Characteristics of the elemental compositions of particulate matter at a subway platform using INAA and XRF

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(Received December 12, 2009; accepted in revised form December 20, 2010)

Air particulate matter / Metals / Iron / Subway platform / Rail wearing / Neutron activation analysis

Summary. In this study, a total of 21 elements were determined from PM_{2.5} and PM₁₀ samples collected at one subway station using INAA and XRF. In order to assess the pollution status and distribution characteristics in a subway station, the absolute concentration levels, concentration ratios, and crustal enrichment factors of these elements were analyzed. PM_{2.5} concentrations in the subway station varied in the range of 24.8 to 72.6 $\mu\text{g m}^{-3}$ (average $\pm$ standard deviation: $42.6 \pm 10.6 \mu\text{g m}^{-3}$), while those of PM₁₀ from 38.0 to 101 $\mu\text{g m}^{-3}$ ($67.2 \pm 15.5 \mu\text{g m}^{-3}$). The relative contribution of elemental components in each particle fraction accounted for about 42 and 44%, respectively. Out of all metals, Fe was predominant to represent about 29 and 27% of each particle fraction. In contrast, the crustal sources were estimated to contribute to about 3.7 and 2.3% of the total Fe concentrations, respectively. Thus, one can conclude that considerable quantities of airborne Fe particles originated mainly from subway sources, probably due to the wearing of the steel products like wheel, rail, brake, etc.

1. Introduction

Because of the potential health impact on the human body, the role of airborne particulate matters (APM) particularly as the carrier of many trace metals (such as As, Be, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, V, and Zn) has been emphasized in recent years [1, 2]. Particulate matter (PM) with aerodynamic diameter equivalent to or less than 2.5 μm (PM_{2.5}) can be deposited in the lower respiratory tract because of its permeability. Thus, it is well known that the health effects of aerosol particles are significantly correlated with their quantities in the fine fraction. When the level of APM and/or the content of the specific metals exceed “no observable adverse effect level” (NOAEL), their effects on human health are insidious both over short- and long-term periods [3]. Therefore, sampling and analysis of APM are needed to evaluate the air quality and contamination status.

As most people spend more than 80% of their time indoors, indoor air quality (IAQ) is an important criterion to

assess the inhalation conditions of toxic substances. Therefore, monitoring of the PM concentration levels and the associated elemental composition can be used as a practical barometer of IAQ in an indoor environment like a subway station. The contaminants originating from indoor pollution sources as well as various outdoor sources are easily accumulated in indoor environment dissimilar to the outdoor. Especially, because natural ventilation is nearly impossible in a subway station, its air quality can be worsened due mainly to the repetitive movement of subway trains [4]. In fact, high levels of PM have been reported in many previous studies throughout the world [4–10]. However, relatively little is known about the distribution of trace elements including Fe and/or many toxic elements. Generally, Fe has been well known as the predominant constituent in many subway systems. Nieuwenhuijsen *et al.* [11] stated that the higher toxicity from inhalation exposure in the metro system may be due to the higher iron content, although Fe is an essential element for human life.

The concentration data of trace metals obtained by long-term monitoring are indispensable for risk assessment and for source identification. Such studies can provide a solid basis for the build-up of various air quality control policies. Hence, an analytical method employed in the determinations of trace elements in APM samples should be sensitive and precise to accurately describe the elemental composition. The source apportionment study can thus be performed using their speciation data (such as carbon, ion, and metal). Although most trace metals (Ba, Br, Cr, Cu, Ni, Pb, Se, V, Zn, etc.) constitute only about 1% of the total particulate mass, they can play a critical role in the identification of diverse source processes. Because large amounts of carbon, ionic components, and major crustal elements are commonly bound to each other in most sources, each source type can be specifically assigned to its tracer [12].

