

Elemental analysis of PM2.5 with energy dispersive X-ray fluorescence spectrometer NEX CG

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1. Introduction

1.1. Elemental analysis of PM2.5

Concerns about the effect of atmospheric aerosol particles have been increasing in recent years and its impact on global climate, air pollution and human health have been studied extensively. Recent reports of extremely high concentration levels of PM2.5 in China have drawn worldwide attention to this issue as well.

PM2.5 are small particles suspended in the atmosphere with diameter less than $2.5\mu\text{m}$. The size is sufficiently small such that breathing can cause the particles to enter deep regions in the lungs where the air and blood are in intimate contact. This has raised concern not only about its effect on the respiratory but also on the cardiovascular system⁽¹⁾.

Elemental analysis of atmospheric aerosols including PM2.5 is an important means that can provide information about its source and environmental impact. In Japan, for the analysis of inorganic elements of PM2.5, acid decomposition of the collected sample followed by inductively coupled plasma-mass spectrometry (ICP-MS) method has been recommended. However, the sample preparation of this analysis method is complicated and analysis error can vary depending on the operator. Furthermore, the sample can not be recovered after measurement since ICP-MS requires that the sample be dissolved in an acid solution.

To overcome these issues, the Japanese ministry of environment established a “Guideline for Component Analysis of PM2.5” in 2007 which is a simple and non-destructive analysis method of inorganic elements by X-ray fluorescence (XRF) analysis. The guideline was partially revised in 2013 which describes the analysis process of PM2.5 by XRF more concretely⁽²⁾.

1.2. Elemental analysis of PM2.5 with XRF

Inorganic components in atmospheric aerosols such as PM2.5 collected on filter can be analyzed easily and non-destructively by XRF. It is also effective when many samples have to be analyzed rapidly. In addition, it has the advantage of being able to easily measure the major component of soil silicon (Si), which is difficult to analyze by the acid decomposition and ICP-MS method.

There are two types of X-ray fluorescence spectrometry methods—energy dispersive and wavelength dispersive XRF (EDXRF and WDXRF). Both types have been demonstrated to be suitable for aerosol analysis^{(3),(4)}, but

EDXRF systems are often times preferred over WDXRF due to fewer installation requirements⁽⁵⁾.

Especially when using the Rigaku EDXRF instrument NEX CG which is equipped with secondary targets for polarized irradiation, superior measurement results can be obtained due to lower background levels and LLD. The characteristics of polarized EDXRF, quantitative calculation process with thin film FP method and analysis results of real samples are introduced.

2. Experimental setup

2.1. System

The Rigaku EDXRF spectrometer NEX CG is shown in Fig.1 and its specifications are shown in Table 1. It does not require any special utilities such as liquid nitrogen or cooling water since it is equipped with a thermoelectrically cooled semiconductor detector and air cooled X-ray tube.

Secondary targets and polarized optics are illustrated in the left panel of Fig. 2. The right panel compares the spectrum of an oil sample for direct excitation to the spectrum obtained with NEX CG. It can be seen that NEX CG has superior peak to background (P/B) ratio resulting in higher sensitivity. The PM2.5 component analysis guideline mentions the use of secondary targets and polarized optics as well⁽²⁾. Since the aerosol filter sample is not irradiated directly, damage to the sample due to X-ray irradiation is reduced.

NEX CG has a wide measurement range from sodium (Na) to uranium (U) with high sensitivity. The monochromatic excitation by the Pd-L α line allows ppm level analysis of the halogen chlorine (Cl) which is difficult to analyze with ICP. The measurement diameter is 20 mm and the measurements are performed under vacuum environment. It is also possible to measure in helium (He) atmosphere to prevent evaporation of volatile components such as Cl. The instrument can be equipped with up to five secondary targets which allows for measurements with high P/B ratio over a wide element range⁽⁶⁾.

2.2. Quantitative analysis method

For quantification, two methods are described in the established XRF guideline—empirical and fundamental parameter (FP) methods, both of which can be performed with NEX CG.

In case of the empirical method which uses standard samples for calibration, it is possible to obtain results with high precision. However, this requires the need to

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Fig. 1. Rigaku EDXRF spectrometer NEX CG.

Table 1. NEX CG specification.

