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Quantitative energy-dispersive electron probe X-ray microanalysis for single-particle analysis and its application for characterizing atmospheric aerosol particles

SHILA MASKEY and CHUL-UN RO*
Department of Chemistry, Inha University, 253 Yonghyun-dong, Incheon 402-751, South Korea
*Corresponding author. E-mail: curo@inha.ac.kr

Abstract. An energy-dispersive electron probe X-ray microanalysis (ED-EPMA) technique using an energy-dispersive X-ray detector with an ultra-thin window, designated as low-Z particle EPMA, has been developed. The low-Z particle EPMA allows the quantitative determination of concentrations of low-Z elements such as C, N and O, as well as higher-Z elements that can be analysed by conventional ED-EPMA. The quantitative determination of low-Z elements (using full Monte Carlo simulations, from the electron impact to the X-ray detection) in individual particles has improved the applicability of single-particle analysis, especially in atmospheric environmental aerosol research; many environmentally important atmospheric particles, e.g. sulphates, nitrates, ammonium and carbonaceous particles, contain low-Z elements. To demonstrate its practical applicability, the application of the low-Z particle EPMA for the characterization of Asian Dust, urban and subway aerosol particles is shown herein. In addition, it is demonstrated that the Monte Carlo calculation can also be applied in a quantitative single-particle analysis using transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectrometry (EDX), showing that the technique is useful and reliable for the characterization of submicron aerosol particles.

Keywords. Low-Z particle electron probe X-ray microanalysis; transmissing electron microscopy/ energy dispersive X-ray spectrometry; Asian Dust; urban aerosol; subway aerosol.

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1. Introduction

In the last decade, both the technological background and the data evaluation methods, i.e. X-ray spectra analysis and quantitative determination of sample composition, have been significantly improved for electron probe X-ray microanalysis (EPMA). One of the most essential breakthroughs in this field was the appearance of commercial silicon-based spectrometers equipped with thin polymer windows which improved the transmission of low-energy X-rays, as well as the newly designed high resolution energy dispersive detectors such as microcalorimeters. Another important improvement can be found in the recently developed evaluation models for quantitative analysis, which can handle various types of target samples. The ultimate goal of this scientific effort has been to increase the X-ray detection efficiency, to broaden the energy range of the X-rays to be analysed, to decrease the irradiated and excited volume in the specimen, and to obtain maximum information about sample composition and structure with application of adequate quantitative model for fast calculation. A quantitative EPMA technique using an energy-dispersive X-ray (EDX) detector with an ultra-thin window, designated as low-Z particle EPMA, has been developed. The low-Z particle EPMA can quantitatively determine concentrations of low-Z elements such as C, N and O, as well as higher-Z elements that can be analysed by conventional energy-dispersive EPMA (ED-EPMA). The morphology and the composition of environmental microparticles are heterogeneous, and therefore detailed quantitative information about both major and trace constituent elements is required. The characteristic X-ray lines of the main components, which are mostly low-Z elements ($Z < 9$), undergo extremely strong attenuation while propagating through the particle volume. Therefore, the estimation of the matrix effect is important. Quantitative determination of low-Z elements was necessary for further research of individual particles: firstly because these elements (C, N, O) are abundant, e.g. in atmospheric particles; and secondly because quantitative information is necessary for speciation of individual microscopic particles. Indeed, many environmental particles contain low-Z elements in the form of nitrates, sulphates, oxides, or mixtures including a carbon matrix.

A number of well-developed and rigorously tested quantification procedures are available in EPMA (e.g. ZAF and $\varphi(\rho z)$ methods), especially for the analysis of bulk samples. However, these procedures are limited for low-Z elements of individual atmospheric microparticles (in view of the small size and variable shape of the particles and the important matrix effect for low-Z elements). Therefore, a quantification method, which employs a Monte Carlo simulation in combination with successive approximations, has been developed. The quantitative determination of low-Z elements in individual environmental particles has improved the applicability of single-particle analysis.

