry. Their average elemental concentrations were analyzed with the program TTSPM (25).

Six typical elemental profiles of the lead emitter sources were shown in Figure 3. Each source was featured with its characteristic elements. The main feature of high calcium concentration (35.5%) was found in cement source. The 280 ppm lead concentration in cement source came from its raw materials in the processing. High iron concentration could be found in the particles from the steel smelters. The lead (810 ppm) and some other toxic elements such as cadmium ( $<10$  ppm) were also found in these industrial pollutant sources. They came from the raw materials used. Figure 4

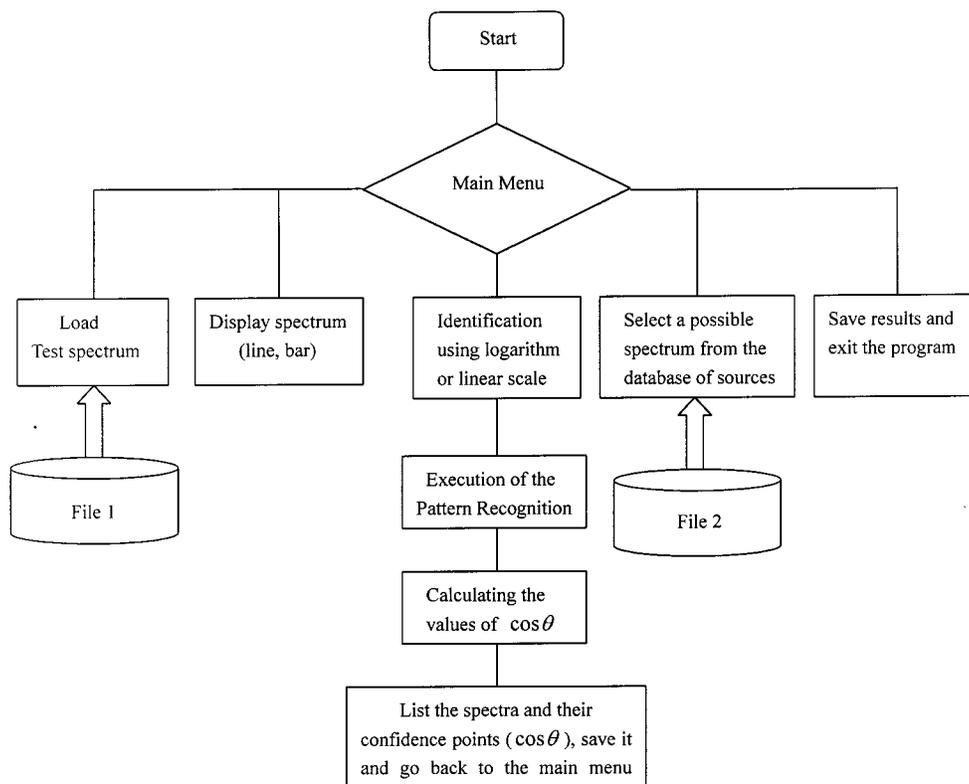


FIGURE 2. The flowchart of the pattern recognition program.

