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Characterization and source identification of fine particulate matter in the atmosphere of downtown Shanghai using μ-SXRF and ICP-MS

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Abstract To investigate the characteristic and sources of the fine particulate matter ($PM_{2.5}$), and the major sources affecting particulate air pollution in Shanghai, China, the individual aerosol particles were analyzed using the synchrotron radiation micro-beam X-ray fluorescence analysis (μ-SXRF), and the $PM_{2.5}$ multi-elements were determined by the inductively coupled plasma mass spectrometer (ICP-MS). The results show that the mass concentration and chemical elements have seasonal variation, and the enrichment factors show that the chemical elements in the inhalable particles could come from the earth crust and anthropogenic pollution. The extent of metal pollution was assessed by comparing the measured concentrations with those reported in the literature. Nine categories of $PM_{2.5}$ pollution sources identified at the center of Shanghai show that the vehicle exhaust, emission of metallurgic industry and coal combustion are important.

Key words $PM_{2.5}$, Enrichment factor, μ-SXRF, ICP-MS

1 Introduction

Along with rapid urbanization, population growth and industrialization, airborne particles study is of growing importance to human health, visibility degradation, and global climate change. The statistical associations of mortality and morbidity to ambient concentrations of particulate matter (PM) show that $PM_{2.5}$ ($\leq$ 2.5-μm aerodynamic diameter) can readily penetrate into the lungs, and likely increase the incidence of respiratory and cardiovascular disease[1,2]. The $PM_{2.5}$ accounts for about 60% mass fraction of inhalable particulate matter (PM_{10}, $\leq$10-μm aerodynamic diameter), and has long residence time in the atmosphere. The $PM_{2.5}$ toxicity is higher than that of coarse airborne particles due to penetrating deeply into the lungs[3]. Over recent years, the respirable PM concentration in ambient air has become a considerable relation to public health[4] since they induce an increase of lung cancer, morbidity and cardio-pulmonary mortality[5–7] with potentially toxic substances, such as heavy metals (Pb, Ni, Zn, Cu, Cd, etc.) of combustion origin, and have a high probability of deep deposition in the respiratory tract[8]. Because the metallurgy and fuel combustion industry, and vehicular traffic, resulted in a substantial increase of trace metal contents in the atmosphere[9,10], the US Environmental Protection Agency (EPA) promulgated a national ambient air quality standard for the $PM_{2.5}$ particles in 1997, and reduced the 24-h $PM_{2.5}$ to 35 $\mu g \cdot m^{-3}$ in 2006 (US Federal Register, 2007). In China, however, there is no standard value for $PM_{2.5}$.

The trace elemental contents in fine particles are of help in knowing the anthropogenic level in urban areas, and have a possible implications for public health[11]. The elemental compositions of atmospheric aerosol at a given location are widely used to characterize the local air conditions[12], but it is

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difficult to determine accurately an element content in the ng·m^{-3} in airborne dust of mg level[13] due to the limitation of the actual concentration exposed to the population or sensitive ecosystems. However, the ICP-MS has such attractive feature as low limits of detection for many elements, measuring isotope ratios, and easily interpretable spectra[14–16].

Traditional source apportionments for air pollutants include chemical mass balance receptor model (CMB) and principal components analysis (PCA), which play an important role in atmospheric environment science, and can be calculated by the PM bulk chemical analysis for many particles of different emission sources, but these efforts, which request measuring a large amount of samples and performing a time-consuming statistical data handling, yield a hazy picture to answer the problems[17]. The individual particle analysis is useful for identifying the origins of airborne particles[18], providing information for the origin, formation, transport, reactivity, transformation reaction of the particles, and these would hardly be possible for the bulk analysis[19]. The μ-SXRF, as a novel analytical technique, has been used to analyze a large number of individual aerosol particles in a non-destructive way for non-conductive samples[20]. Due to the extremely high intensity of photon beams from the synchrotron, the characteristic X-ray spectra can be obtained in a shorter time than other microprobe methods based on a conventional X-ray source or focused proton beams. In addition, with the μ-SXRF, the excitation energy can be tuned to have great detection sensitivity for elements of interest.

