# Trace elements in particles of motor vehicle exhaust in Shanghai

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**Abstract** A nuclear microprobe with high spatial resolution and high analytical sensitivity was applied to analyze trace elements, especially lead, in vehicle exhaust of Shanghai city. The result shows that the chemical composition and its corresponding x-ray relative intensity are different among different vehicle exhausts. There are many kinds of metal elements in particles of vehicle exhaust, most are harmful to people, such as Ti, Cr, Mn, Pb, etc. We found that the lead concentration was 6820 $\mu$g/g and the bromine concentration was 5300 $\mu$g/g in the exhaust from Santana using leaded gasoline (SULG), which is higher than any other kinds of vehicle exhausts. We have also detected the minimum lead in the particles of unleaded gasoline and its content varies from one to another. Its mean concentration was 450 $\mu$g/g and the highest reached 6210 $\mu$g/g. The unleaded gasoline's Pb existed in the whole particle while the leaded gasoline's enriched in the surface of the particle and was more harmful to the human beings.

**Keywords** Nuclear microprobe, Particles of motor vehicle exhaust, Leaded gasoline and unleaded gasoline

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## 1 INTRODUCTION

Shanghai is a famous economic and industrial center of China. With the improvement of the traffic requirement, the number of vehicles has increased rapidly by 100,000 per year in Shanghai. The enhancement of the burden of vehicle exhaust directly affects the atmospheric environmental quality of Shanghai city.

Some elements in vehicle exhaust are deleterious to human beings. For example, tantalum in the particles of vehicle exhaust deeply influence the people's physiological

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functions; lead could not only damage the haematogenous system, kidney and neural system, but also induce cerebral stunt and affect the person's intelligence; the chrome in the cells could induce the transfer of the genetic code and the induced mutation of the cells. Before 1996, the plumbic pollution was serious, 80% of the lead came from the combustion of leaded gasoline, so the government has advanced the unleaded gasoline for vehicles since Oct. 1, 1997.

How about the content of the deleterious metals in the particles of vehicle exhaust after using the unleaded gasoline? This is the purpose of our work. Furthermore, we should learn the distribution of metal elements in the particles because the biologic activity and toxicity of an element depend on the distribution to some extent.

There have been many reports on the elemental analysis of vehicle exhaust based on the bulk analysis.[1] Although the bulk analytical methods constitute useful tools for analyzing the aerosol particles, they still have some limitations. Because many different particles were measured as a whole in the bulk analytical methods, ambiguities of the elemental distributions occurred even if a large number of sample measurements and a time consuming statistical data handling were used.[2]

The limitation of bulk analytical method can be avoided by the method of single aerosol particle (SAP) analysis.[3] The association of certain elements in a particle can be observed directly by the single particle measurement. Some elements tend to occur at relatively high concentration in a small particle. However, in a bulk measurement, the concentration of these elements may be at a level lower than the detection limit. If these particles are measured individually, the associated elements can be determined easily. More advantages of the single particle analysis have been discussed by Orlic[4] and Grime.[5] Although the electron microprobe can measure SAP very efficiently, its relatively low analytical sensitivity restricted its application, because some important trace element features in SAP may be lost.[6]

A nuclear microprobe is suitable for SAP analysis because of its reasonable spatial resolution (1 $\mu$m), high analytical sensitivity, and versatile analytical techniques.[7,8] Some successful analyses of SAP by the nuclear microprobe have been reported.[9-11] However, accurate quantification of the element concentration in a single particle is very difficult due to the geometrical and morphological influences of a single particle. Some calculation methods, which try to reduce these influences, have been discussed, but the accuracy is still not ideal.[12,13] We can analyze each particle directly by its spectrum instead of its chemical composition.

