



Rapid and Simple Determination of Multi-Elements in Aerosol Samples Collected on Quartz Fiber Filters by Using EDXRF Coupled with Fundamental Parameter Quantification Technique

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ABSTRACT

It would be convenient if we could achieve multi-component (organic and inorganic species) analysis using just one quartz fiber filter (QFF) as an aerosol collection medium. In general, QFF have been used for analyzing carbonaceous materials in aerosols. This study shows a nondestructive, rapid, and simple method using EDXRF (Energy Dispersive X-Ray Fluorescence spectrometry) that has secondary targets and three-dimensional polarization optics for analyzing inorganic multi-elements in aerosols collected on QFFs. Multi-element analysis can be achieved by using EDXRF coupled with fundamental parameter (FP) quantification, as speed of up to 900 s (15 min) per sample. The EDXRF-FP method shows good repeatability, with generally less than 5% variation when measuring each analyzed element. While the elemental concentrations in the blank QFFs in any lots examined in this study could be considered to be lower than the actual samples, the blank level of Ni cannot be ignored. The EDXRF-FP results for each element of the aerosols collected on QFF agreed well with ICP-MS and ICP-AES results. The temporal variations of the selected elements in aerosols obtained by EDXRF-FP showed very good agreement with those obtained by ICP-MS and AES, and thus this method is suitable for elucidating day-to-day variations of multi-elements in aerosols.

Keywords: Aerosols; Asian mega-city; Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF); Nondestructive analytical method; Three-dimensional polarization optics.

INTRODUCTION

Air pollutants such as atmospheric aerosol and hazardous chemical species adversely affect many cities around the world. In particular, many kinds of metals and metallic compounds in aerosol are harmful and carcinogenic to humans. Therefore, exposure to atmospheric metals is of a serious concern to human health. According to the

International Agency for Research on Cancer (IARC, 2012), arsenic and inorganic arsenic compounds, beryllium and beryllium compounds, cadmium and cadmium compounds, chromium (VI) compounds, and nickel compounds are classified into Group 1 (carcinogenic to humans), inorganic lead compounds are classified into Group 2A (probably carcinogenic to humans), and many other metals and metallic compounds are classified into Group 2B (possibly carcinogenic to humans). From another aspect, it is well known that trace metals are specific to their emission sources (Okuda *et al.*, 2006a; 2007; 2008). Trace metals are transported together with aerosols that are also harmful, without volatilization or decomposition. Therefore, it is very important to measure trace metals for elucidating their

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health impacts and the source identification of hazardous chemical species.

Different types of filters have been used for collecting aerosols. In general, fluoropolymer or cellulose membrane filters have been used for multi-elemental analysis because these kinds of filters usually contain very little amount of inorganic impurities (Calzolari *et al.*, 2008; Niu *et al.*, 2010; López *et al.*, 2011; Öztürk *et al.*, 2011). On the other hand, quartz fiber filters (QFFs) have not often been used because they are considered to contain silicon and many other metal impurities (Baron and Willeke, 2001). QFFs have been used to analyze carbonaceous materials in aerosols, such as elemental carbon, organic carbon, and many other organic compounds (Baron and Willeke, 2001; Okuda *et al.*, 2002; 2006b). In order to make simultaneous measurements of carbonaceous and inorganic components, many researchers have achieved parallel samplings using QFFs and other filter materials at the same time (Okuda *et al.*, 2009; Perrino *et al.*, 2009). However, it is obvious that it would be quite convenient if we could achieve multi-component analysis using just one filter as an aerosol collection medium.

A variety of methods has been used for analyzing multi-elements in aerosols (Baron and Willeke, 2001). Mass spectrometry or atomic emission spectrometry coupled with inductively coupled plasma technique (ICP-MS or ICP-AES) have been used for many years as highly sensitive and reliable methods of multi-elemental analysis. However, in order to apply these techniques to aerosol samples, time-consuming pretreatment procedures such as acid decomposition are required. Instrumental neutron activation analysis (INAA) and particle-induced X-ray emission (PIXE) are also highly sensitive multi-elemental analytical methods (Chiari *et al.*, 2006; Salma *et al.*, 1997); however, these techniques need a nuclear reactor or an accelerator facility that cannot fit within the bench-top scale of a laboratory. X-ray fluorescence spectrometry (XRF) has been used for measuring major elements in aerosols for many years. XRF can be classified into two groups, energy-dispersive (EDXRF) and wavelength-dispersive (WDXRF), by the detecting mechanisms. In general, EDXRF requires less laboratory space due to the simple concept of the instrument. WDXRF spectrometers tend to be larger and more expensive. Synchrotron radiation XRF (SR-XRF), which has very high sensitivity, is another candidate (Bukowiecki *et al.*, 2008; López *et al.*, 2011; Osan *et al.*, 2010; Richard *et al.*, 2011); however, it requires proximity to such a facility. Traditionally, it is thought that the bench-top type EDXRF is unsuitable for trace element analyses because of its relatively low sensitivity; however, it has increasingly been applied to aerosol multi-element measurements because of the improvements in sensitivity associated with the utilization of many new techniques such as secondary targets and three-dimensional polarization optics (Okuda *et al.*, 2013; Spolnik *et al.*, 2005; Zhang *et al.*, 2012).

Recently, Yatkin *et al.* (2011) reported an intensive study on the evaluation of the potential of EDXRF to be competitive to graphite furnace atomic absorption spectrometry (GF-AAS) and ICP-MS for the measurements of heavy metals in particulate matter. They concluded that EDXRF could be

considered as an alternative method to ICP-MS for measurements of elements in aerosols. The report was quite comprehensive and informative, but we found at least two issues remain open, i.e., sample matrix and analytical time. The EDXRF results can be affected by sample matrix. Yatkin *et al.* (2011) targeted aerosols collected in Europe, but they did not analyze aerosols collected in Asian region. The Asian region is one of the most diverse areas in the world, and many Asian cities have undergone rapid development in recent years; therefore, the aerosol sample matrix which is associated with each city individually would be different from other regions. The applicability of analytical methods should be independent of geography; in other words, EDXRF is required to be able to analyze any samples that have different sample matrices. Therefore, it is worth investigating the applicability of EDXRF to Asian aerosol samples as examples that have diverse sample matrices. The analysis time per one sample was 5,500 s (92 min) as reported by Yatkin *et al.* (2011). It would be considered much faster than the analytical time needed by the entire process for ICP-MS, but it would be quite convenient if we could analyze each sample in much shorter time.

This study shows a nondestructive, rapid, and simple method using EDXRF for analyzing multiple elements in aerosols collected on QFFs. Aerosol samples collected on QFFs in several large Asian cities were analyzed to validate the multi-elemental analytical method developed in this study. We achieved the multi-elemental analysis by using EDXRF coupled with fundamental parameter (FP) quantification as fast as 900 s (15 min) per sample. Systematic experiments for elucidating the applicability of QFFs to multi-elemental analysis by EDXRF have been carried out by comparing the analytical results obtained by EDXRF to those obtained by ICP-MS and ICP-AES. We selected aerosols samples collected on QFFs in different cities in Asia, so that the EDXRF method developed in this study might allow researchers to monitor the dramatic changes in the atmospheric environment of Asian cities in a much easier way.