In this study, a total of 60 samples (both PM_{2.5} and PM₁₀) were collected in the spring and summer seasons of 2009 with two annular denuder samplers at one subway station in Daejeon, Korea. Field campaigns were carried out during a 3 month period in spring (April–May) and summer season (July) in 2009. The measurements were made to cover up to 21 elements in both PM fractions using an instrumental neutron activation analysis (INAA)

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and X-ray fluorescence (XRF). INAA has been favored for many advantages in metal analysis (*e.g.*, high-precision, non-destruction, and multi-elemental capabilities) [13]. In order to assess the pollution status and distribution characteristics of PM-bound metals in a subway station, their absolute concentration level, concentration ratio, and crustal enrichment factor were also evaluated based on our measurement data.

2. Analytical methods

2.1 Sampling

The collection of all PM samples was made simultaneously with low volume air samplers from one subway station in Daejeon city, Korea. The Daejeon city subway system (approximately 94,000 passengers per day) consists of a single line with about 22.6 km tunnel path that crosses the central part of the city. The platform was equipped with a screen door to prevent the intrusion of the pollutants from the tunnel. The target sampling station (Yuseong spa station) is surrounded by a highly populated residential and commercial sector in the Yuseong hot spring region.

A total of 60 samples (both PM_{2.5} and PM₁₀) were collected in parallel from a platform of Yuseong spa subway station during the spring (22 April–5 May) and summer season (1 July–15 July) in 2009. For the collection of both PM fractions, two annular denuder samplers (URG, 3000C model) with polycarbonate filter (47 mm, 0.4 μ m pore size, Nuclepore) were used. The air flow rates for each sampler were adjusted to 16.7 L min⁻¹ and were operated continuously on a 24-h basis. Each filter was placed and weighed in a controlled atmosphere (20 °C and 50% relative humidity) for 24-h both before and after exposure to air sampling. These filters were weighed three times with a calibrated microbalance with a readability of 1 μ g (MT5 model, Mettler-Toledo Ltd.) of which electrostatic charges are controlled by a ²¹⁰Po radioactive source.

2.2 Elemental analysis

In the course of this research, a total of 21 trace elemental species were analyzed quantitatively from both PM fractions. The PM-bound concentrations of most elements (Al, As, Ba, Br, Cl, Cr, Cu, Fe, I, In, K, La, Mg, Mn, Na, Sm, Ti, V, and Zn) were analyzed by INAA. In case of Ca and Si, XRF (SEA2220A model, SII SEIKO Instruments Inc.) analysis was made prior to INAA. For the INAA, PM samples were irradiated in the thermal neutron field with the Pneumatic Transfer System (PTS, $\Phi_{th} = 2.95 \times 10^{13}$ cm⁻² s⁻¹, $R_{Cd} = 250$) at the HANARO research reactor at the Korea Atomic Energy Research Institute (KAERI). For neutron flux monitoring, activation wires were made up of such material as Au-Al, Co, Fe, and Mn (Reactor Experiments Inc., R/X activation wire, 99.99% purity). The optimum analytical conditions for various operations (*e.g.*, neutron flux, irradiation facilities, irradiation time, cooling time, counting time, *etc.*) were pre-estimated based on procedures established from our previous studies [14, 15]. For the determination of short-lived nuclides, the whole filter fraction was

irradiated for 1 min. After γ -ray counting of short-lived nuclides, it was re-irradiated for another 4 h to determine long-lived nuclides. The measurements were carried out using a high purity Ge detector with relative efficiency of 25%. This analytical system has 1.9 keV resolution (FWHM) at 1332 keV of ⁶⁰Co with the peak to Compton ratio of 45:1. During the measurement of the activated samples, dead time is maintained below 10%. Energy and efficiency calibrations were performed using multi-nuclide reference sources (NEN Products Inc., NES-602, 2.54 cm diameter disc type) that are certified by the National Institute of Standards and Technology (NIST, USA). A Gamma Vision software (EG&G ORTEC) was used on the basis of: (1) energy and efficiency calibrations, (2) the acquisition of gamma-ray spectra, and (3) peak analysis. The absolute concentrations of elements were estimated by the absolute approach with an aid of a new calculation-based PC code (*e.g.*, HYPERGAM [16]) with the nuclear data library in which a new PC code is adopted with HYPERMET [17]. The counting losses of both short (such as Al and V) and long half-life species were corrected by the inverse value of the mean decay ratio (F_m). For instance, the activity of Al can be computed by $1/F_m$ value (2.87), while it is negligible for long half-life species.