## 2 EXPERIMENT

### 2.1 Sample collection and preparation

The individual particles of vehicle exhaust were collected from three kinds of vehicles and five kinds of exhausts, i.e., exhaust of Santana using leaded gasoline (SULG), exhaust of new and old Santana using unleaded gasoline (NSUUG and OSUUG), exhaust of buses using diesel oil (BUDO) and exhaust of scooter using unleaded gasoline (SUUG). The exhaust of OSUUG means the particles let out from the Santana that used leaded gasoline previously and now uses unleaded gasoline; the exhaust of NSUUG means the particles let out from the Santana that has used the unleaded gasoline since leaving factory. The MEXA−324M vehicle exhaust analyzer is used in the vent of the vehicle for two hours and the samples are collected on polystyrene fiber filters.

In order to measure the single particles one by one, it is 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 requirements in mind, a new method for single particles 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 stretched and a very thin (0.2 $\mu$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 dropped dispersively from the filter onto the sticky foil by a small shaker. After five minutes 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, tant and flat nylon foil. After 24 hours baking at a temperature of 60°C, the single aerosol particle sample was ready for individual particle analysis by the nuclear microprobe.

More than 90% of the collected particles are smaller than 10 $\mu$m and 70% of them are smaller than 3 $\mu$m. So those bigger than 3 $\mu$m are used for pointing analysis and those smaller than 3 $\mu$m are used for scanning analysis.

### 2.2 Single aerosol particle measurement by nuclear microprobe

A reliable and efficient experiment for single aerosol particle analysis demands good performance of the nuclear microprobe. Because most of the particles are smaller than 3 $\mu$m, both high spatial resolution and high beam current are needed. The Leipzig nuclear microprobe, LIPSION, satisfies the experimental requirements. A detailed description of LIPSION can be found elsewhere.[14] A 100$\mu$m object diaphragm and a 100 $\mu$m aperture diaphragm were used to produce a focused beam spot with 1 $\mu$m size and 80pA beam current for most single particle measurements. The particles are so small that it could be considered as thin target measurements. The 2.5 MeV protons could penetrate most of the particles. The beam charge was collected by a downstream Faraday cup. There was 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. Much experimental time was spent on searching for isolated small particles. A proper searching procedure was important for high efficiency of this work. At first, a big scan in steps like 70 $\mu$m was needed to survey the sample in order to find areas where the isolated small particles were cultivated with high distribution density. The coordinates of each small particle in the big scanned area were digitized and recorded for further small scans. And then, set up the small scan area in size of 6–10 $\mu$m and moved one or more isolated small particles into the area. The three dimensional movement of the sample stage was precisely digitally controlled. The accuracy of the sample displacement was better than 1 $\mu$m. One or more isolated small particles were covered by the beam within the scanning areas. Each single particle measurement took about 15 minutes. The characteristic spectrum of single particle was extracted from raw data according to the particle shape in the small scanning area.

## 3 RESULTS AND DISCUSSIONS

More than 100 particles of different vehicle exhausts were analyzed. Fig.1 shows the representative micro-PIXE spectra. From the spectra we can find that the chemical composition and x-ray relative intensity are different because the crude oil's abstraction, preparation and combustion processions were different. In order to quantitatively analyze the difference among the chemical elements of the particles, SPSCAN software was used to calculate the elemental contents of the particles. The design and theoretical background of that software can be found in Ref.[15]. Table 1 gives the result of this quantitative analysis. From this table we can see there are many kinds of metal elements in vehicle exhaust, most of which are harmful to people, such as Ti, Cr, Mn, Pb, etc. And the lead concentration was $6820\times10^{-6}$ and the bromine concentration was $5300\times10^{-6}$ in the SULG, which were higher than those in any other kinds of vehicle exhausts because there are antiknock with tetraethyl lead and purificant with bibromide ethylene in the leaded gasoline. So we can make lead and bromine as the "fingerprints" of leaded vehicle exhaust. But in the OSUUG we also detected the high lead concentration—$1430\times10^{-6}$ and a little bromine concentration—$95\times10^{-6}$. It means that there was still a little vestige of leaded gasoline in the engine although having been changed to unleaded gasoline. When the engine operated, the remainder leaded gasoline was let out. To our surprise, we have detected the minimum lead in the particles of NSUUG and its content varied from one to another. Its average concentration was $450\times10^{-6}$ and the highest reached $6210\times10^{-6}$. We consider that there is minimum lead in the unleaded gasoline from the crude oil. This lead has the enrichment effect in some single particles during the contribution process, thereby resulting in high concentration lead in some particles and no lead in other ones. The same conclusion is applicable in the diesel engine exhaust, and the lead concentration