METHODS

Details of the EDXRF Analysis

Filter samples were analyzed by EDXRF without any pretreatment using an EDXL300 spectrometer manufactured by Rigaku Corp., Japan. For emitting primary radiation, an X-ray tube ($I_{\max} = 2$ mA, $V_{\max} = 50$ kV) with a 50 W Pd anode was used. EDXL300 has three-dimensional (Cartesian geometry) polarization optics. The primary beam from the X-ray tube first irradiates a polarizing target (secondary target) placed along the first axis, and then the 90°-scattered X-rays go along the second axis to the sample. After scattering at 90° at the sample surface again, the X-rays reach the semiconductor detector, which is placed along the third axis. By scattering at 90° two times, the primary beam is eliminated by polarization, thereby reducing the spectral background considerably. The secondary targets allow the researcher to optimize the excitation source for the analytes of interest. In this study, we used three secondary

targets. The secondary targets, X-ray current, voltage, and duration time were Mo: 1 mA, 50 kV, and 400 s; Cu: 1 mA, 50 kV, and 400 s; and RX9 (graphite crystal): 0.7 mA, 25 kV, and 100 s. Prior to the analysis, the sample chamber was pumped out to reach a vacuum of 1 Pa in order to avoid the X-ray interferences caused by the air.

The quantification of each element in aerosol samples was performed using the fundamental parameter (FP) method. The general concept for the FP quantification is described elsewhere (Beckhoff *et al.*, 2006), but in brief, the FP quantification is based on the theoretical relation between the measured X-ray intensities and the concentrations of the elements in the sample. The FP quantification considers many parameters in the calculations such as the interaction and absorption between photons and atoms, the thickness of atomic layer, the elemental compositions. EDXL300 has a powerful FP algorithm called as Rigaku Profile Fitting-Spectra Quant X (RPF-SQX) that allows the users to achieve standardless analysis whereby all parameters are based upon theoretical equations, the fundamental parameter database, and precise modeling of the detector, X-ray tube, and instrumental geometry; however, the details of the actual algorithm is secret for users since RPF-SQX is a commercial product. Although users cannot alter the FP algorithm itself, there are still many choices in terms of setting calculating parameters. Therefore, it is very important to seek the optimum settings for the practical use of FP quantification for EDXRF analysis. One of the advantages of using FP standardless analysis is that we do not need to prepare standard materials of each target element. Yatkin *et al.* (2011) concluded that the standardless EDXRF analysis was found to be more efficient than linear calibration for the quantification of most of the studied elements. Hence, we decided to use the standardless analysis for our study. For the routine analysis, instrument calibration was performed daily using a Herzog glass pellet with known elemental composition. In order to check the instrument condition, SRM2783 (Air Particulate on Filter Media, provided by NIST) was analyzed daily.

EDXRF Instrumental Performance Checked by Analyzing SRM2783

We checked if standardless EDXRF analysis could measure correctly multi-elements in SRM2783, which has certified values of elemental content of aerosol deposited on polycarbonate thin-film. Five replicate analyses were made, and then analytical results were compared to the certified (or reference) values of elements in SRM2783. This procedure was repeated several times in different days

in order to check the day-to-day variation of the EDXRF performance.

Evaluation of the Effect of Elements That are Contained in Blank QFFs

Commercially available QFF products may contain impurities differing from lot to lot, and from filter to filter in the same lot. In this study, we tried to make the level of impurities contents clear. We prepared 25 blank QFFs, which were the sample set of 5 different filters from 5 different lots (Pallflex 2500QAT-UP, Lot#50613, 55355, 55624, 55688, and 56076), and then the blank QFFs were analyzed by EDXRF. We compared the X-ray intensities obtained from the blank QFFs to those from the actual aerosol samples collected in four Asian cities described below.

Field Campaign 1: Comparison between the Two EDXRF-FP Methods for Aerosol Samples Collected from Four Asian Cities

Total suspended particles (TSP) were collected in four different Asian cities (Table 1). Beijing (BJW and BJS): The sampling site was Tsinghua University, located 15 km in a northwesterly direction from the center of Beijing City, China. We collected one sample in the summer and winter because the air pollution levels in the summer and winter differ (Okuda *et al.*, 2006b; 2008). Hanoi (HAN): The sampling site was a private house, located 4km in a southwesterly direction from the center of Hanoi City, Vietnam. Kolkata (KKT): The sampling site was a private house in the center of Kolkata City, India. Tokyo (TKY): The sampling site was the University of Tokyo, located in the center of the Tokyo metropolitan area, Japan. QFF (Pallflex 2500QAT-UP, 8 × 10 inch) was used for collecting the aerosol samples. High-volume air samplers were operated for 24 h at an air flow rate of 800 L/min. We cut a 47 mm (in diameter) round part of the QFF filter, and then the samples were subjected to the following analytical procedure. A photograph for these samples is shown in Fig. 1.

Practically, the RPF-SQX requires the sample thickness to be entered as an essential parameter for FP calculation. In this study, we tested two types of FP methods: FP1 (total fixed), and FP2 (Si-measured). In FP1 (total fixed), first, the actual filter mass per unit area ($7.68 \pm 0.23 \text{ mg/cm}^2$, which was the mean value of weights of ten blank QFFs) was entered as the total amount that represents the thickness of the atomic layer, and then the Si amount was calculated by subtracting the measured amount of all elements other than Si from the entered total amount. In FP2 (Si-measured), Si amount was measured by the actual fluorescent X-ray counts

Table 1. Description of the samples subjected to EDXRF and ICP-MS analyses.