The elemental concentrations in PM samples, blank filters, and standard samples were determined for quality control purposes under the same analytical conditions. The final elemental concentrations were calculated after the subtraction of analytical blank values in polycarbonate filters used in this study (refer to Table 1). The analytical blank values for each target element were significantly lower than those of samples. Considering that the detectabilities are highly variable between different target elements, the net concentration data (signal) close to the analytical blank (noise) are subject to higher uncertainty. The method detection limit (MDL) was evaluated from blank filter values with a confi-

Table 1. Summary of elemental concentrations in blank polycarbonate filter and the corresponding method detection limit (ng/filter).

	Mean	RSD (%)	N	MDL ^a
Al	73.2	44.6	6	137
As	0.037	62.3	5	0.08
Ba	3.1	73.5	4	7.7
Br	21.9	27.0	6	33.4
Ca	6217	1.7	5	6427
Cl	185.0	8.5	6	216
Cr	214.3	28.2	6	333
Cu	2.3	39.2	6	4.08
Fe	256.9	53.9	4	528
I	1.0	24.8	6	1.55
In	0.006	59.4	5	0.01
K	42.7	45.8	6	81.1
La	0.031	57.5	5	0.07
Mg	68.9	18.7	6	94.1
Mn	1.6	37.1	5	2.79
Na	113.2	10.4	6	136
Si	15 969	14.3	5	20 430
Sm	0.008	74.5	4	0.02
Ti	14.1	46.7	6	27.0
V	0.1	24.8	6	0.18
Zn	51.0	83.3	2	134

a: Method detection limit (MDL).

dence interval of 95% (e.g., mean +2× standard deviation). The MDL is also presented in Table 1.

In this study, the standard reference materials (SRM2783 and 1648) of the NIST were analyzed by the same method as that for the quality control purposes. The elemental concentrations were compared statistically with the certified (or recommended) values. The deviation between the two values generally fell below 5% for most metal species. As such, the analytical results derived for most elemental components were fairly reliable.

3. Results and discussion

3.1 PM_{2.5} and PM₁₀ concentration

The PM_{2.5} concentrations in the platform area of subway station varied in the range of 24.8 to 72.6 $\mu\text{g m}^{-3}$ with an average ($\pm$ standard deviation) of $42.6 \pm 10.6 \mu\text{g m}^{-3}$. In contrast, the PM₁₀ concentration fell in the range of 38.0 to 101 $\mu\text{g m}^{-3}$ ($67.2 \pm 15.5 \mu\text{g m}^{-3}$). The average concentrations of PM₁₀ at subway station did not exceed the PM₁₀ guidelines set for both annual ($70 \mu\text{g m}^{-3}$) and daily intervals ($150 \mu\text{g m}^{-3}$) in Korea. However, the pollution levels of PM_{2.5} in the study area exceeded the strengthened daily PM_{2.5} guideline of US National Ambient Air Quality Standard (NAAQS) ($35 \mu\text{g m}^{-3}$) [18]. About 76% of our daily PM_{2.5} concentration data were higher than such guideline. The general features of PM distribution are presented in Fig. 1. Differences in concentration levels between PM_{2.5} and PM₁₀ are statistically significant at 99% confidence interval. The average concentration ratio of PM_{2.5}/PM₁₀ was estimated to be 0.64 ± 0.09 (range: 0.53 to 0.83). Furthermore, the daily concentration data for both PM fractions exhibited a moderately strong correlation (correlation coefficient (r) = 0.69, $p < 0.01$). These findings reflect that the

Fig. 1. Absolute concentrations of PM_{2.5} and PM₁₀ measured in the model subway station.

particle mass in the fine fraction (with anthropogenic origin) should be dominant over its counterpart with crustal origin.