is relatively low—$90\times10^{-6}$. From Table 1, we also find that Ni exists only in unleaded gasoline. Because the crude oil's abstraction and preparation processions were different between leaded and unleaded gasoline, Ni was left over in the unleaded gasoline, but abstracted out from the leaded gasoline. In scooter exhaust, there were relatively high concentrations of rare earth metals, such as Rb, Sr, Nd, etc, but no lead. These rare earth metals perhaps came from the catalytic and purificatory equipment of gasoline. There the lead concentration was so low relative to these rare metals that we could not detect it.

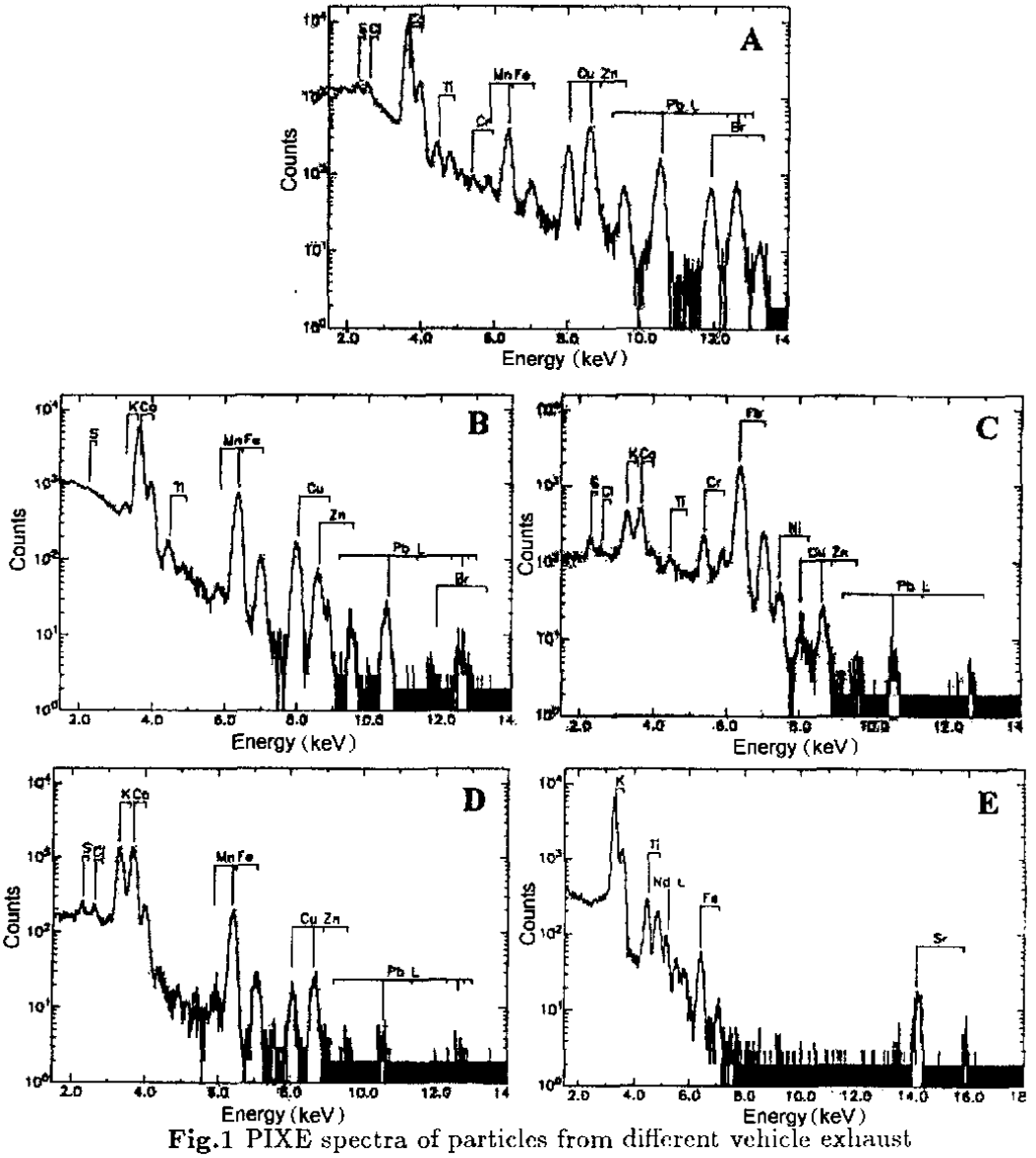


Fig.1 PIXE spectra of particles from different vehicle exhaust

A. Santana using leaded gasoline (SULG), B.Old Stantana using unleaded gasoline (OSUUG). C. New Stantana using unleaded gasoline (NSUUG), D. Bus using diesel oil (BUDO), E. Scooter using unleaded gasoline (SUUG)

**Table 1** Elemental mass percentages of exhausts from different vehicles ($\times 10^{-6}$)

| Ele | SULG ($N$ = 25) | | | OSUUG ($N$ = 25) | | | NSUUG ($N$ = 25) | | | BUDO ($N$ = 25) | | | SUUG ($N$ = 25) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CR | Mean | SD | CR | Mean | SD | CR | Mean | SD | CR | Mean | SD | CR | Mean | SD |
| S | 80-1620 | 630 | 570 | /-700 | 120 | 300 | /-150 | 40 | 50 | 5950-19000 | 11750 | 9510 | /-2500 | 880 | 1320 |
| Cl | 440-1440 | 940 | 730 | /-150 | 25 | 40 | /-45 | 15 | 25 | /-9100 | 2850 | 3990 | / 15 | 2 | 5 |