2. Low-Z particle EPMA

Cautious sampling of airborne particles is the first step in the application of low-Z particle EPMA, which aims for the quantitative determination of elemental concentrations, both for low-Z and higher-Z elements, of individual aerosol particles. The measurements are carried out in a scanning electron microscope (SEM) equipped with an ultra-thin window EDX detector. To achieve optimal experimental conditions, such as a low background level in the spectra and high sensitivity for low-Z element analysis, an accelerating voltage of 10 kV is chosen. The beam current is 1 nA for all measurements. To obtain the statistically sufficient number of counts in the X-ray spectra while limiting the beam damage on sensitive particles, a typical measuring time of 10 s is used. A more detailed discussion of the measurement conditions is given elsewhere [1]. The net X-ray intensities for chemical elements are obtained by nonlinear, least-squares fitting of the collected spectra using AXIL program [2]. The elemental concentrations of individual particles are determined from their X-ray intensities by applying a Monte Carlo calculation combined with reverse successive approximations [1,3]. The quantification procedure provided results with an accuracy of less than 12% relative deviations between the calculated and nominal elemental concentrations for various standard particles [3–5]. The low-Z particle EPMA method can provide quantitative information on the chemical composition and particles can be classified based on their chemical species. The analytical procedure for determining chemical species and assigning individual particles to specific types is described in more detail elsewhere [6,7].

3. Monte Carlo calculation for quantitative TEM/EDX analysis

The Monte Carlo calculation has been proven to be an excellent tool for accurately simulating electron–solid interactions in atmospheric individual particles of micrometre size. In Monte Carlo calculations, electron trajectories are simulated, the generated characteristic and bremsstrahulung X-rays are calculated for spherical, hemispherical and hexahedral particles sitting on a flat surface, and the concentrations of chemical elements of single particles can be accurately determined. Although it was designed for SEM application, the Monte Carlo calculation could be used also for the quantitative single-particle analysis using transmission electron microscopy (TEM) with an ultra-thin window EDX with a high accelerating voltage (200 kV) [8]. For TEM measurements, formvar/carbon-coated TEM grids have been widely used as a collecting substrate of airborne particles. The formvar/carbon film, consisting of formvar resin for film resilience and a carbon layer for film stability under the electron beam, is composed of C, O and H, and has a density of about 1.2 g/cm^3. When formvar/carbon-coated TEM grids are used, the correction for the interference of C and O X-rays from the formvar/carbon film is critical for the quantitative single-particle analysis using TEM-EDX. Monte Carlo calculation is very good as a quantification procedure, because it can deal with sample systems with complex geometry, such as a single particle sitting on a thin film, which is not feasible for conventional EPMA quantification procedures such as those based on ZAF and $\varphi(\rho z)$ corrections. In a Monte Carlo calculation program newly modified for TEM-EDX application, electron trajectories for a particle sitting on the thin film can be simulated and X-rays generated both from the particle and the film can be calculated (figure 1). The simulated X-ray spectra for particles with different chemical compositions and sizes showed that the intensities of C and O X-rays were nearly constant for particles without C and O elements such as NaCl and KCl particles, whereas X-ray intensities of chemical elements of the particles (e.g. Na, Cl, K) as well as the bremsstrahlung background increased with the increase of particle size. For particles containing O and/or C such as SiO_2, Fe_2O_3, K_2SO_4 and $CaCO_3$, the intensities of O and/or C X-rays increased with the increase of particle size, indicating that the contribution was mainly from particles (possibly a small fraction from the formvar/carbon films). Thus, the C and O X-ray intensities of the particle were calculated separately from those of the film, and the extent of the contribution of X-rays from the collecting film was estimated and corrected through the Monte Carlo simulation. The accuracy of the quantification procedure, including the correction for C and O X-ray intensities of the formvar/carbon film, was evaluated by investigating various types of standard particles, and good accuracy of the methodology was demonstrated