In this study, the combination of ICP-MS with a strong acid digestion was employed to measure the $PM_{2.5}$ trace elements. Enrichment factors (*EF*) were calculated to determine the origin of trace elements in atmospheric particles. Further, the μ-SXRF was used to analyze the individual particle to identify the emission sources of $PM_{2.5}$ particles.

2 Experimental

2.1 Sampling

The $PM_{2.5}$ was sampled by a medium volume sampler from January 2007 to December 2007, and collected by polytetrafluoroethylene (PTFE) filters (90-mm diameter, and 0.45-μm pore size) due to its low blank concentrations for determination of trace elements. The sampler on rooftop was about 15-m from the ground near the People's square, which is a standard sampling location of dense residential area in Shanghai, and where three major streets with heavy traffic are intersected. The PTFE filters were changed every two weeks. Twenty-two $PM_{2.5}$ samples collected in 2007 were analyzed by ICP-MS. And $PM_{2.5}$ samples collected in winter of 2008 were employed for individual particle analysis using μ-SXRF.

In Shanghai, the climate is subtropical humid because of the Asian monsoon system. Its monthly averaged ambient temperature in July and January is about 27.8°C and 3.6°C, and relative humidity is 75% and 83%, respectively. The atmospheric pressure is higher in winter than in summer. The meteorological data during sampling were downloaded from National Climate Data Center (http://cdc.cma. gov.cn).

In order to establish a fingerprint database of pollution sources, samples were also collected from possible sources of $PM_{2.5}$ emission in Shanghai, including the metallurgic facilities of the converter, electric furnace, the coke oven and sintering plant, and other sources of vehicle exhaust, coal combustion (the coal-fired power plants and coal-fired boilers), cement dust, and soil dust.

3 Analytical technique

3.1 ICP-MS analysis

The $PM_{2.5}$ mass was determined by gravimetry. The PTFE filters were weighed by an analytical balance with a reading precision of 0.01 mg. Before weighing, the samples were put in the weighing room for 24 h to reach 50±6% relative humidity and 23±2°C equilibrium. The samples were kept in desiccators until chemical analysis. All particle loaded filters and the field blank were appropriately cut using a special round hand punch made of high purity molybdnum. The HNO_3 (70%), H_2O_2 (30%) and HF (40%) were commercially ultra-pure, and used for chemical digestion by a high pressure microwave digestion system (Ethos 320; Mile stone, Italy). The resultant solution was evaporated by a hot plate to remove HF, and properly diluted by pure water to analyze trace elements using the ICP-MS (X-7, Thermo-elemental, USA). Indium (10 ng·mL^{-1}) was used as an internal standard for quantitative elemental analysis. It was added on-line via a Y-type canal. Accuracy of the trace elemental analysis was evaluated using a standard reference material (SRM 1648, Urban Particulate Matter, National Institute of Standards and Technology, USA), and the analytical results were in good agreement with the certified values (data not shown). The instrumental settings are shown in Table 1.

Table1 ICP-MS operating conditions and measurement parameters for the trace elements in acid digested filter samples.

Sample introduction		Plasma conditions		Measurement parameters	
Sample uptake	0.80 mL·min^{-1}	RF power	1300 W	Data acquisition	Peak hoping
Nebulizer	Concentric nebulizer	Coolant gas	13.5 L·min^{-1}	Dwell time	10 ms
Nebulizer gas	0.85 L·min^{-1}	Nebulizer gas	0.85 L·min^{-1}	Runs/replicates	3
Sampling cones	Ni	Auxiliary gas	0.76 L·min^{-1}	Internal standard	^{115}In

3.2 μ-SXRF analysis

When electrons in relativistic speed in the storage ring of a synchrotron are forced to change directions in an undulator, electromagnetic radiations from IR to hard X-ray (synchrotron radiation, SR) with high intensity and directionality occur, and the X-rays are an ideal source for microbeam X-ray fluorescence analysis.

The samples of individual PM$_{2.5}$ particles were prepared as follows[21]. A nylon powder was dissolved in iso-butyl alcohol (m:m=1:99) at 80°C. The solution was dropped onto surface of deionized water at room temperature to form a thin nylon foil due to its rapid stretch. The foil was taken out of the water using an aluminum frame of 10 mm in inner diameter. The particles were transferred onto the foil to become a μ-SXRF target.