Sample Code	Description	Date	Sampling Volume [m ³]	Sampling Duration [h]
BJW	Beijing - Winter/Dry Season	2008/1/3	1005	24
BJS	Beijing - Summer/Wet season	2009/9/24	1152	24
HAN	Hanoi - Wet Season	2009/9/29	1152	24
KKT	Kolkata - Dry Season	2010/1/1	1152	24
TKY	Tokyo - Winter/Dry Season	2009/12/24	1152	24
BLK	Blank, Pallflex 2500QAT-UP			

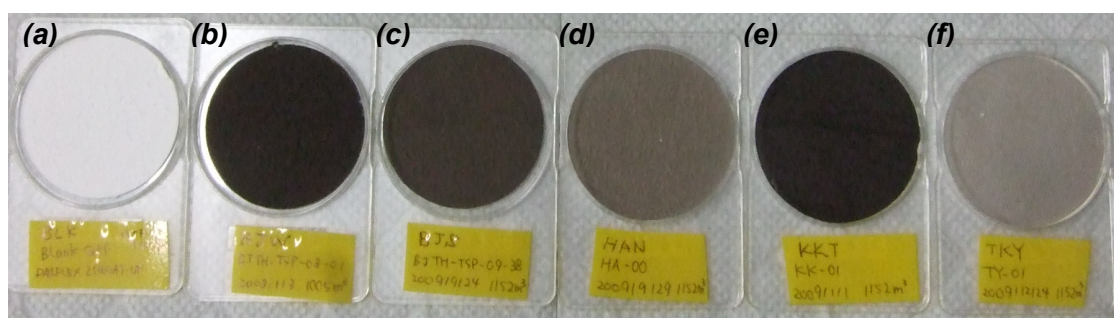


Fig. 1. Photograph for (a) blank QFF and (b) Beijing winter (BJW), (c) Beijing Summer (BJS), (d) Hanoi (HAN), (e) Kolkata (KKT), and (f) Tokyo (TKY) samples. The sample descriptions are shown in Table 1.

as well as the other elements, so that sample thickness was calculated by using measured Si amount. The analytical conditions of the EDXRF are shown in Table 2.

ICP-MS analysis was performed by following conventional methods. The samples were digested by HF, HNO₃, and H₂O₂, and then introduced to ICP-MS (Agilent 7500cx). Recovery tests were done using CRM#28 (Urban Aerosols, NIES, Japan) and DC73308 (Stream Sediment, NCS, China). The recovery of each element through the entire procedure was 90–101%. In this campaign, each set of results by EDXRF and ICP-MS was obtained from exactly the same part of the filter. We compared the multi-element concentrations in QFF-laden aerosol samples analyzed by EDXRF and ICP-MS.

Field Campaign 2: Day-to-Day Variation in an Urban City in Japan

Particulate matter less than 10 μm in diameter was collected in the urban city of Nagoya, Japan. The sampling site for this campaign was in Nagoya University, located near a residential area in Nagoya City. QFF (Advantec QR-100) was used for collecting the aerosol samples. A high-volume air sampler equipped with a 10 μm cutoff plate (Shibata HV-500F-10) was operated for 10 h at an air flow rate of 800 L/min. We collected 26 samples during the autumn of 2004. The sampled filter was cut into two pieces, and then half of the sample was subjected to EDXRF analysis (FP2 method mentioned above). Another part of the sample was subjected to acid digestion followed by ICP-MS or ICP-

AES analysis. The samples were digested by HF, HClO₄, and HNO₃, and then analyzed by ICP-MS (Agilent HP4500) or ICP-AES (Jarrell Ash Model Plasma AtomCorp Mk II). Recovery tests have been done using SRM1648 (Urban Particulate Matter, NIST, USA). The recovery of each element through the entire procedure was 95–105%. Detailed descriptions for this procedure were shown elsewhere (Fujimori *et al.*, 2007; Fukai *et al.*, 2007). In this campaign, each set of the EDXRF and ICP-MS data was obtained from different parts of the same filter. We compared the multi-element concentrations in QFF-laden aerosol samples analyzed by EDXRF and ICP-MS/AES.

RESULTS AND DISCUSSION

Detection Limit and Repeatability for EDXRF-FP Analysis

In general, the detection limit (DL) of each element analyzed by EDXRF can be expressed as

$$DL \text{ (counts)} = 3 \times N^{1/2}, \quad (1)$$

where N (counts) are the background photons (Beckhoff *et al.*, 2006). The X-ray counts N are the product of counting rate (cps) × counting time (s). This concept can be applied when the quantification is performed by using the X-ray counts directly. However, the FP quantification depends not only on the X-ray counts but also on many other factors, and therefore, it is not easy to determine the detection limit if the FP method is used. In order to determine the detection

Table 2. Analytical conditions of the measurement of elements in aerosols on QFF by EDXRF.

Instrument	Rigaku EDXL300
X-ray Source	Pd-50W
Detector	SDD (Silicon Drift Detector)
X-Ray Irradiation Area	20 mm-i.d.
Sample Chamber Pressure	Vacuum (1 Pa)
Secondary targets	Mo: 50 kV - 1 mA (auto), 400 sec Cu: 50 kV - 1 mA (auto), 400 sec RX9 ^a : 25 kV - 0.7 mA (auto), 100 sec
Quantification Method	FP (Fundamental Parameter): RPF-SQX (Rigaku Profile Fitting - Spectra Quant X)
Quantification Parameter	FP1: Total Fixed, Si - Calculated (Balanced) FP2: Total Measured, Si - Measured

a. RX9 is a graphite crystal.

limit of each element in this study, we compared the statistical standard deviations calculated from the X-ray counts to those of the actual EDXRF-FP2 responses for replicate analyses of a blank filter.

First, we analyzed multiple elements in a blank QFF by the EDXRF-FP2 method five times. The minimum counting rate among all elements (K-line) was 0.4 cps for Ti. In this study, Ti was measured using a Cu secondary target; therefore, the counting time was 400 s. In this case, the total X-ray counts for Ti from the blank QFF analysis were 160 counts. Consequently, the statistical standard deviation σ is 12.6 counts ($160^{1/2}$), and then the statistical relative standard deviation (RSD%) is 7.9% ($12.6/160 \times 100$). Second, we obtained analytical values (expressed as $\mu\text{g}/\text{cm}^2$) for multiple elements from five replicate analyses of the blank QFF. The analytical values for S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn were obtained from the blank QFF by the EDXRF-FP2 method. The RSD% for each element from five replicate analyses were generally less than 10%, but sometimes those were larger than 10%. We considered that the level of deviation for the analytical data obtained from the replicate analyses of the blank QFF by EDXRF-FP2 was almost the same or slightly higher than the statistical standard deviation calculated from the X-ray counts in this study. Third, the RSD% for each element from five replicate analyses of SRM2783 were obtained. These RSD values for SRM2783 were almost always higher than those for the blank QFF. Hence, we decided to use the standard deviations for the analytical data for each element obtained by analyzing SRM2783 using EDXRF-FP2 to determine the detection limits in this study.

The detection limits (ng/cm^2) for each element in this study are shown in Table 3, and are also expressed as the atmospheric concentrations (ng/m^3). Overall, the detection limits for each element in this study have been determined as 7.2–193 ng/cm^2 , and also 2.4–29 ng/m^3 for the campaign 1 and 1.1–32 ng/m^3 for the campaign 2. These detection limit levels are similar to previous studies that have used fluoropolymer (PTFE) and also to equivalent to cellulose

filter as the sampling media for EDXRF analysis (Cuccia et al., 2010; Öztürk et al., 2011).