| K | /-285 | 75 | 90 | /-5840 | 430 | 1090 | /-550 | 95 | 165 | 3160-90300 | 10500 | 18080 | 550-40150 | 5300 | 11080 |
| Ca | 7320-54270 | 41600 | 68180 | 1640-9740 | 5890 | 3710 | / 2650 | 640 | 1000 | 800-20800 | 17250 | 23950 | 750-1660 | 1090 | 880 |
| Ti | /-1260 | 370 | 440 | / 320 | 100 | 90 | /-430 | 100 | 140 | /-540 | 90 | 160 | 730-2040 | 1470 | 1770 |
| Cr | /-430 | 120 | 170 | /-1080 | 70 | 210 | /-760 | 220 | 230 | /-30 | 10 | 20 | / | / | / |
| Mn | /-770 | 200 | 260 | / 950 | 70 | 200 | / 140 | 50 | 50 | /-210 | 60 | 80 | /-100 | 40 | 40 |
| Fe | 600-15730 | 11380 | 15980 | 380-10310 | 2960 | 3670 | 820-3350 | 2680 | 2050 | 980-7130 | 3110 | 2090 | 100-4620 | 1930 | 1570 |
| Ni | / | / | / | /-170 | 30 | 30 | /-200 | 50 | 60 | / | / | / | / | / | / |
| Cu | /-3490 | 1060 | 1840 | /-7630 | 3900 | 5760 | /-60 | 10 | 20 | 540-17270 | 5430 | 7600 | /-10 | 1 | 3 |
| Zn | /-34150 | 2770 | 8750 | /-8260 | 1070 | 2160 | /-340 | 80 | 100 | 610-8350 | 3190 | 2470 | /-240 | 70 | 110 |
| Br | /-29270 | 5300 | 13760 | /-690 | 100 | 180 | / | / | / | / | / | / | / | / | / |
| Rb | / | / | / | / | / | / | / | / | / | / | / | / | /-80 | 20 | 30 |
| Sr | / | / | / | /-70 | 10 | 30 | /-190 | 40 | 60 | / | / | / | / 5900 | 1760 | 2090 |
| Pb | /-60730 | 6820 | 16310 | /-8120 | 1430 | 1900 | /-6210 | 590 | 1270 | /-640 | 90 | 110 | / | / | / |
| Nd | / | / | / | / | / | / | / | / | / | / | / | / | / 220 | 20 | 70 |