The individual particles were measured by the X-ray fluorescence station of BL-4A beam line at Photon Factory of High Energy Accelerator Research Organization, Japan (Fig.1). The electron energy and ring current were 2.5 GeV and 310–430 mA. The experimental station uses either a double crystal monochromator, i.e. a layer pair of [Si(111), Si(111)]), for high-resolution experiments; or a multilayer-pair monochromator of W/B$_4$C for high-flux experiments. The latter was utilized in this work. To determine the trace elements in the fine particles, the X-rays were monochromatized into 17.4-keV X-ray, which was focused by Kirkpatric-Baez optics (K-B mirror), offering a square spot of 5 μm×5 μm, with the photon flux of about 5×10^9 ph·s^{-1}/300 mA at the sample position. A Si(Li) detector was mounted in the orbital plane perpendicular to the beam incidence.

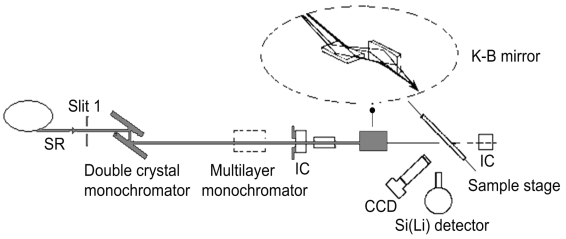

Fig.1 A schematic diagram of the μ-SXRF at BL-4A beamline of PF, Japan. Either a double crystal monochromator or a synthetic multilayer monochromator was used as the monochromator

The sample frame was mounted on a computer -controlled stage to maneuver the sample relative to the incoming X-ray microbeam. The beam spot on the sample surface was monitored using an optical microscope and a CCD camera, which can be operated in reflected and transmitted light mode. Because of the high photon fluxes using spot analysis mode, a 60-s irradiation was used to measure each of random PM$_{2.5}$ particles on the foil target.

4 Results and discussion

4.1 Mass concentration of PM$_{2.5}$

Fig.2 shows the seasonal variation in the PM$_{2.5}$ mass concentrations in downtown Shanghai, being 80.6, 71.4, 48.9, and 41.2 μg·m^{-3} in spring, winter, autumn, and summer, respectively, in 2007. The annual average mass concentration of 54.8 μg·m^{-3} is approximately three times higher than the 15 μg·m^{-3} reported by US EPA[22], but is lower than those in Beijing, China[23–25]. This could be assigned to difference of geographical location and meteorological conditions. Located at the Great North China Plain, Beijing is close to the Mongolian Desert in the north, and the significant northwest seasonal winds from November to April lead to dry and dusty in Beijing, with a mean annual precipitation of 584 mm, relative to the 1040 mm of Shanghai at the Yangtze River mouth. In addition, Beijing is easily impacted by regional and/or local deserts and arid loess-lands, while Shanghai is rarely influenced by the dust of long-range transport.

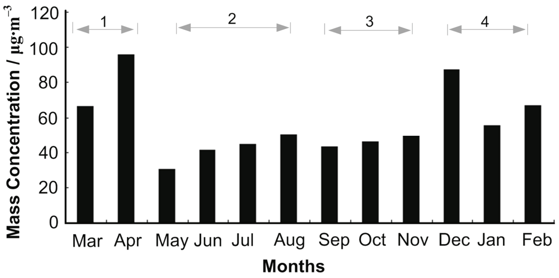

Fig.2 Mass concentration of PM2.5 in downtown Shanghai (average two weeks per month) in spring (1), summer (2), autumn (3), and winter (4) in 2007.

4.2 Elemental contents in $PM_{2.5}$ of Shanghai

The $PM_{2.5}$ samples were analyzed by ICP-MS. The total mass concentrations of detected elements were 4.5, 3.7, 2.4 and 2.0 μg·m^{-3} in spring, winter, autumn and summer, respectively. Results of the elemental analysis are given in Fig.3. The main elements were Mg, Ti, Cr, Mn, Fe, Cu, Zn, Ba, Pb and Ca, and the $PM_{2.5}$ trace elemental contents in Shanghai were ranked as Fe > Ca >Ti = Zn > Mg > Pb > Mn > Cr > Cu > Ba > V > Sr > Sn > Rb >Se> As > Zr > Ce > La > Cd > Co > U. The high Fe and Ca contents in the $PM_{2.5}$ might be attributed to the steel industry of Shanghai, such as Baostell Group, the largest steel complex in China.