X-ray tube	Pd target, air cooled
Tube Power	50 W: 50 kV–2 mA (max)
Secondary targets	5 targets (max)
Detector	High performance Silicon Drift Detector (SDD)

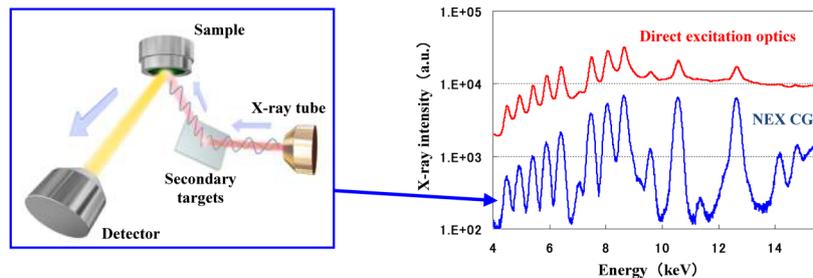


Fig. 2. Polarized optics and comparison to direct excitation optics of an oil sample (Spectra are normalized at Mo-K α Compton scattered X-ray intensity).

prepare many standard samples especially when there are many elements of interest⁽²⁾. In addition, when peaks of elements of interest are overlapped by peaks from other elements, or if the amount of collected sample varies in weight, additional corrections need to be applied and reliability of analysis result decreases. Actual aerosol samples consist of many components resulting in complex spectra with many overlapping peaks.

On the other hand, if FP method is used to perform semi-quantitative analysis, there is no need for standard samples since quantification is carried out based on the sensitivities that are pre-registered in the instrument. FP method is therefore also referred to as “standardless analysis.” When performing quantitative analysis with FP method, absorption and excitation effects due to co-existing elements are taken into account when calculating concentrations (or amount deposited on filter). Therefore, accurate analysis results can be obtained without the need to apply complex corrections even for samples which contain many elements. NEX CG is equipped with a FP calculation program that allows accurate quantitative calculation for thin film samples as described below⁽⁷⁾.

2.3. Outline for semi-quantitative analysis software “RPF-SQX”

The RPF-SQX (Rigaku Profile Fitting-Spectra Quant X) software⁽⁸⁾ for standardless analysis combines FP method with full profile fitting. The sensitivities are pre-calibrated using pure materials to cover the analysis of elements Na to U.

The computational scheme of RPF-SQX is summarized in Fig. 3. First (1), a sample is measured to obtain its spectrum. Next (2), the initial values of

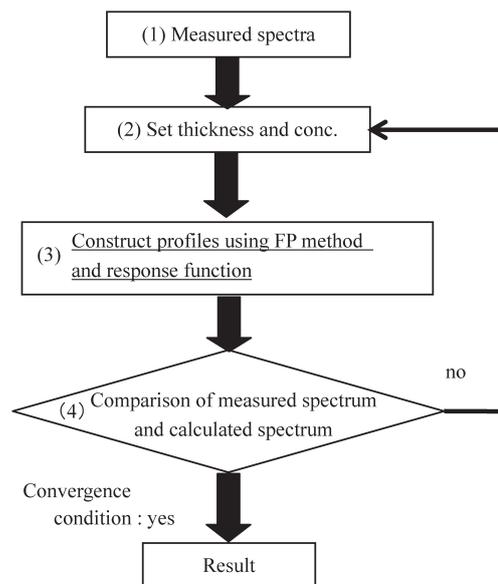


Fig. 3. Computational scheme of RPF-SQX⁽⁸⁾.

the thickness and contents of the sample is set. Then (3), a profile is constructed for each individual set element using the intensity obtained by the FP method and response function. The total spectrum is then calculated by summing up each individual profile. (4) The calculated total spectrum is then compared with the actual measured spectrum. The sample content and thickness are adjusted until both calculated and measured spectra match. The final result is obtained by fitting the entire spectrum, not just the peak intensity. The profile of each individual element is calculated using the FP method and the response function of the detector to match the measured spectrum.

Since this method utilizes the theoretically calculated

peak profile for each element in the fitting process, accurate quantitative results can be obtained even when complex overlaps exist. Analysis results can be further improved by calibrating the sensitivities using the matching library function⁽⁵⁾.

2.4. RPF-SQX analysis for thin film sample

For filter samples, it is necessary to use the thin film FP analysis method. RPF-SQX is also applicable to thin film samples by calculating theoretical XRF intensities with an additional term for sample thickness⁽⁹⁾.

The XRF intensity ratio of different line types varies with sample thickness. Figure 4 shows the Pb-L β and Pb-L α intensity ratio for varying sample thickness. Due to self-absorption of Pb the intensity ratio of L β to L α decreases as the sample becomes thinner. Therefore, in order to obtain accurate full profile fitting, it is necessary to perform profile fitting using the thin film FP method to reflect the effect of self-absorption.

Figure 5 shows the measured and fitted spectra by the RPF-SQX method for polyethylene standard samples with different thicknesses. This sample contains not only Pb but also As, which Pb-L α and As-K α lines overlap with each other.