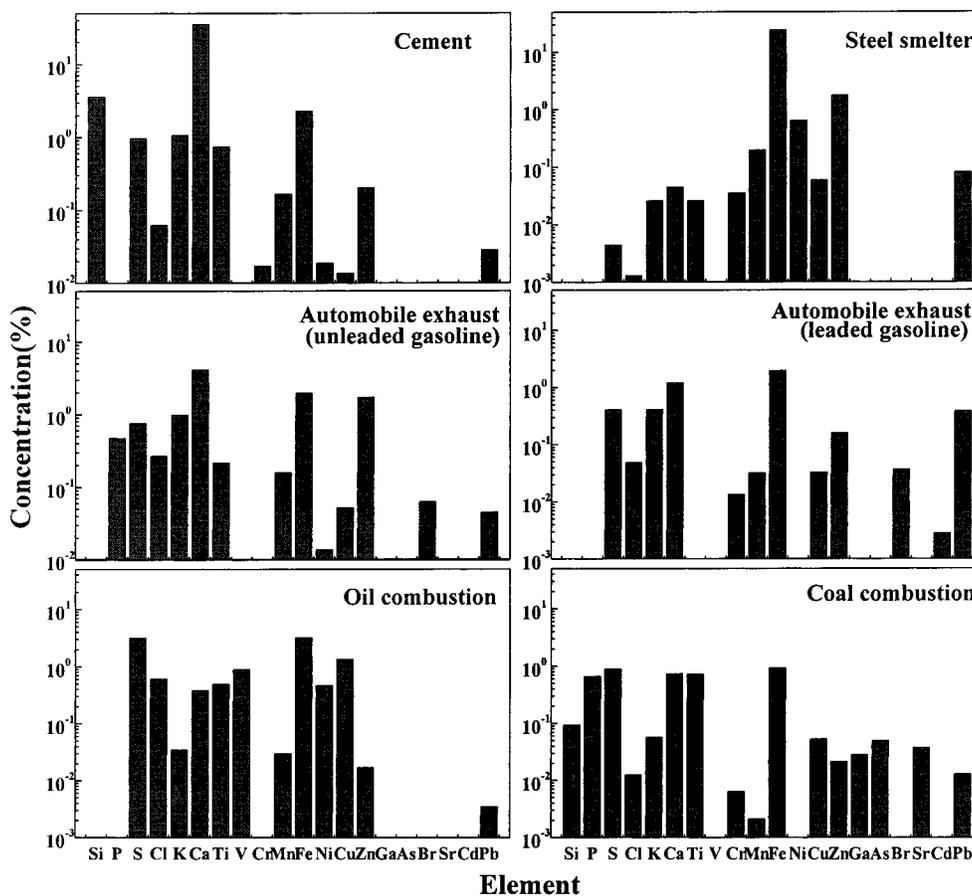


FIGURE 3. Six typical elemental profiles of the lead emitter sources.

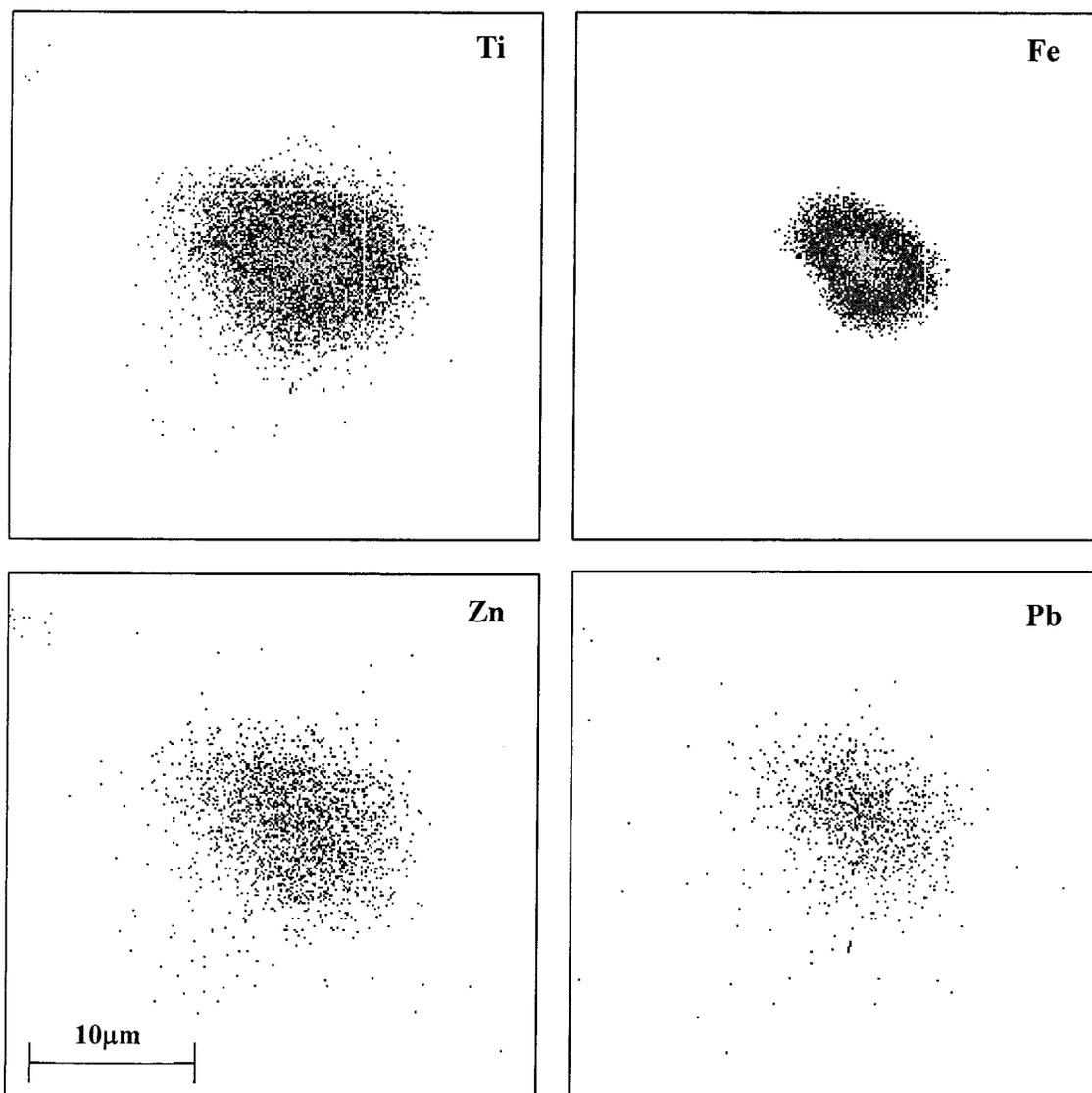


FIGURE 4. The elemental distribution maps of an individual particle from a steel smelter.