3.2 Elemental concentration

Table 2 summarizes PM and the associated elemental concentration data measured from all PM samples collected at our target subway station in Daejeon city, Korea. To describe the distribution patterns of 21 elements, their concentration data were simply evaluated by their magnitude. The results can be grouped arbitrarily into five different categories: 1) $< 10^0 \text{ ng m}^{-3}$: In, La, and Sm; 2) $< 10^1 \text{ ng m}^{-3}$: As, Br, I, and V; 3) $< 10^2 \text{ ng m}^{-3}$: Cr and Ti; 4) $< 10^3 \text{ ng m}^{-3}$: Al, Cl, Cu, K, Mg, Mn, Na, and Zn; and 5) $> 10^3 \text{ ng m}^{-3}$: Ba, Ca, Fe, and Si. The concentrations of As, Cr, Cu, Mn, and Zn in PM_{2.5} averaged as 1.57 ± 0.80 , 41.1 ± 7.28 , 178 ± 45.3 ,

Table 2. Statistical summary of PM_{2.5} and PM₁₀ concentrations and the associated elemental components at the target subway station. The unit of PM is $\mu\text{g m}^{-3}$, while all the rest are in ng m^{-3} .

	PM _{2.5}					PM ₁₀				
	Mean	SD	Min	Max	N	Mean	SD	Min	Max	N
Al	286	179	96	860	29	550	260	222	1111	29
As	1.57	0.80	0.61	3.71	29	2.16	0.90	0.91	4.88	29
Ba	705	191	384	1092	28	1112	291	492	1627	29
Br	6.18	2.77	1.82	13.4	29	9.22	3.81	4.60	21	26
Ca	994	277	429	1535	29	2130	272	1567	2606	29
Cl	171	68.1	84.2	358	29	518	244	239	1237	29
Cr	41.1	7.28	27.0	58.6	29	62.2	10.5	44.0	78.6	27
Cu	178	45.3	89.6	248	29	291	77.6	132	396	29
Fe	12 165	2916	5801	16 683	29	17 969	4823	7481	26 158	29
I	2.58	1.83	0.55	8.58	29	3.72	1.93	0.82	9.27	29
In	0.01	0.01	0.00	0.03	27	0.02	0.01	0.01	0.05	27
K	239	253	10	1255	29	417	318	107	1396	29
La	0.37	0.25	0.10	1.25	29	0.68	0.35	0.17	1.53	29
Mg	161	50	96	296	29	278	84	113	426	27
Mn	98.5	27.2	49	144	28	157	45.7	67.1	239	29
Na	115	70.6	35	329	29	235	157	69.8	707	29
Si	2402	864	1248	4585	29	5446	1061	3786	8141	29
Sm	0.04	0.04	0.01	0.24	29	0.07	0.05	0.02	0.19	29
Ti	21	11	5.28	47.5	29	45	18.2	20.3	87.8	28
V	2.40	1.09	0.89	4.98	29	3.43	1.51	1.48	7.85	29
Zn	173	44.4	90.5	280	29	250	52.3	133	364	29
PM	42.6	10.6	24.8	72.6	29	67.2	15.5	38.0	101	29

Fig. 2. Average daily elemental concentration ratios between daily of PM2.5 and PM10.

98.5 ± 27.2 , and $173 \pm 44.4 \text{ ng m}^{-3}$, respectively, while their PM10 counterparts were 2.16 ± 0.90 , 62.2 ± 10.5 , 291 ± 77.6 , 157 ± 45.7 , and $250 \pm 52.3 \text{ ng m}^{-3}$, respectively.