The precision (repeatability) for each element in the actual samples is shown in Table 4. We used the data from five replicate analyses of each aerosol sample collected on QFF for campaign 1. According to these data, the repeatability as RSD% was less than 10%, except for V and Cr. Two possible reasons for the relatively higher RSD% for V and Cr are considered. First, the overlapping of the fluorescent X-rays, for example, Ti-K β overlaps with V-K α , and Cr-K β overlaps with Mn-K α , may cause adverse effects on the analytical results since the FP algorithm uses not only α X-rays but also β ones for the calculation. Second, uncertainty of the X-ray counts would be increased since the atmospheric concentrations for V and Cr were relatively low. However, except this, the EDXRF-FP method showed good repeatability that was less than 10%, and in many cases, less than 5%.

EDXRF Instrumental Performance by Analyzing SRM2783

The matrix effect caused by filter material could be important, for example, polycarbonate (SRM2783) would have a different matrix effect from quartz fiber (used in this study). Apparently, polycarbonate filter would have less sample matrix effect than QFF since polycarbonate filter is thinner and contains much lighter elements than QFF. Ideally, the matrix effects for both polycarbonate and QFF should be examined, but unfortunately, QFF-laden standard reference material of aerosol is currently not available. Therefore, we tested the EDXRF instrumental performance by analyzing SRM2783, which is polycarbonate-laden reference material for aerosol.

Table 5 shows the analytical results by EDXRF-FP2 and the certified (or reference) values of elements in SRM2783. The measured/certified ratio for each element was 0.9–1.1, except for V, Mn, Ni and Pb. The low concentration level of V and Ni may cause the large uncertainty of the X-ray counts. EDXRF-FP2 gave always higher values for Mn and Pb, however the reproducibility of the results was quite

Table 3. Detection limits by EDXRF-FP2 method for each element collected on QFF for each campaign.

Element	Detection Limit ^a [ng/cm^2]	Detection Limit [ng/m^3]	
		Campaign 1	Campaign 2
		Filter: 8" \times 10" Air Volume: 1152 m^3	Filter: 110 mm Φ Air Volume: 480 m^3
S	39.7	13.9	6.5
K	82.2	28.7	13.4
Ca	193	67	31.5
Ti	28.7	10.0	4.7
V	9.1	3.2	1.49
Cr	13.0	4.5	2.1
Mn	7.2	2.5	1.2
Fe	67.0	23.4	11.0
Ni	6.9	2.4	1.1
Cu	25.9	9.1	4.2
Zn	16.2	5.7	2.7
Pb	23.1	8.1	3.8

a. Detection limits were determined as [(SD of 5 replicate analysis of SRM2783) \times 3].

Table 4. Repeatability by the EDXRF-FP2 method for each element collected on QFFs.

Element	Repeatability in RSD% by 5 replicate EDXRF-FP2 analysis ^a	
	Mean	SD
S	2.8%	3.0%
K	2.1%	1.5%
Ca	1.7%	2.2%
Ti	3.8%	2.0%
V	28%	20%
Cr	12%	11%
Mn	3.5%	1.4%
Fe	2.0%	1.9%
Ni	4.2%	1.5%
Cu	3.7%	2.0%
Zn	2.6%	2.0%
Pb	3.8%	2.5%

a. Five aerosol samples collected on QFF at four Asian cities (Beijing, Hanoi, Kolkata, and Tokyo). SD means standard deviation among five samples.

Table 5. Analytical results for each element on SRM2783 by EDXRF-FP2.

Element	Certified/Reference Values on SRM2783 ^a [ng/cm ²]		Analytical Results by EDXRF-FP2 [ng/cm ²]		Measured/Certified Ratio	
	Mean	SD ^b	Mean	SD ^c	Mean	SD ^c
S	105	26	112	13	1.1	0.1
K	530	52.2	487	27.4	0.9	0.1
Ca	1325	171	1287	64.2	1.0	0.0
Ti	150	24.1	140	9.6	0.9	0.1
V	4.9	0.60	8.2	3.0	1.7	0.6
Cr	13.6	2.5	12.8	4.3	0.9	0.3
Mn	32.1	1.2	65.4	2.4	2.0	0.1
Fe	2661	161	2384	22.3	0.9	0.0
Ni	6.8	1.2	8.8	2.3	1.3	0.3
Cu	40.6	4.2	41.8	8.6	1.0	0.2
Zn	180	13.1	187.7	5.4	1.0	0.0
Pb	31.8	5.42	79.8	7.7	2.5	0.2

a. Air Particulate on Polycarbonate Filter.

b. This SD means uncertainty described in the certification document for SRM2783.

c. This SD means standard deviation for five replicate measurements.

good. Improvement of FP algorithm would reduce these backgrounds. Another possible reason for the higher background of Mn and Pb is due to the primary beam from the X-ray tube that is not completely eliminated by three-dimensional polarization optics. In this case, the problem that has to be solved would be physical geometry of optics instead of the FP algorithm. Consequently, EDXRF-FP2 showed good results for analyzing S, K, Ca, Ti, Cr, Fe, Cu and Zn, but the improvement of the hardware and/or software of the instrument would be open for further study.

Evaluation of the Effect of Elements in Blank QFF

Representative X-ray spectra are shown in Fig. 2. Note that the Si peak for blank QFF was much higher than that for the actual sample. This was because the filter surface of the actual sample was covered by aerosol layer so that the fluorescent X-ray from Si of filter would decrease. However, this phenomenon would not affect the analytical results for other elements since the peak resolution among Si and

other elements was good enough as shown in Fig. 2. Table 6 shows the X-ray intensities from different lots of blank QFFs and five actual TSP samples collected on QFFs in Asian cities. Some elements have large lot-to-lot variations; however, the ratios of the X-ray intensities of actual samples to those of blank QFFs (in other words, signal-to-background ratios) were 7.8–266, except for Ni. Therefore, the elemental concentrations in the blank filters in any lots examined in this study could be considered to be lower than the actual samples. However, the blank level of Ni could not be ignored if QFFs are the collection media.

Campaign 1: Comparison between the Two EDXRF-FP Methods for Aerosol Samples Collected from Four Asian Cities

The results of the comparative measurements for the different FP methods are shown in Fig. 3. These have been displayed as the mass concentrations of each element by ICP-MS on the x-axis and those by EDXRF for each FP