It can be seen in Fig. 5(b) that the profiles of both analytical lines are constructed separately. Since the combined profiles to form the spectrum matches the

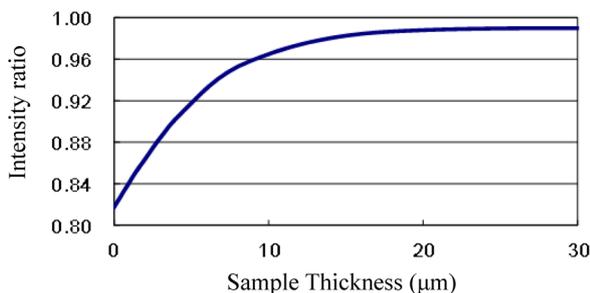


Fig. 4. Relationship between Pb-L β to Pb-L α intensity ratio and sample thickness.

measured spectrum, accurate quantification results can be obtained even if sample thickness varies. This result demonstrates that RPF-SQX is able to calculate accurate results even when complicated overlaps exist or sample thickness varies⁽⁷⁾.

3. Aerosol filter sample analysis

3.1. Analytical procedure for aerosol filter sample

The analysis procedure of an actual aerosol filter sample is shown in Fig. 6. The aerosol filter is placed in a sample cup with the collected sample side facing down and an aluminum cup is placed on top to hold the filter. The sample cup is then placed in the turret.

Information regarding the sample is set in the software. If “EZ analysis” mode is selected, measurement can be carried out with only a minimum amount of settings such as sample position or application type. Measurement time is typically several minutes to 1 hour. After measurement, the software automatically carries out spectral identification and RPF-SQX calculation to display the standardless analysis result. By using XRF method, analysis result can be obtained easily without any tedious sample preparation.

3.2. Analysis result for aerosol filter samples

The spectra of an aerosol filter standard sample (NIST SRM2783) measured with NEX CG are shown in Fig. 7. The energy ranges where the sensitivity is optimum for each secondary target are shown. Spectra with good P/B ratio are obtained over a wide energy range from light to heavy elements. The Na-K α line can be clearly seen although the Zn-L α and Zn-L β lines overlap. This shows that it is important to correct for line overlaps in order to obtain accurate analysis results.

Table 2 shows the RPF-SQX result based on the spectra shown in Fig. 7. The result demonstrates that accurate analysis values can be obtained even without the use of standard samples. Since the effect of the immeasurable elements is not taken into consideration,

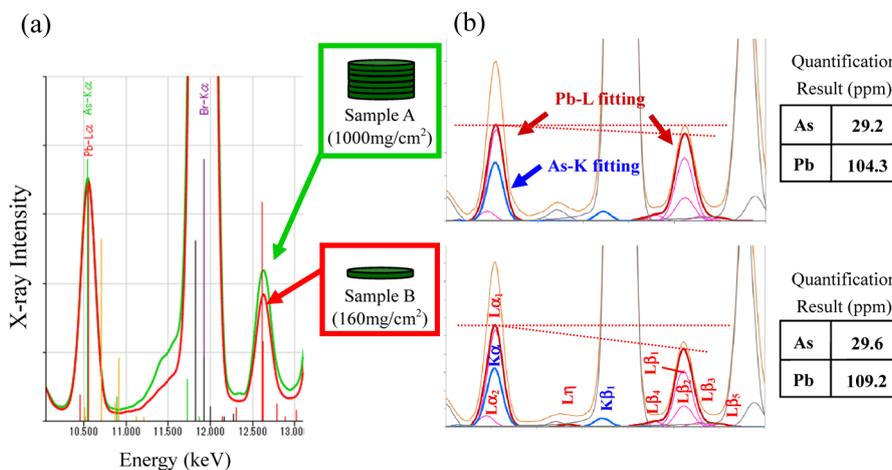


Fig. 5. Spectra of polymer samples (BCR680: As 30.6ppm Pb 107.6ppm) with different thickness. (a) Measured spectra (b) Individual fitted spectra and quantified values obtained by RPF-SQX⁽⁷⁾.