Ele=elements, CR=Concentration Range, SD=Standard Deviation, SULG=Santana Using Leaded Gasoline, OSUUG=Old Santana Using Unleaded Gasoline, NSUUG=New Santana Using Unleaded Gasoline, BUDO=Bus Using Diesel Oil; SUUG=Scooter Using Unleaded Gasoline.

"/ " =Having not been detected, $N$= the number of the samples

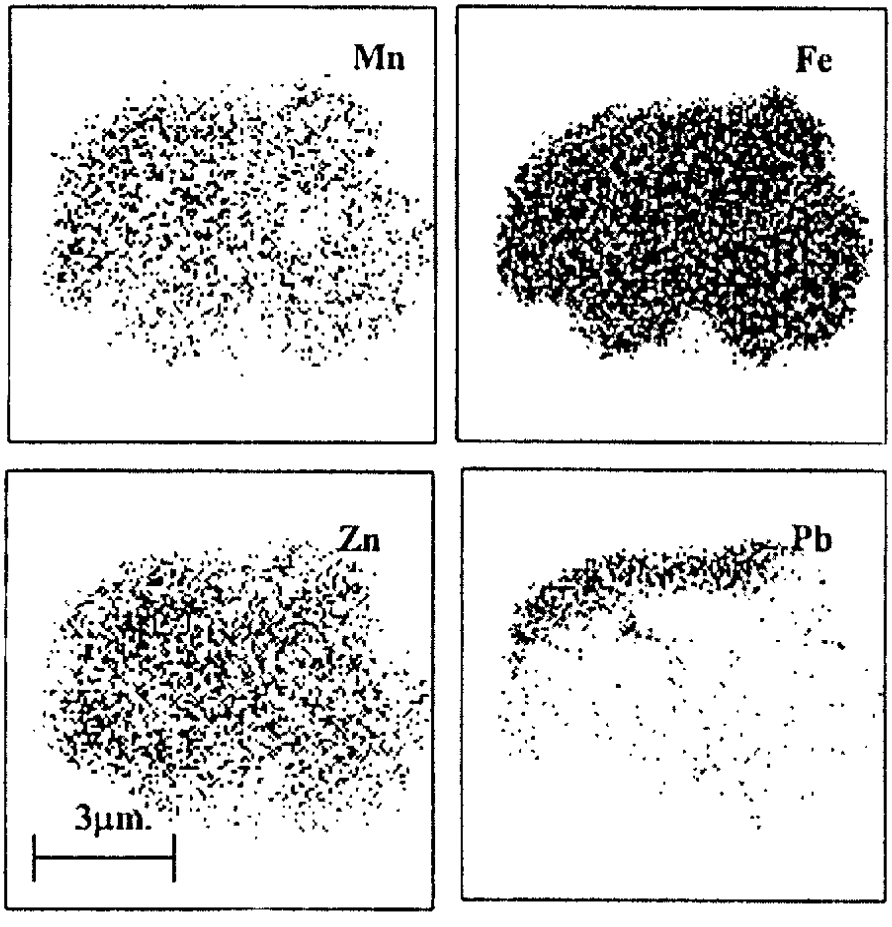


**Fig.2** Elemental distributions of a single particle from Santana using leaded gasoline (SULG, scanning range: $10\mu m \times 10\mu m$)