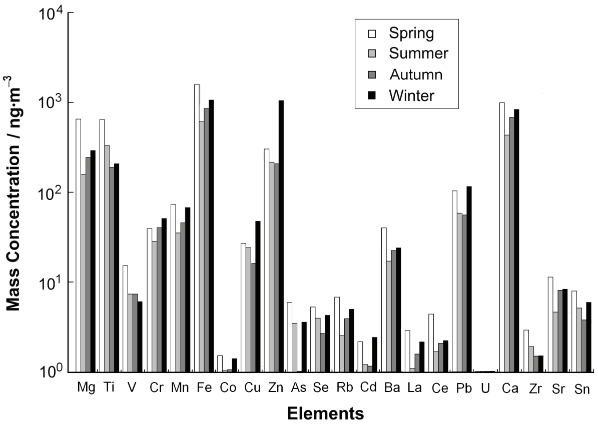

Fig.3 Mass concentration of elements in $PM_{2.5}$.

The lethal Pb contents in $PM_{2.5}$ of Shanghai in winter, spring, autumn, and summer were 114.4, 100.2, 57.9, and 56.3 ng·m^{-3}, respectively, with an annual average value of around 72.4 ng·m^{-3}, which is lower than that of 1533 ng·m^{-3} reported by Long *et al.* in 2003[26]. This shows a considerable decrease of the Pb pollution since the phasing out of leaded gasoline in 1997 by the government.

Table 2 Metal contents (ng·m^{-3}) in particulate matter of different cities in the world.

References*	[29]	[30]	[27]	[31]	[32]	[33]	[34]	[35]	[36]	[37]	[38]	This study
Samples	261	47–108	—	—	—	110	17	>7 years	—	—	—	22.1 year
Mass	7.3	—	—	—	—	—	48.6	6.2	—	—	—	54.8
As	—	1.5	—	—	—	4.2	—	—	—	2.83	38.33	2.9
Ba	—	—	—	—	—	—	—	—	—	—	—	23.8
Cd	—	0.1	—	—	—	—	—	—	—	1.22	6.38	1.5
Cr	—	3.2	2.9	2.3	6	—	—	0.1	—	2.165	26.67	36.7
Co	—	3.3	—	—	—	—	—	—	—	—	2.25	1.15
Cu	—	—	7.2	8.4	99	—	—	1.4	3.7	22.84	58.33	25.1
Fe	51.1	100	100	150	24	114	194	4	1,135	258.37	1,140	922.2
Mn	4.1	4.9	8.4	6.7	4	9.9	27.7	0.7	97	16.73	73.33	49.6
Pb	—	71	33	60	292	—	—	1.1	319.5	49.755	218.3	72.4
Sr	—	—	—	—	—	—	—	—	—	—	—	7.2
Zn	26.3	16	53	33	144	297	112	1.2	525	198.59	503.3	331.1
V	—	3.9	3.9	5.4	19	4.9	—	1	—	6.705	28.9	8.7
Ti	5.1	—	10	7.2	5	4.7	24.3	1	—	4.15	55	331.1

* Places in the Refs. [29] Brisbane, Australia, [30] Ankara, Turkey, [27] Kyoto, Japan, [31] Vienna, Austria, [32] Mexico City, Mexico, [33] Birmingham, UK, [34] California, USA, [35] Tasmania, Australia, [36] Beijing, China in 2002, [37]Honkong,China, in 2006, [38] Beijing, China, in 2006.