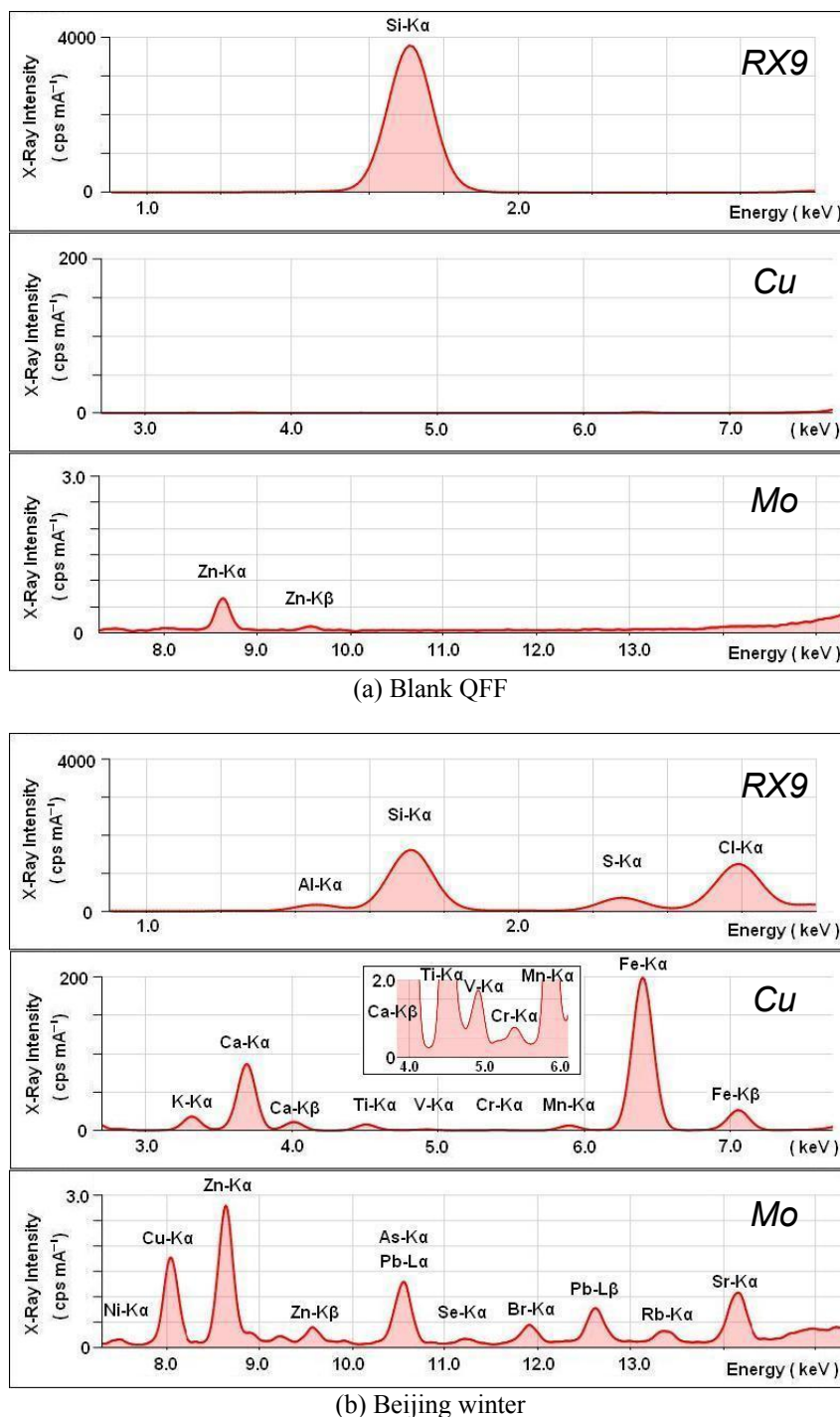


Fig. 2. Representative X-ray spectra for (a) blank QFF and (b) Beijing winter (BJW) sample. The sample descriptions and analytical conditions are shown in Tables 1 and 2.

method on the y-axis. Plot symbols correspond to the sampling sites (and each season for the Beijing samples). Note that this figure contains all the data even if the analytical values are sometimes less than the detection limits described above. This is because we simply wanted to show all the data we obtained so that the reader could have an idea how these two FP methods worked (or did not work) when the analytical values were low. At first glance both EDXRF-FP methods agreed well with the ICP-MS

results. By taking a closer look, however, the results obtained by the FP2 method seem to be much better than those by FP1. The EDXRF-FP1 method nearly always gave much higher values than ICP-MS. With RPF-SQX algorithm, FP1 seems to overestimate the absorption effect on the atomic layer than it should actually consider in FP calculation. Besides, the log-log linear correlation coefficient for FP2 ($r^2 = 0.94$) was higher than that for FP1 ($r^2 = 0.79$). The FP2 method can calculate the amount of each element on

Table 6. X-ray intensities from blank and sampled QFFs.

Secondary Fluorescent Targets	X-Ray Intensities [cps/mA]																					
	Blank QFF Lot#50613			Blank QFF Lot#55355			Blank QFF Lot#55624			Blank QFF Lot#55688			Blank QFF Lot#56076			Inter-lot variation of blank QFFs			Actual TSP samples collected on QFFs ^a			Actual /Blank Ratio
	Mean	SD	RSD%	Mean	SD	RSD%	Mean	SD	RSD%	Mean	SD	RSD%	Mean	SD	RSD%	Mean	SD	RSD%	Mean	SD	RSD%	
RX9	67.6	7.1	11%	16.3	4.1	25%	15.2	1.0	7%	13.8	3.0	22%	14.6	0.5	3%	25.5	23.5	92%	6783	3509	52%	
Cu	1.6	0.1	4%	1.6	0.2	13%	1.8	0.1	4%	2.1	0.1	6%	3.0	0.1	3%	2.0	0.6	30%	190	140	74%	94
Cu	6.4	0.2	3%	3.5	2.3	65%	2.4	0.1	4%	2.4	0.2	10%	2.6	0.2	6%	3.5	1.7	50%	771	555	72%	223
Cu	0.5	0.1	13%	1.2	0.1	9%	0.4	0.1	12%	0.6	0.2	25%	1.5	0.2	13%	0.9	0.5	55%	79.7	63.8	80%	94
Cu	n.d. ^b			n.d.			n.d.			n.d.			n.d.			n.d.			1.4	1.0	69%	∞
Cu	0.6	0.1	9%	0.7	0.1	14%	0.6	0.1	14%	0.6	0.1	23%	0.6	0.1	11%	0.6	0.1	9%	6.5	5.3	81%	10
Cu	7.3	0.7	10%	7.5	0.7	9%	7.4	0.1	1%	7.6	0.4	6%	7.2	0.3	4%	7.4	0.1	2%	57.9	33.9	59%	7.8
Cu	23.0	1.1	5%	29.2	6.4	22%	24.9	1.0	4%	25.2	1.5	6%	25.8	0.5	2%	25.6	2.2	9%	1774	1368	77%	69
Mo	1.6	0.1	3%	2.8	0.1	4%	1.8	0.1	6%	1.6	0.1	5%	1.6	0.1	7%	1.9	0.5	27%	3.0	1.0	34%	1.6
Mo	2.2	0.2	9%	2.0	0.1	6%	2.0	0.1	6%	2.0	0.2	7%	2.2	0.1	4%	2.1	0.1	4%	46.6	76.5	164%	22
Mo	2.5	0.1	4%	4.7	0.5	10%	1.8	0.2	8%	2.5	0.3	10%	7.5	0.7	9%	3.8	2.3	61%	65.4	44.3	68%	17
Mo	n.d.			n.d.			n.d.			n.d.			n.d.			n.d.			33.5	38.4	115%	∞

a. Mean value of each X-ray from five Asian aerosol QFF samples.

b. Not detected.

c. This SD means standard deviation for five replicate measurements.

d. This SD means standard deviation for each mean value for each lot.

e. This SD means standard deviation among five Asian aerosol samples.