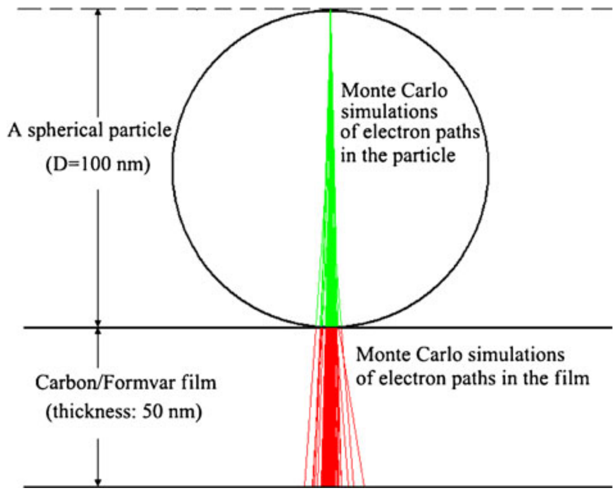

Figure 1. Electron paths obtained by Monte Carlo calculation under TEM-EDX measurement condition for a spherical particle sitting on carbon/formvar film (adapted from Geng *et al* [8]).

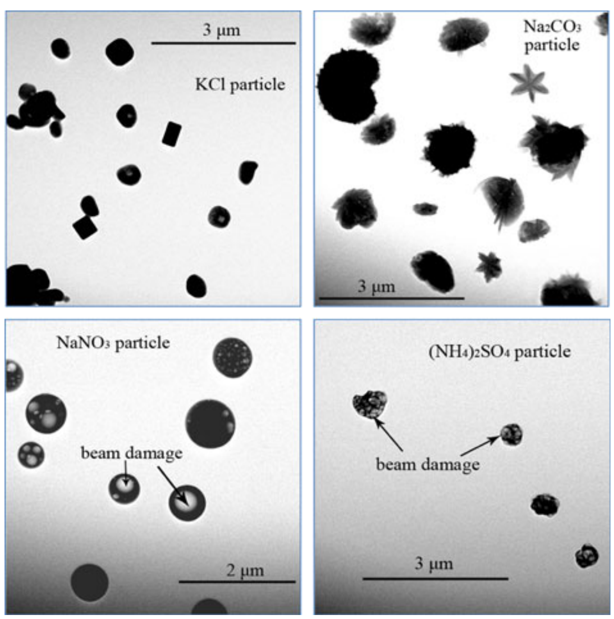

Figure 2. TEM images of KCl, Na_2CO_3, $NaNO_3$ and $(NH_4)_2SO_4$ standard particles (adapted from Geng *et al* [8]).

for beam-refractory particles such as $CaCO_3$, SiO_2, NaCl, Na_2CO_3, KCl and $CaSO_4$ [8]. However, for electron beam-sensitive particles such as $NaNO_3$ and $Ca(NO_3)_2{\cdot}4H_2O$, the deviations were quite large, because of the electron beam damage on the particles as electron beams of high energy and current were employed in TEM-EDX measurements. Figure 2 shows white bubbles in beam-sensitive $NaNO_3$ and $(NH_4)_2SO_4$ particles, which clearly indicates the electron beam-damage on the particles. Based on quantitative X-ray analysis together with morphological information from TEM image, overall 1638 submicron individual particles from 10 sets of aerosol samples collected in Incheon, Korea were identified. Figure 3 shows the relative abundances of various types of particles encountered in ten seasonal samples. The most frequently encountered particle types are carbonaceous and $(NH_4)_2SO_4/NH_4HSO_4$-containing particles, followed by soil-derived (e.g. aluminosilicate, SiO_2, $CaCO_3$), sea salt, K-rich (e.g. K_2SO_4 and KCl), Fe-rich, fly ash, and transition or heavy metal-containing (e.g. $ZnSO_4$, $ZnCl_2$, $PbSO_4$) particles. The relative abundances of the submicron particle types varied among samples collected in different seasons and also depended on different air mass transport routes. This study demonstrates that the quantitative TEM-EDX individual particle analysis is a useful and reliable technique for characterizing submicron aerosol particles.