Table 2 shows metal contents ($ng\cdot m^{-3}$) in particulate matter of different cities in the world. The Pb concentration in Beijing is three times higher than in Shanghai. Sun *et al*[28] concluded that the high Pb concentrations in winter were likely attributed to the large consumption of coal for house heating, and the high emission of exhaust due to the incomplete combustion of fuel. However, this is not the case in Shanghai, where the winter is relatively warm. The Pb content difference between winter and summer in Shanghai was likely due to meteorological conditions and the steel industry zone. Unlike in summer with high wind speed and high temperature favoring the air convection and pollutant dispersion, the low wind speed and ambient temperature in winter favor the accumulation of pollutants. Moreover, as a coastal city, the southeast wind from the sea in summer of Shanghai can dilute or blow the air pollutants from the steel industry zone in North Shanghai, whereas the northwest wind in winter of Shanghai brings pollutants from inland and the steel industry zone, hence the high Pb concentrations in winter.

Comparatively, the metal concentrations for different studies reveal the difference of metal diversity and the magnitude of variable concentration. In our study, the extent of pollution is significant for several metals of different sites based on the absolute metal contents. In Table 2, concentrations of the crustal metals, such as Fe and Mn, are the highest except Beijing. The airborne particles of crustal elements in Shanghai are mainly derived from local construction and land reclamation activities. The anthropogenic elements, such as Cr, Cu and Zn, come from vehicle emission, and Zn is likely also from wearing of car tyres, and their concentrations are as high as other cities except Beijing.

4.3 Enrichment factors

Atmospheric particles are mainly derived from low-temperature crustal weathering, soil remobilization (crustal source), and a variety of high-temperature anthropogenic source. The enrichment factors (*EF*) is used to establish the chemical character and the principal sources of trace elements to aerosols by incorporating reference elements, and evaluate the strength of the crustal and non-crustal sources using Eq.(1), which are indicators of a specific source. Ti is used as an element of crustal indicator.

$$EF_x = [C_{xp}/C_{\mathrm{Tip}}]/[C_{xc}/C_{\mathrm{Tic}}] \qquad (1)$$

where, C_{xp} and C_{Tip} are the concentrations of x element and Ti in an aerosol, respectively. C_{xc} and C_{Tic} are their concentrations in an average crustal material.

If the EF_x approaches unity, crustal soils are likely predominant source for x elements. Except for crustal materials, other EF_x of trace elements in sources are expected to be greater than 1.0. However, since the types of crustal materials and soils come from different areas, and little is known about uncertainties of fractionation during weathering, the EF_x are better resolvable within 10 or a little larger from crustal materials (Fig.4)[39]. Continentally crustal values of eastern China were referenced using Ti as a crustal tracer[40]. *EF* of elements, such as Mg, V, Mn, Fe, Co, Ba, La, Ce, Zn, Sr and Rb are close to unity or less than 10, suggesting that they are attributable mainly to soil and road dust of dispersion and re-suspension. The high enrichment for Cr, Cu, Zn, As, Se, Cd, Pb and Sn, which suggests that their dominant sources are non-crustal and a variety of pollutant emissions, may contribute to their loading in the air. This enrichment analysis confirms that the trace elements come from a blend of crustal particles and anthropogenic source in the ambient air of Shanghai.

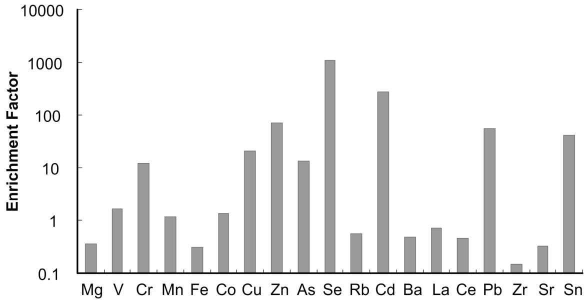

Fig.4 Enrichment factors of elements in $PM_{2.5}$.

4.4 Source identification of $PM_{2.5}$ particles

The element compositions for individual airborne particles characterized by their X-ray spectra show that they vary with emission sources[18]. These can be used as fingerprint to identify an unknown source of individual particles, by comparing their spectra with those of emission sources. In our earlier study[41], PIXE spectra were used as pattern recognition (PR) system for identifying the sources of individual airborne particles. In this work, μ-SXRF spectra of individual particles were measured and recorded into a fingerprint database of the emission sources by the PR system. Similarly, individual particles for the environmental monitoring sites were measured, and the spectra were recorded into another database by the PR system. The latter were identified by comparing both PR systems. Fig.5 compares the μ-SXRF spectrum of an unknown $PM_{2.5}$ with that of a vehicle exhaust particle in the fingerprint database, which implies the former is derived from vehicle exhaust due to similar chemical compositions. Eight categories of pollution sources recognized in this work were shown in Fig.6.