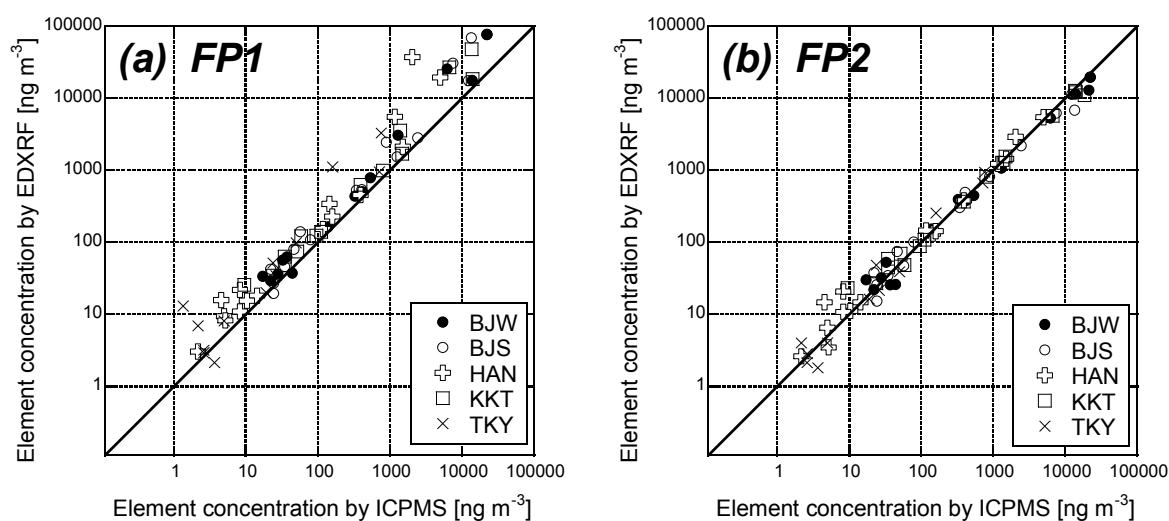


Fig. 3. The mass concentration [ng/m^3] of each element in aerosols collected on QFFs in four Asian cities by EDXRF (y-axis) and by ICP-MS (x-axis). The detailed information for the FP1 and the FP2 are described in the main text. BJW: Beijing winter, BJS: Beijing summer, HAN: Hanoi, KKT: Kolkata, and TKY: Tokyo. See also Table 7 for the detailed results.

the filter much more accurately even though the Si of QFF emits intense fluorescent X-rays more than any other element. It seems that elements having concentrations higher than $100 \text{ ng}/\text{m}^3$ show very good agreement between EDXRF and ICP-MS. We did not find an “upper-limit” in the concentration in terms of the agreement between the compared results. This means that at least we do not have to concern ourselves with particulate matter “overload” on the filter, within the range of the element concentrations presented in this study. This is especially important when we want to collect the aerosol samples in Asian region and analyze them by EDXRF because sometimes the aerosol concentrations could be high in developing areas in this region. We did not find any site-specific anomalies among the five samples from the four Asian cities. This means that this method can be easily applied to multi-elemental analysis for aerosols collected on QFF obtained in a variety of sites in Asian region. Table 7 shows the detailed analytical results obtained by the EDXRF-FP2 method and ICP-MS. This table includes additional results for three other samples in order to show reliability and robustness of the method; BJ3: collected at the same site as BJW and BJS on August 27, 2010; HA2: collected at the same site as HAN on May 14, 2010; and YKH: collected on the rooftop of Keio University, Yokohama, Japan on April 5, 2010. Both methods agreed well for all elements for these eight samples (the EDXRF/ICP-MS ratio ranged from 0.8 to 1.3). Overall, the EDXRF-FP2 method gave very good results for a wide range of concentrations in a variety of elements in aerosols in different cities/seasons.

Campaign 2: Day-to-Day Variation in an Urban City in Japan

First, we should note that the obtained analytical data for 15 elements were determined by EDXRF whereas 38 elements were determined by ICP-AES and ICP-MS since the latter two methods provided much better analytical detection limits for each element (Fujimori *et al.*, 2007; Fukai *et al.*,

2007). We compared the analytical results for the elements that were measured by both XRF and ICP. The results of the comparative measurements are shown in Table 8 and Fig. 4. In this figure, different symbols correspond to various elements. Fig 4 also shows the results of campaign 1 in the same plot style. It can be seen that the EDXRF results agree well with the ICP-MS for S, Ni, and Pb and ICP-AES for Ca, Ti, Mn, Fe, Cu, and Zn. Similar to campaign 1, the elements having concentrations higher than $100 \text{ ng}/\text{m}^3$ show very good agreement. Both methods agreed very well for all elements except for Mn, Pb, and Ni. The results for Mn and Pb showed similar features. The degree of overestimation by EDXRF was enhanced when the concentrations decreased. For the Ni case, the degree of underestimation by EDXRF increased when the concentrations decreased. These problems could be explained by the overlapping of the fluorescent X-rays. For example, Mn- $\text{K}\beta$ overlaps with Fe- $\text{K}\alpha$, Pb- $\text{L}\alpha$ overlaps with As- $\text{K}\alpha$, and Ni- $\text{K}\beta$ overlaps with Cu- $\text{K}\alpha$. Such overlapping has an adverse effect in calculating elemental compositions by the FP quantification with RPF-SQX algorithm. Besides, Ni concentrations in campaign 2 were often lower than the detection limit as defined above. Scatter plots for Mn and Pb from campaign 2 are shown in Fig. 5. The slopes of regression lines for Mn and Pb are close to unity, but have specific intercepts. Therefore, we can practically correct the analytical values for Mn and Pb that were obtained by the EDXRF-FP2 method using these linear regression lines. Note that we did not find these anomalies for Mn, Pb, and Ni in campaign 1. One possible reason for this difference between two campaigns was the difference in concentration levels for these elements. The concentrations of Mn, Pb, and Ni in Beijing, Hanoi, and Kolkata were almost one order of magnitude higher than those in Tokyo and Nagoya (see Tables 7 and 8). It can be thought that the instrumental backgrounds for Mn and Pb found in campaign 2 (intercepts found in Fig. 5) could be neglected in campaign 1 due to relatively higher element

Table 7. Analytical results for the element concentrations in aerosols collected on QFFs in Asian cities by ICP-MS and EDXRF (campaign 1).