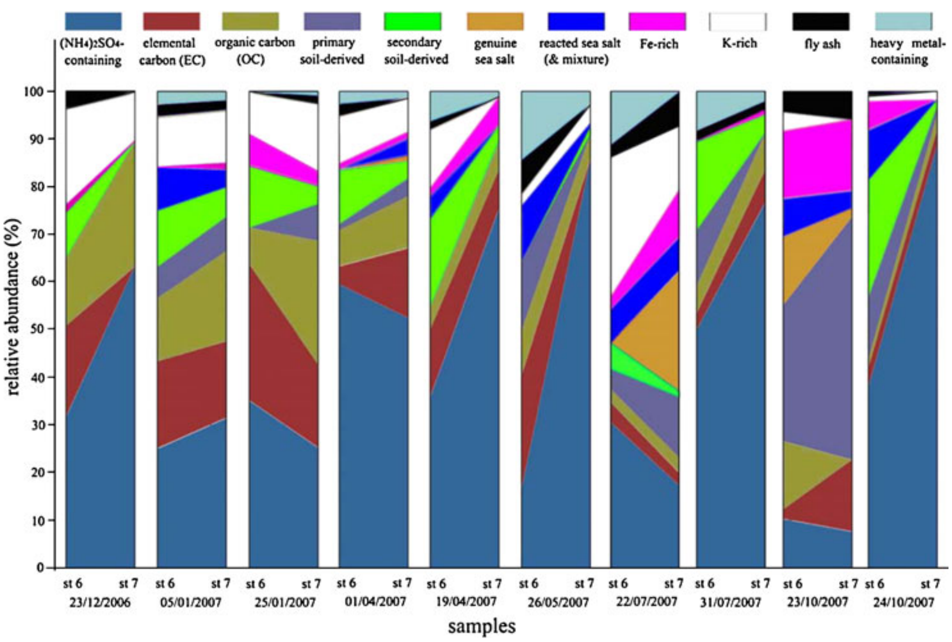

Figure 3. Relative abundances of various types of particles encountered in 10 seasonal samples (adapted from Geng *et al* [8]).

4. Application of low-Z particle EPMA for the characterization of aerosol particles

The low-Z particle EPMA has been proven to be very useful for the characterization of airborne particles. Herein, three different types of airborne samples, such as Asian Dust, urban aerosols and subway particles, are discussed as typical examples to show the practical applicability of low-Z particle EPMA technique.

4.1 *Characterization of Asian Dust particles*

Low-Z particle EPMA was used to characterize Asian Dust samples, collected in Chun-Cheon, Korea, during four Asian Dust storm events on 21 March, 9 April, 17 April and 11 November in 2002 [9]. In figures 4 and 5, relative abundances of the chemical species at different impactor stages for samples 'April_17' and 'Nov_11', respectively, are shown. For the samples, the most abundantly encountered particles, both in coarse and fine fractions, were soil-derived particles such as aluminosilicates (AlSi) and silicon dioxide (SiO_2), except for the sample collected on 11 November 2002, where the reacted $CaCO_3$ particles were the most abundant. All four samples found to have experienced chemical modifications during long-range transport because the samples contained particles composed of chemical species, such as nitrate and sulphate, which resulted from atmospheric reactions of $CaCO_3$ and sea-salt particles because $CaCO_3$ and sea-salt particles reacted with sulphur and nitrogen oxide species during long-range transport. The sample collected on 11 November 2002 experienced the most extensive chemical modification during its transport. For this sample, the overall relative abundances of the reacted $CaCO_3$ and reacted sea-salt particles were 29.9% and 23.2%, respectively. In addition to the reacted $CaCO_3$ and sea-salt particles, reacted K-containing particles were also encountered in this sample. In this work, it was observed that chemical modification of sea-salt particles was more extensive than that of $CaCO_3$ particles. By considering the

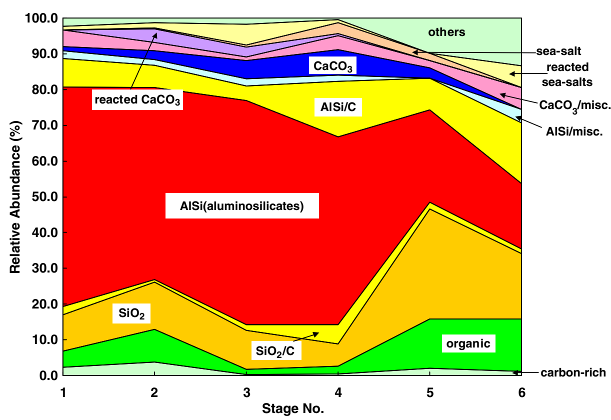

Figure 4. Relative abundances of each chemical species in the 'April_17' sample (cut-off diameters of stages 1–6: 16, 8, 4, 2, 1 and 0.5 μm) (adapted from Hwang *et al*, 2005).