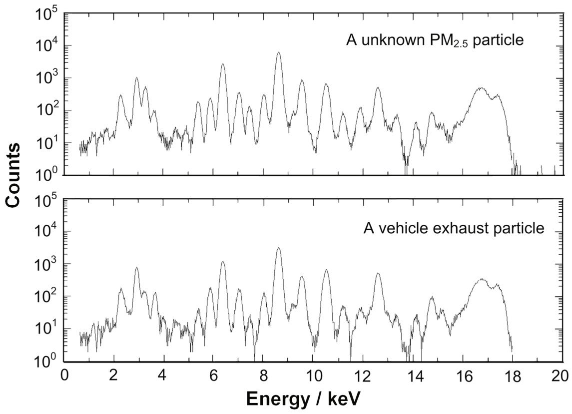

Fig.5 A comparison of the μ-SXRF spectrum of an unknown particle with that of a vehicle exhaust particle.

In Shanghai, the highest contribution of vehicle exhaust may be attributed to heavy traffic due to over 2 million motor vehicles and the annual gasoline consumption of about 6.2 million tons in 2006. This suggests that the vehicle exhaust is the most important pollution source of $PM_{2.5}$. The 21% contributions of metallurgical activities are from converter and electric furnace for steelmaking, coke oven and sintering plant, which may be attributed to the steel industry in Shanghai. The 12% contribution of converter for steelmaking is much more than that of electric furnace for steelmaking, the coke oven and the sintering plant. Thus, the control of the emission from converter for steel making is important to improve the air quality of Shanghai in future. The contributions of the coal-fired power plant and boiler are 6% and 4%, respectively. The soil dust in a city is often caused from uncovered ground surfaces, municipal construction sites. Yue *et al*[42] found in 2004 that the $PM_{2.5}$ contribution of soil dust was 13% at the center of Shanghai. In this study, its contribution has decreased to 5%, this may be attributed to the tree and grass planting on a large scale, and the setting of dust proof enclosures at the construction sites.

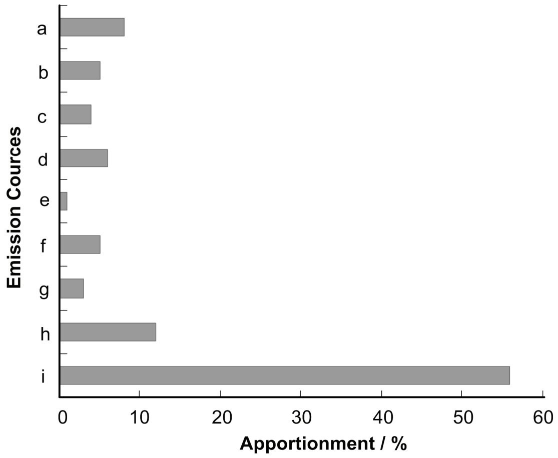

Fig.6 Individual $PM_{2.5}$ particle from Shanghai.
(a) unidentified, (b) soil dust, (c)coal-fired boilers,
(d) coal-fired power plants, (e) sintering plant, (f) coke oven,
(g, h) electric furnace and converter for steelmaking,
(i) vehicle exhaust.

5 Conclusions

In Shanghai, the $PM_{2.5}$ were analyzed by the μ-SXRF and ICP-MS, and revealed seasonal variation in mass concentration and chemical elements. The EF_x showed that the Mg, V, Mn, Fe, Co, Ba, La, Ce, Zn, Sr and Rb were close to unity or less than 10, and the Cr, Cu, Zn, As, Se, Cd, Pb and Sn were larger than 10, this suggests that the chemical elements in the ambient air of Shanghai resulted from a blend of crustal particles and anthropogenic source. The $PM_{2.5}$ particles were recognized in eight categories of emission sources. The results showed that most of $PM_{2.5}$ particles were derived from the vehicle exhaust and metallurgic emissions.

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