As shown in Fig. 2, the average PM2.5/PM10 concentration ratios for each element ranged from 0.37 (Cl) to 0.77 (In) in this study. Concentration ratios of most elements exhibited above 0.6 except for crustal origin (Al, Ca, K, Ti, and Si) and sea salt (Cl). One can thus confirm that elements of crustal origin fell mainly in coarse particle fraction, while those of anthropogenic origin are more dominant in fine particle fraction. This relative pattern observed in our target subway is thus comparable to that of ambient air in certain respects.

To account for the relative contribution of elemental components to the PM mass, the concentrations of 21 elements, determined in this study, were summed up and compared with the mass of the corresponding PM fractions; each fraction accounted for about 42% (PM2.5) and 44% (PM10). As such, the relative contribution of elements to PM mass is significantly different between subway and ambient air. The speciation of the measured elements in each PM fraction is shown in Fig. 3. For the clarity, the elements were divided into four groups: 1) Fe; 2) major crustal elements: Al, Ca, K, Mg, and Si; 3) minor elements: Ba, Cl, Cr, Cu, Na, Mn, Ti, and Zn; and 4) trace elements: As, Br, I, In, La, Sm, and V. Major components of PM (*e.g.*, elemental and organic carbon or soluble ions in airborne particles) which were not determined in this study appeared to occupy the remaining 56–58%.

From the Table 2 data (and Fig. 3), it was found that the concentrations of Fe in both fractions were substantially larger than all other elements. One may note that Fe is generally the most abundant element in indoor environment of a subway station, as it can be released by the wearing of steel products [19]. The Fe concentrations in PM2.5 varied in the range of 5.8 to $16.7 \text{ } \mu\text{g m}^{-3}$ with average ($\pm$ standard deviation) of $12.2 \pm 2.9 \text{ } \mu\text{g m}^{-3}$, while those in PM10 ranged from 7.5 to $26.2 \text{ } \mu\text{g m}^{-3}$ ($18.0 \pm 4.8 \text{ } \mu\text{g m}^{-3}$). The concentrations of Fe alone accounted for 29 and 27% of PM2.5 and PM10, respectively, while those of the major crustal elements were about 10 and 13%, respectively. The proportion of other minor and trace elements was significantly lower on the other hand (by about 4%).

As shown in Fig. 3, the predominant element, Fe tends to occur in the form of magnetite (Fe_3O_4). Seaton *et al.* [20] studied the toxicological aspects of PM10 collected in a London subway station; they found that Fe-enriched dust has a cytotoxic and inflammatory potential. Thus, in order to evaluate the relative contribution of anthropogenic sources to the observed Fe levels, its proportion was calculated by the equation shown below [5].

$$\text{Crustal amount of (Fe)}_{\text{APM}} = \left(\frac{\text{Fe}}{\text{Si}} \right)_{\text{crust}} \times (\text{Si})_{\text{APM}}$$

Here, $(\text{Si})_{\text{APM}}$ and $(\text{Fe})_{\text{APM}}$ denote the concentrations of Si and Fe in APM, while $(\text{Si})_{\text{crust}}$ and $(\text{Fe})_{\text{(crust)}}$ represent their global average concentrations in earth crust [21]. The contributions of crustal sources to the observed Fe levels were estimated as 3.7 (PM2.5) and 2.3% (PM10) of the total Fe. Thus, one can conclude that considerable amount of airborne Fe in subway stations was mainly derived by the wearing of steel products (*e.g.*, wheel, rail, and brake).

Typically, Ba is an element added to the lubricating oil to prevent smoke and engine abrasion of diesel vehicles [22]. Thus, it has been used as one of the marker species of road dust in ambient air [12]. It is also known that Ba (and Mn) can also be enriched in subway station [11, 19, 20, 23]. The pollution level of Ba (1112 ng m^{-3}) in PM10 was significantly higher (about 26 times) than that measured at an industrial area (43.4 ng m^{-3}) in the same city [12]. The relative enrichment of Mn was not observed in the subway station, which is suspected to arise from insignificant role of subway sources relative to outdoor ones (*e.g.*, antiknock agent in gasoline vehicles) [23].