Method	ICP-MS [ng/m ³]									EDXRF-FP2 [ng/m ³]							
	Site	BJW	BJS	BJ3	HAN	HA2	KKT	TKY	YKH	BJW		BJS		BJ3		HAN	
										Mean	SD ^b	Mean	SD ^b	Mean	SD ^b	Mean	SD ^b
K	6231	7450	1408	1163	914	6677	159	170	5305	175	6204	30.8	1714	34.6	1228	23.9	
Ca	22156	22147	8370	4954	3075	13569	754	67	19560	732	19557	66.3	9778	24.8	5414	34.0	
Ti	1292	886	255	144	142	1378	49.5	5.3	1058	41.8	820	11.5	358	6.9	131	9.0	
V	27.7	24.2	5.9	5.0	3.9	34.5	2.2	3.1	32.2	4.7	25.5	3.5	7.9	2.8	6.5	2.1	
Cr	36.9	56.4	15.7	5.2	3.3	58.2	5.0	1.1	25.6	2.28	47.1	2.5	16.1	0.8	3.5	2.2	
Mn	531	342	101	157	43	388	25.8	9.4	444	17.9	302	6.3	127	2.6	142	6.9	
Fe	13847	12282	3115	1508	1548	14000	711	141	11350	396	11344	47.8	3693	10.1	1445	12.7	
Ni	21.9	34.2	5.2	2.15	4.8	23.7	3.7	1.1	22.0	3.7	34.4	3.5	4.4	0.5	2.6	3.4	
Cu	415	2416	31	14.2	7.2	110	19.0	4.2	377	13.8	2188	15.2	44.5	1.6	14.7	4.0	
Zn	415	1248	390	388	40	797	n.d.	33	397	25.1	1235	8.8	432	6.5	381	10.8	
Pb	323	403	101	116	11	1465	23.7	12.2	395	34.8	493	7.99	119	3.2	145	6.8	

Method	EDXRF-FP2 [ng/m ³]								EDXRF/ICP-MS										
	Site	HA2		KKT		TKY		YKH		BJW	BJS	BJ3	HAN	HA2	KKT	TKY	YKH	8 samples	
		Mean	SD ^b	Mean	SD ^b	Mean	SD ^b	Mean	SD ^b									Mean	SD ^c
K	925	19.8	5642	130	255	13.8	123	3.7	0.9	0.8	1.2	1.1	1.0	0.8	1.6	0.7	1.0	0.3	
Ca	3123	54.4	12603	246	939	16.2	69	1.9	0.9	0.9	1.2	1.1	1.0	0.9	1.2	1.0	1.0	0.1	
Ti	146	5.5	1260	41.5	38.7	5.4	7.6	1.0	0.8	0.9	1.4	0.9	1.0	0.9	0.8	1.4	1.0	0.2	
V	3.9	1.1	44.6	3.5	4.02	1.7	3.1	0.3	1.2	1.1	1.3	1.3	1.0	1.3	1.9	1.0	1.3	0.3	
Cr	3.3	0.4	48.2	2.5	3.99	1.9	1.1	0.3	0.7	0.8	1.0	0.7	1.0	0.8	0.8	0.9	0.8	0.1	
Mn	43	1.5	365	11.2	21.5	3.5	7.9	0.3	0.8	0.9	1.3	0.9	1.0	0.9	0.8	0.8	0.9	0.1	
Fe	1454	28.7	12149	246	662	15.7	120	1.3	0.8	0.9	1.2	1.0	0.9	0.9	0.9	0.9	0.9	0.1	
Ni	4.8	0.2	26.9	3.9	n.d. ^a		1.7	0.6	1.0	1.0	0.9	1.2	1.0	1.1		1.6	1.1	0.2	
Cu	7.2	0.3	108	5.4	16.2	4.2	4.4	0.2	0.9	0.9	1.4	1.0	1.0	1.0	0.9	1.0	1.0	0.2	
Zn	40	1.0	806	23.3	n.d.		31	0.4	1.0	1.0	1.1	1.0	1.0	1.0		1.0	1.0	0.1	
Pb	11	0.4	1546	36.2	48.1	2.8	12.9	0.7	1.2	1.2	1.2	1.2	1.0	1.1	2.0	1.1	1.3	0.3	

a. Not detected.

b. This SD means standard deviation for five replicate measurements.

c. This SD means standard deviation among eight Asian aerosol samples.

Table 8. Analytical results for the element concentrations in aerosols collected on QFF in Nagoya by ICP-MS/AES and EDXRF (campaign 2, n = 26).

Method	ICP [ng/m ³]			XRF [ng/m ³]		EDXRF/ICP	
	Instrument	Mean	SD ^a	Mean	SD ^a	Mean	SD ^a
S	MS	1206	536	1360	595	1.2	0.2
Ca	AES	234	136	249	131	1.2	0.4
Ti	AES	27.5	14.1	28.9	14.5	1.1	0.3
Mn	AES	15.5	9.4	33.4	10.4	2.5	0.7
Fe	AES	313	149	251	117	0.8	0.2
Ni	MS	2.4	1.4	2.2	1.8	0.7	0.4
Cu	AES	12.3	5.59	12.7	6.27	1.0	0.2
Zn	AES	112	87.5	98.5	80.8	0.9	0.1
Pb	MS	16.7	10.2	30.0	10.4	2.2	0.9

a. SD means standard deviation for 26 aerosol samples.

concentrations. Higher X-ray intensity led by higher concentrations of Ni could also contribute to the improvement of repeatability of the measurement. Another difference in the two campaigns was the type of QFF; however, we cannot find a reasonable explanation of this difference. Further study will be required to elucidate how the types of QFF affect the EDXRF-FP quantification.

Finally, the temporal variation of the selected elements in aerosols obtained by EDXRF and ICP-AES are shown in Fig. 6. The results obtained by the EDXRF-FP2 method showed very good agreement with those obtained by ICP-AES; therefore, the EDXRF-FP2 method is suitable for elucidating day-to-day variations of multiple elements in aerosols.