showed the elemental distribution maps of titanium, iron, zinc, and lead in an individual particle from the steel smelter. The scan size was  $30\ \mu\text{m} \times 30\ \mu\text{m}$ . It showed from the maps that these elements seemed to be homogeneously distributed in the individual particle.

The individual particles from automobile exhaust using both leaded and unleaded gasoline were measured as different categories of the pollutant sources. The average lead concentration (3800 ppm) in the particles from leaded gasoline was much higher than that of the particles from the other lead pollutant sources. It seemed to dominate the lead input into the atmosphere. Low lead concentration in average (450 ppm) was detected in the particles from unleaded gasoline. However, the lead value of each particle varied wildly from a few tens to hundreds ppm. It was surprising to detect a particle having 1500 ppm lead concentration. The lead in the particles from unleaded gasoline is derived from the crude oil. It was different from the situation of leaded gasoline, in which lead had been added to the oil as the lead-based antiknock compounds. The toxic metal cadmium was also found in the particles from leaded gasoline. Bromine and chlorine could be found in particles from automobile exhaust using both leaded and unleaded gasoline. It was a feature used to distinguish them from other lead pollutant sources.

The elemental distribution maps from an individual particle of automobile exhaust using leaded gasoline were

shown in Figure 5. The distribution of manganese, iron, and zinc in the particle seemed to be homogeneous, but the lead seemed not. This observation indicated that lead is attached at the surface of the particle during combustion. It had been clear that many toxic elements having boiling points below the normal combustion temperature were volatilized in the process of combustion (26). They condensed onto the surrounding particles after cooling, and thus it was expected that the surfaces of the particles from automobile exhaust were enriched with these elements. The lead distribution of these particles were quite different from that of the particles from the steel smelter (Figure 4). The biological toxicity of SAP depended upon the toxic element concentration and its distribution profile in the particle. The lead enrichment at the particle surface would make it more soluble than that buried in the particle. Therefore, it would be more harmful to the local residents (27).

The characteristic elements for SAPs from oil combustion were vanadium, nickel, and copper. Those from coal combustion were arsenic and strontium. They contained relatively low lead at concentrations of 40 and 130 ppm, respectively. The pollutant source of coal combustion included some subfingerprints, which depended upon the chemical composition of raw coal used and the type of the combustion process.