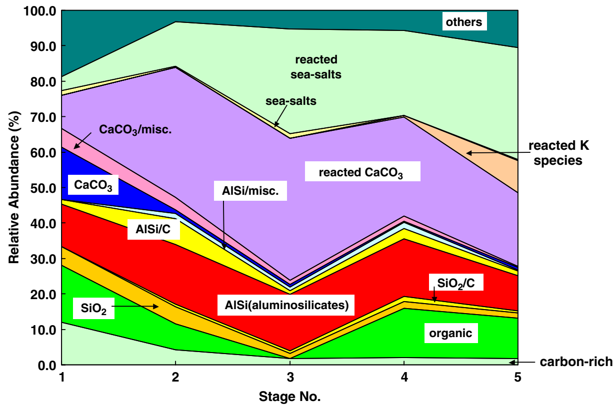

Figure 5. Relative abundances of each chemical species in the 'Nov_11' sample (cut-off diameters of stages 1–5: 16, 8, 4, 2 and 1 μm) (adapted from Hwang *et al*, 2005).

relative abundances of nitrate- and sulphate-containing particles, nitrate formation from $CaCO_3$ and sea-salt particles in the air is found to be more favourable than sulphate formation. This example demonstrates that the single-particle analysis using low-Z particle EPMA can provide detailed information on various types of chemical species in the samples [9].

4.2 *Characterization of urban aerosol particles*

The low-Z particle EPMA, combined with the utilization of morphological information on individual particles, was used to characterize six aerosol samples collected in the Korean city, Incheon, during 9–15 March 2006 [10]. Incheon is densely populated (population: 2.7 million, area: 427 km^2) and has many local emission sources, including seven industrial complexes, two seaports with ten wharfs, and one international airport. A new town (area: $\sim$33 km^2) has been under construction with major building activity and heavy transport. Incheon is on the coast of the Yellow Sea and adjacent to the megacity of Seoul. The sampling site was regarded as being susceptible to various urban source processes, including high areal traffic loads. The collected supermicron aerosol particles were classified based on their chemical species and morphology on a single-particle basis. Table 1 shows particle types based on their chemical species and morphology and their frequencies in the urban samples. Different particle types were identified and their emission source, transport and reactivity in the air were elucidated. In the samples, particles in the 'soil-derived particles' group were the most abundant, followed by 'reacted sea-salts', 'reacted $CaCO_3$-containing particles', 'genuine sea-salts', 'reacted sea-salts + others', 'Fe-containing particles', 'anthropogenic organics', $(NH_4)_2SO_4$, 'K-containing particles', and 'fly ash'. The application of the single-particle analysis, fully utilizing their chemical, compositional and morphological data of individual particles, clearly revealed the different characteristics of the six aerosol samples. For samples S3 and S5,

Table 1. Particle types based on their chemical species and morphology and their frequencies in the urban samples (adapted from Kang *et al* [10]).

	Sample S1		Sample S2		Sample S3		Sample S4		Sample S5		Sample S6		Total
	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	
(1) Soil-derived primary particles													
Aluminosilicate-containing	20	13	3	4	39	46	15	8	58	45	4	4	259
SiO_2-containing	1	1			5	1			1	3			12
$CaCO_3$-containing	3	5	1		3	3	3	2	5	2	1		28
$CaSO_4$(gypsum)	3		2				1						6
Carbonaceous		2	1					1	1	6			11
Other species	2	2	1	1	1			1	2	1	1		12
(2) Reacted $CaCO_3$-containing	5	1	7	3	2		2		1	1	12	5	39
(3) Genuine sea-salts							18	16	1		1		36
(4) Reacted sea-salts	4	2	15	11			13	13	1		15	12	86
(5) Reacted sea-salts + others	3	2	2	3			5	5			8	4	32
(6) Anthropogenic organics	2	4	2	2		3					5	8	26
(7) Biogenic aerosols		1		1	1								3
(8) Soot		1											1
(9) $(NH_4)_2SO_4$		3		5		1		1				2	12
(10) K-containing particles			2	3				2				5	12
(11) Fe-containing particles	1	6	1	6	1	2	3	1	2	1	1	3	28
(12) fly ashes	2	2	1	2				1				1	9
Total	46	45	38	41	52	56	60	51	72	59	48	44	612