To evaluate a certain element or compound's influence to the environment, we need to know not only its content, but also its distribution in the single aerosol particles. In this paper, we emphasize on the elemental distributions in the particles of the SULG and NSUUG. Fig.2 shows the distributions of Mn, Fe, Zn, Pb in the particles of the leaded gasoline. From this figure, we can find that Mn, Fe and Zn seem to have similar distributions and they distribute equably in the particles, but Pb distributes mostly at one end of the surface of the particle. If the particles of the exhaust of the leaded gasoline are breathed in the human body, Pb is more likely to be brought into contact with the stomach and intestines. That is, Pb in the leaded gasoline is more easily to be absorbed into human body. Fig.3 is the elemental distributions in the particles of NSUUG. Two particles were analyzed at the same time. The left one has the higher concentrations of Cu and K, and the right one has the higher concentrations of S and Pb. Meanwhile, S and Pb in the right particle have the same distributions, which means perhaps Pb exists in the form of sulfide. This figure also proves that Pb has the enrichment effect in some particles, and as a result the lead concentration increases in these particles.

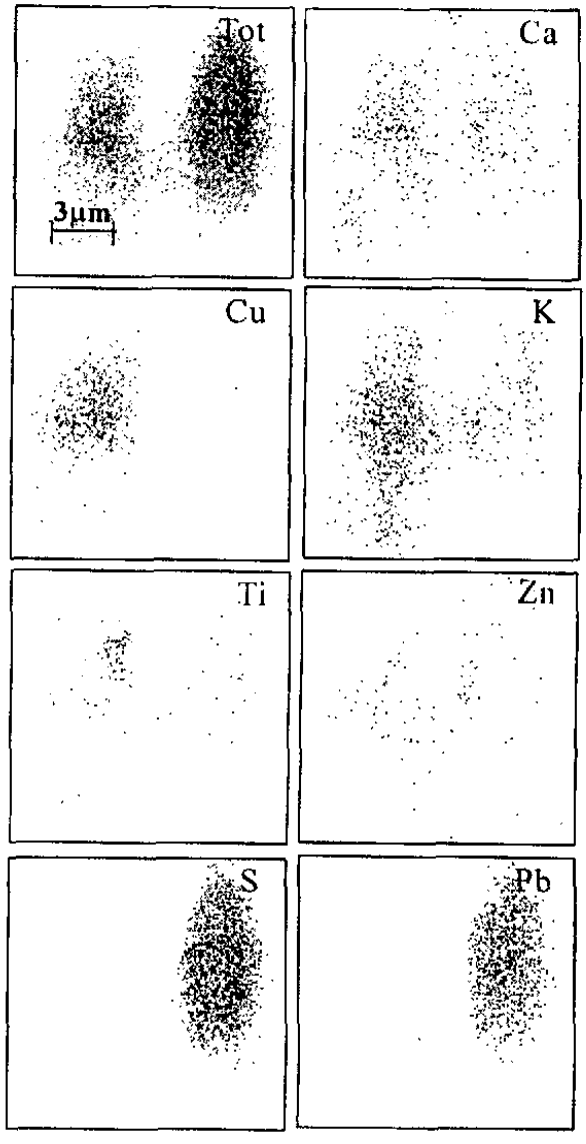


**Fig.3** Elemental distributions of particles from new Santana using unleaded gasoline (scanning range: $10\mu m \times 10\mu m$)
Tot: Scanning figure of two particles

## 4 CONCLUSIONS

There are many kinds of metal elements in vehicle exhaust, most of which are harmful to people, such as Ti, Cr, Mn, Pb, etc. Although the lead concentration in the

unleaded exhaust is lower than that in the leaded exhaust, it is still high in some Pb-enriched particles. So the 'unleaded' gasoline is not really unleaded because its exhaust has some Pb-enriched particles.

Due to the different sources of Pb in the leaded gasoline and unleaded gasoline, Pb exists in different forms after gasoline burning. The unleaded gasoline's Pb exists in the whole particle, and the leaded gasoline's enriches in the surface of the particle and is much more easily absorbed by the body. Therefore, leaded exhaust is more harmful to the atmosphere and we must enhance the control of the leaded exhaust.

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