Fig. 3. Comparison of elemental compositions in PM2.5 and PM10 samples.

Fig. 4. Crustal enrichment factor (EF) values for all elements in PM10 and PM2.5 fractions.

The concept of enrichment factor (EF) can be introduced to help distinguish some elements with well-defined sources (e.g., Si as the major component of the earth's crust) from other ones with different origins [21]. By comparing the concentration of a target element to a reference element like Si [$EF = (X/Si)_{PM} / (X/Si)_{crust}$], one can evaluate the extent of enrichment for a given element. Because Si is the most abundant element in the crustal composition or is affected less significantly by anthropogenic sources, it was selected as a reference element in this study. It is acknowledged that EF values of elements are associated with some degree of uncertainty due to the natural variation of the crustal composition. However, one may assume that the EF value larger by an order of magnitude than unity can signal the potent role of anthropogenic origin [24, 25]. By setting the arbitrary EF value of 10, we attempted to sort out such a signal from several metals (e.g., As, Ba, Br, Cl, Cr, Cu, Fe, I, Mn and Zn) for both PM fractions. The EF values for almost all elements in the PM10 samples were lower than those in PM2.5 samples. It was noteworthy that most elements with higher EF values (e.g., As, Br, Cl, Cu, I, and Zn) are typically classified as the key components of major anthropogenic processes with different characteristics such as industrial activities, fossil fuel combustion, and high traffic activities. Because Ba, Cr, Fe, and Mn can be generally classified into elements of crustal origin, their relative enrichment in subway station should be accounted for by the resuspension of crustal particulates through incoming passengers (penetration of outdoor APM) as well as anthropogenic sources within subway station (steel friction of railway and wheel).

4. Conclusion

In this study, PM2.5 and PM10 samples were collected at one subway station in Daejeon, Korea, and the concentrations of the associated elements (up to 21) were determined using INAA and XRF. Based on our measurement, the pollution status and the distribution characteristics of diverse metal components in subway particles were evaluated in many respects. The contents of analytical blank and MDL for target elements were significantly lower than their average content determined from the actual samples. If one considers the fact that the relative error of SRM samples (for quality control) generally fell below 5% for most metal species, the analytical results derived for most elemental components in PM samples were fairly reliable.

The PM2.5 concentrations in the subway station varied in the range of 24.8 to 72.6 $\mu\text{g m}^{-3}$ with average ($\pm$ standard deviation) of $42.6 \pm 10.6 \mu\text{g m}^{-3}$. The PM10 concentrations were seen at moderately enhanced levels from 38.0 to 101 $\mu\text{g m}^{-3}$ with average ($\pm$ standard deviation) of $67.2 \pm 15.5 \mu\text{g m}^{-3}$. The pollution levels of PM2.5 in the target subway exceeded the strengthened US NAAQS daily PM2.5 guideline (35 $\mu\text{g m}^{-3}$); 76% of our daily PM2.5 data are higher than such guideline. Unlike the case of ambient air, the relative contribution of elemental components was significant enough to account for about 42 and 44% of PM mass in PM2.5 and PM10 fractions, respectively. The proportion of Fe in those PM fractions were apportioned to 29 and 27%, respectively. However, the crustal sources were estimated as 3.7 and 2.3% of the total Fe concentrations, respectively. Thus, one can conclude that airborne Fe in subway station should come mainly from the wearing of steel products in subway systems (e.g., wheel, rail, and brake), regardless of particle size. Evaluation of elemental concentration ratios led us to conclude that crustal elements are still associated with coarse particle fraction, while Fe and most elements with anthropogenic origin are tightly linked to fine particle fraction produced in the subway station. Data from this study can be used further to apportion different sources and to assess health risk so that one can establish or improve policies and strategies for an indoor air quality management in the public transportation system.

Acknowledgment. This research was supported by the Nuclear R&D Program by the Ministry of Science and Technology, Republic of Korea.

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