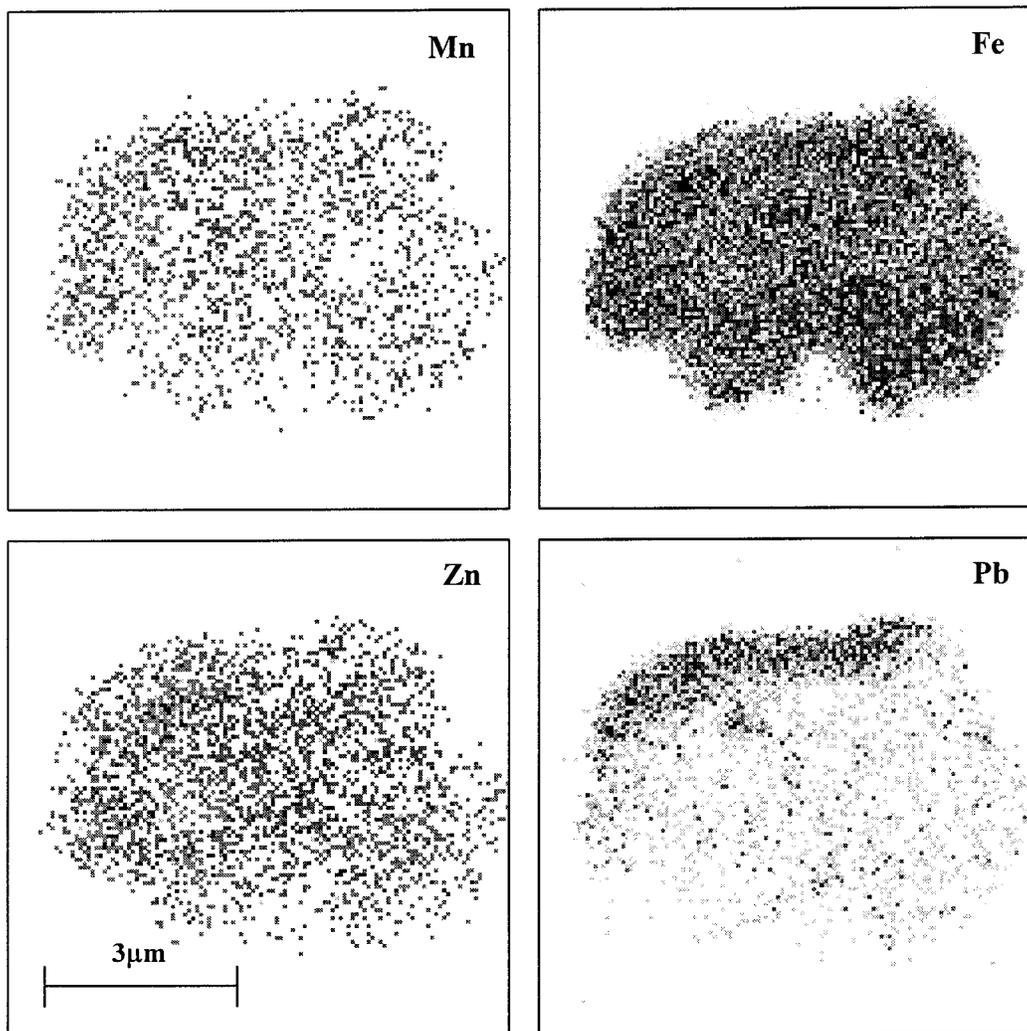


FIGURE 5. The elemental distribution maps of an individual particle from leaded gasoline.

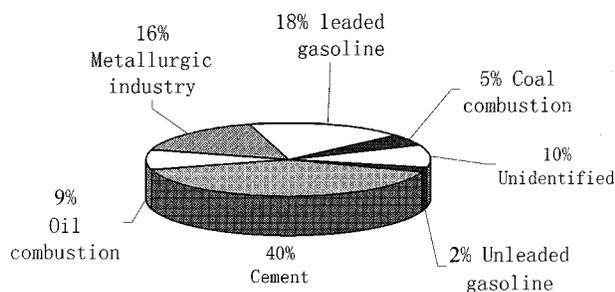


FIGURE 6. The origins of lead contaminated particles in the atmosphere of Shanghai City.

**Environmental Samples Identification.** Five hundred SAPs of environmental monitor samples were collected from the center of Shanghai. These samples were analyzed with the same facilities as before. Their micro-PIXE spectra were compared with the spectra of the pollutant source particles by the PR program. The origins of these particles were then identified. About 50 lead contaminated particles were found in the environmental samples. These particles belonged to seven categories of pollution sources. They were the cement industry, automobile exhaust using both leaded and unleaded gasoline, oil combustion, coal combustion, the metallurgic industry, and some unidentified sources. Figure 6 showed the relative contributions of these lead pollution sources to the local atmosphere. About 40% of lead contaminated particles were derived from the cement industry. It was true

because the municipal construction had been the largest business in the city recently. About 20% of them came from automobile exhaust due to the heavy traffic in the sampling area. Most of them belonged to the leaded gasoline category. Shanghai government had phased out of the leaded gasoline since 1997. However, the SAP analyzing results indicated that the contribution of the leaded gasoline still dominated the lead input to the local atmosphere. Shanghai is a busy metropolis. A lot of vehicles transit through the city from other areas, where the leaded gasoline is still used. The illegal supply of the leaded gasoline in the city might be continued. Another reason for the high contribution of the leaded gasoline might be the earlier lead contaminated particles blown up by the heavy traffic.

About 10% of the lead contaminated particles could not be identified. It was suggested that they might come from other lead pollution sources, which had not yet included in our investigation list. It gave hints for discovering new lead pollutant sources.

In conclusion, the discrimination of different pollutant sources could be enhanced by the combination of SAP analysis and pattern recognition technique. The features of SAPs were characterized with their micro-PIXE spectra. The original source of any SAP could be recognized by its spectrum pattern in comparing with the source spectra, which had been compiled in a library. The results showed that the automobile exhaust still contributed most of the lead pollution to the Shanghai atmosphere, though the usage of

leaded gasoline had been officially prohibited for 2 years in the city. Another important lead contributor in the city was the cement industry. Although its average lead concentration was not so high, more attention must be paid on it because a large amount of lead containing SAPs were given out from the cement factories.

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