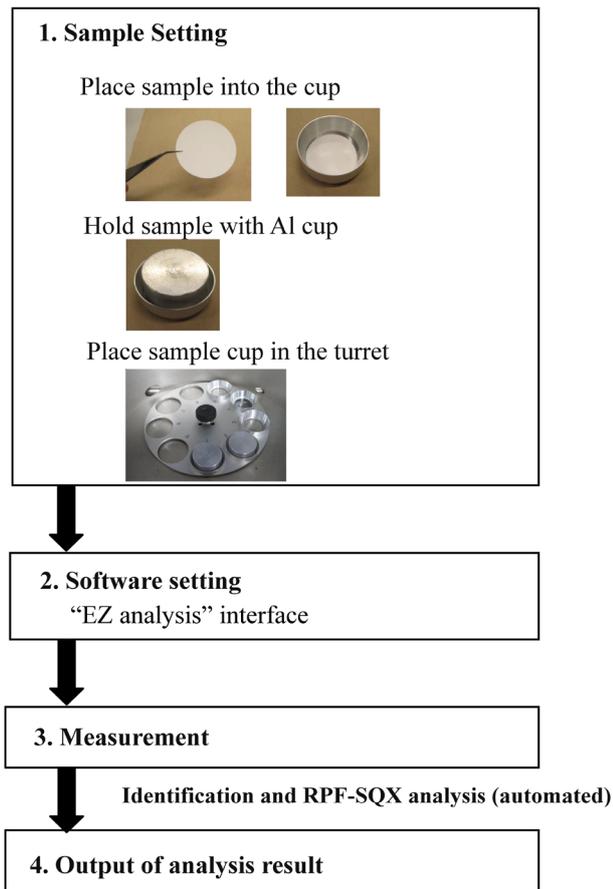


Fig. 6. Flow chart of aerosol filter sample analysis with NEX CG.

the results for light elements are low. Reliability of analysis results of inorganic elements such as Al, K, Ca, V, Fe, Zn by the FP method has previously been confirmed by finding that the results correlate with ICP-MS analysis results^{(5),(10)}.

3.3. Lower Limit of Detection

Figure 8 shows the LLDs for various elements for NEX CG. These values were determined by measuring MICROMATTER™ thin film standard samples. Measurement time is 300sec for each secondary target. The LLDs are lower than 10ng/cm², which corresponds to 5.2ng/m³ when converted to concentration in air assuming that the aerosol particles are collected on the

Table 2. Analysis results of aerosol filter standard sample (NIST SRM 2783) using RPF-SQX analysis. Unit: ng/cm²

	Na	Mg	Al	Si	P	S
Standard value	187	865	2330	(5880)	—	(105)
Analysis result	95	610	2220	6400	100	206
	Cl	K	Ca	Ti	Cr	Mn
Standard value	—	530	1325	150	13.5	32.1
Analysis result	46	540	1490	180	16.6	31
	Fe	Ni	Cu	Zn	Pb	
Standard value	2660	6.83	40.7	180	31.8	
Analysis result	2760	8.3	48.4	208	38.9	

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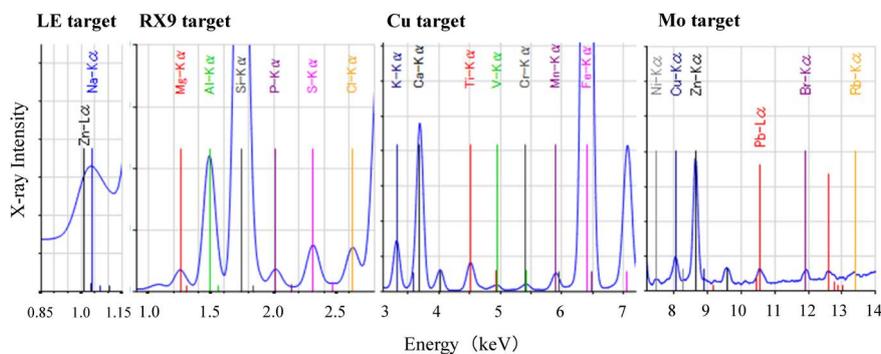


Fig. 7. Spectra of aerosol filter standard sample (NIST SRM 2783).

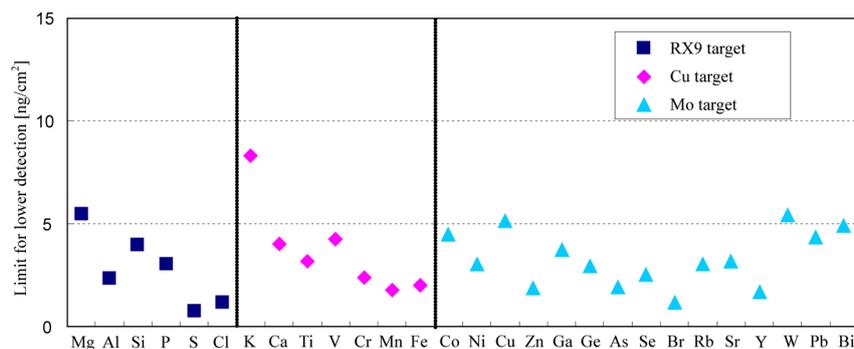


Fig. 8. LLDs for each element.

filter paper (diameter 47 mm, effective diameter 40 mm) at a flow rate of 16.7 L/min for 24 hours.

4. Summary

Using NEX CG, analysis of atmospheric aerosol such as PM2.5 collected on filters can be easily and non-destructively carried out for a wide element range. RPF-SQX allows accurate analysis even if complicated line overlaps exist. In addition, analysis can be performed without the need to prepare standard samples since FP method assures sufficiently accurate results. NEX CG is therefore an effective tool for the analysis of PM2.5 and is expected to contribute to the advancement in this field.

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