which were sampled during two Asian Dust storm events, almost all particles were of soil origin that had not experienced chemical modification and that did not entrain sea-salts during their long-range transport. For sample S1, collected at an episodic period of high PM_{10} concentration and haze, anthropogenic, secondary and soil-derived particles emitted from local sources were predominant. For samples S2, S4 and S6, which were collected on average spring days with respect to their PM_{10} concentrations, marine-originated particles were the most abundant. Sample S2 seemed to have been strongly influenced by emissions from the Yellow Sea and Korean peninsula, sample S4 had the minimum anthropogenic influence among the four samples collected in the absence of any Asian Dust storm event and sample S6 seemed to have entrained air pollutants that had been transported from mainland China over the Yellow Sea to Korea [10].

4.3 *Characterization of subway particles*

The low-Z particle EPMA was used to characterize seasonal indoor aerosol samples collected at a subway station in Seoul, Korea [11]. Overall, some 10,400 particles for eight seasonal samples collected at the Hyehwa subway station platform were analysed and classified on the basis of their chemical species. Four major types of particles, based on their chemical compositions, were significantly encountered: Fe-containing, soil-derived, carbonaceous, and secondary nitrate and/or sulphate particles. In table 2, the overall relative abundances of those particle types encountered in the subway platform samples are shown. Fe-containing particles are the most abundant, with a relative abundance in the range of 61–79%. Fe-containing particles were generated from wear processes at rail–wheel–brake interfaces, whereas the others might be introduced mostly from the outdoor urban atmosphere. Most of the Fe-containing particles were found in either partially or fully oxidized state. The relative abundance of Fe-containing particles increases as particle size decreases. In samples collected in the summer, Fe-containing particles were the most abundant, whereas soil-derived and nitrate/sulphate particles were the lowest. This indicates that the air-exchange between indoor and outdoor environments is limited in the summer, owing to the air-conditioning in the subway system. In addition, it was observed that the relative abundance of particles of outdoor origin varied somewhat among seasonal samples to a lesser degree, reflecting that indoor emission sources predominated. To clearly identify indoor sources of subway particles, samples were collected at four different locations of four subway stations, namely the Jegi, Seouldae, Yangjae and Chungmuro stations in Seoul [12]. The four sampling locations were in tunnel, at platform, at ticket office and outdoors. Figure 6 shows the relative abundances of major particle types for samples collected at different locations of the four underground subway stations. For the samples collected in tunnels, Fe-containing particles were the most abundant, with relative abundance of 75–91% for the four stations. For the samples collected at the platform, at the ticket office and outdoors, the relative abundance of Fe-containing particles decreased as the distance of the sampling sites from the tunnel increased. In addition, samples collected at the platform of subway stations with platform screen doors that limit air-mixing between the platform and the tunnel, showed a marked decrease in the relative abundance of Fe-containing particles, clearly indicating that Fe-containing subway particles were generated in the tunnel.

Table 2. Overall relative abundances of subway particle types observed in the eight samples (adapted from Kang *et al* [11]).