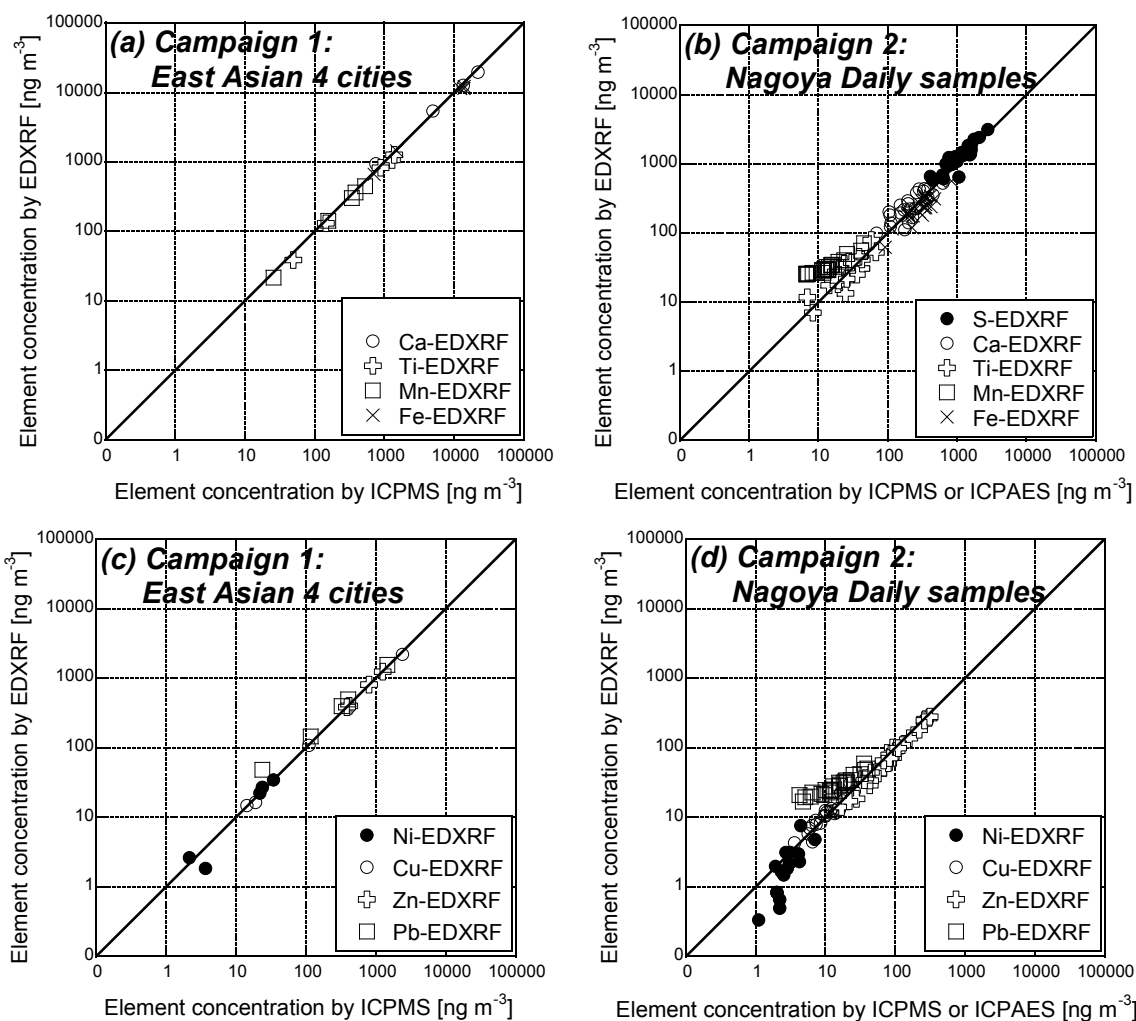


Fig. 4. The mass concentration [ng/m^3] of each element in aerosols collected on QFFs by the EDXRF-FP2 method (y-axis) and by ICP-MS or ICP-AES (x-axis). See also Tables 7 and 8 for the detailed results.

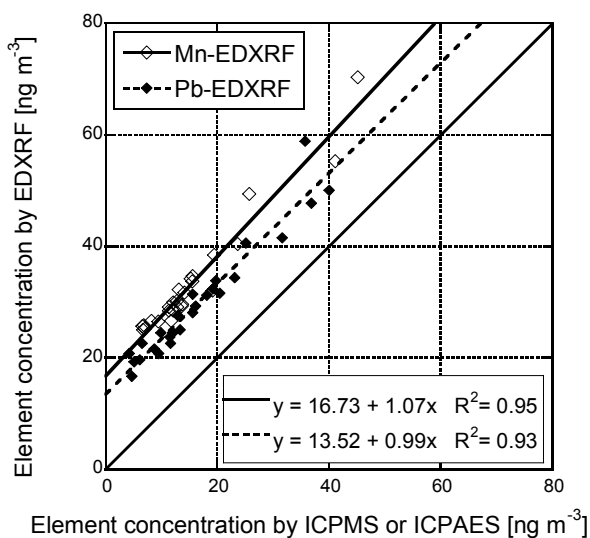


Fig. 5. The mass concentration [ng/m^3] of Mn and Pb in aerosols in Nagoya, Japan (campaign 2) collected on QFFs by the EDXRF-FP2 method (y-axis) and by ICP-MS or ICP-AES (x-axis).

CONCLUSIONS

This study shows a nondestructive, rapid, and simple method using EDXRF for analyzing inorganic multi-elements in aerosols collected on QFFs. Multi-elemental analysis can be achieved by using the EDXRF-FP quantification as fast as 900 s (15 min) per sample. The elemental concentrations in the blank QFFs in any lots examined in this study could be considered to be lower than the actual samples; however, the blank level of Ni could not be ignored. EDXRF-FP results for each element in aerosols collected on QFFs agreed well with ICP-MS and ICP-AES results. Elements having concentrations higher than $100 \text{ ng}/\text{m}^3$ show very good agreement between EDXRF and ICP-MS. We did not find an “upper-limit” in the concentration in terms of the agreement between the compared results. This means that at least we do not have to concern ourselves with particulate matter “overload” on the filter, within the range of the element concentrations presented in this study. This study offers researchers the possibility to achieve the simultaneous measurement of carbonaceous and inorganic components in aerosols collected on QFF by using rapid and nondestructive

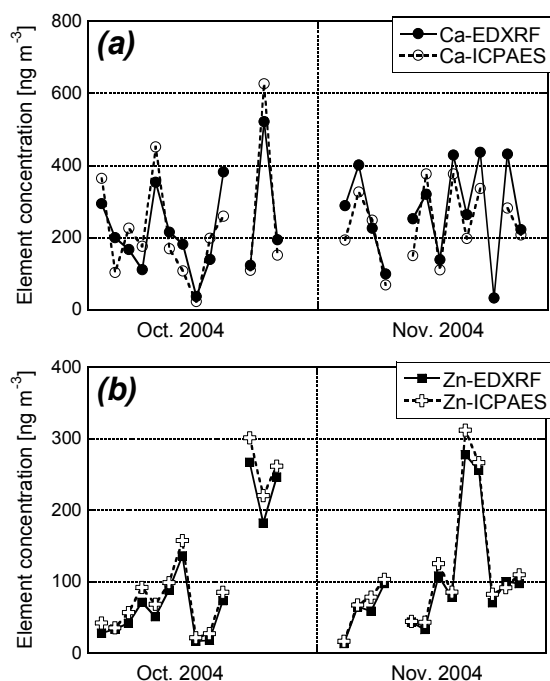


Fig. 6. The temporal variation of the concentrations [ng/m^3] of the selected elements in aerosols collected on QFFs in Nagoya, Japan (campaign 2) obtained by the EDXRF-FP2 method and ICP-AES.

EDXRF-FP method followed by further analysis of other components.

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