Particle types	Dec. 16, 2004	Dec. 17, 2004	May 3, 2005	May 5, 2005	July 4, 2005	July 6, 2005	Nov. 23, 2005	Nov. 25, 2005
Iron-containing	60.5	71.5	70.8	71.4	79.1	78.0	71.1	74.6
Carbonaceous	13.2	7.7	9.0	9.2	10.5	8.6	5.4	7.4
Soil-derived (sum)	14.0	11.4	10.7	11.5	6.0	7.5	13.1	9.4
Aluminosilicates	5.1	4.6	3.8	3.8	2.0	2.6	4.6	2.5
Aluminosilicates/C	2.8	1.5	2.2	1.8	1.0	1.3	2.0	1.1
$CaCO_3$	0.8	1.0	0.1	0.7	0.5	0.7	1.5	1.0
$CaCO_3$/C	1.2	0.8	0.4	0.6	0.5	0.4	1.3	0.8
SiO_2	1.8	1.3	2.7	2.8	0.8	1.4	1.5	2.5
SiO_2/C	2.5	2.2	1.5	1.8	1.2	1.1	2.2	1.5
Secondary nitrates/sulphates (sum)	8.0	6.8	5.1	4.0	1.3	2.7	6.0	4.1
$Ca(NO_3,SO_4)$	4.2	2.5	1.5	2.2	0.8	1.1	2.6	1.2
$(Na,Mg)(NO_3,SO_4)$	1.5	1.0	3.6	1.8	0.5	1.2	3.2	2.7
$(NH_4)_2SO_4$	2.3	3.3	–	–	–	0.4	0.2	0.2
Others	4.2	2.6	4.5	3.9	3.1	3.3	4.3	4.5
Total	100	100	100	100	100	100	100	100

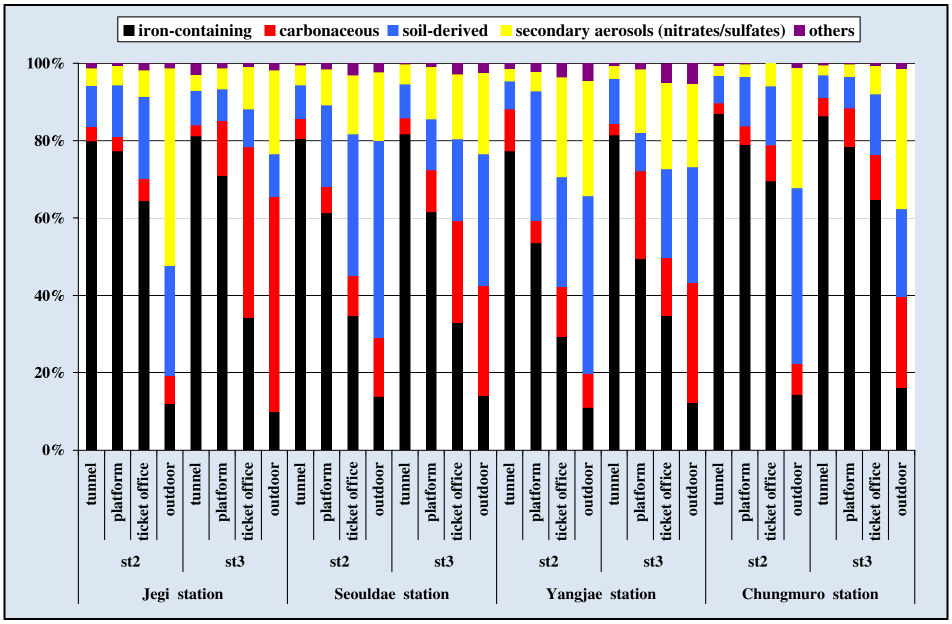

Figure 6. The relative abundances of major particle types for samples collected at different locations at four underground subway stations.

5. Conclusion

We introduced a single-particle analytical technique, named low-Z particle EPMA. The low-Z particle EPMA allows the quantitative determination of concentrations of low-Z elements such as C, N and O. The quantitative determination of low-Z elements (using full Monte Carlo simulations, from the electron impact to the X-ray detection) in individual particles has improved the applicability of single-particle analysis, especially in atmospheric environmental aerosol research; many environmentally important atmospheric particles, e.g. sulphates, nitrates, ammonium and carbonaceous particles, contain low-Z elements. In order to demonstrate its practical applicability, the application of the low-Z particle EPMA for characterizing Asian Dust, urban and subway aerosol particles is shown herein. In addition, it is demonstrated that the Monte Carlo calculation method can also be applied in a quantitative single-particle analysis using TEM/EDX, showing that the technique is useful and reliable for the characterization of submicron aerosol particles.

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