

Application News

No. X244A

X-ray Analysis

EDXRF Analysis of PM_{2.5} (Particle Matter)

In Japan, there is a standard that limits the size of suspended particulate matter (SPM) to 10 μm or less, and in September, 2009, the PM_{2.5} air quality standard (particles 2.5 μm or smaller) was established as an environmental standard to be monitored constantly in order to investigate the impact on health and farmland. Following is an example of analysis using the energy dispersive X-ray fluorescence spectrometer, one of the instruments designated for conducting such measurements.

Standard Samples

NIST SRM2783 Air Particulate on Filter Media

(1) #2048 (PM_{2.5} deposited sample)

(2) Blank (blank filter)

(Overview) An actual PM_{2.5} sample is one in which 50 % or more of the particles are 2.5 μm or smaller, rather than all of them being 2.5 μm or smaller. This particulate matter is deposited to a polycarbonate membrane filter.

Deposit area: 9.96 cm²

Mass loading: 485 μg (48.69 μg/cm²)

Sample Preparation and Placement

As there is no preparation required, the sample was measured as is. The method of placement is shown in Fig. 1.

(1) Measurement of Light Elements with High Sensitivity

To prevent sample contamination, a piece of 4 μm Prolene* film is spread over the sample stage so that the sample placement area (13 mm dia.) remains exposed, and the sample surface is placed face down on top of the film. Another piece of 4 μm Prolene* film is then spread over the same area, also excluding the measurement area, and a fixing jig is used to secure these and prevent any movement during evacuation. As light elements such as ¹¹Na, ¹²Mg and ¹³Al do not pass through the film, they are measured with high sensitivity. However, there is a possibility that the deposit can fall through the opening.

(2) Measurement where Deposit is Prevented from Falling

The 4 μm Prolene* film is spread over the entire sample stage, including the sample placement area, and the rest of the preparation is as described in (1). The deposit is prevented from falling due to the film, however, due to this shielding film, the sensitivity of light elements such as ¹¹Na and ¹²Mg decreases by about one half.

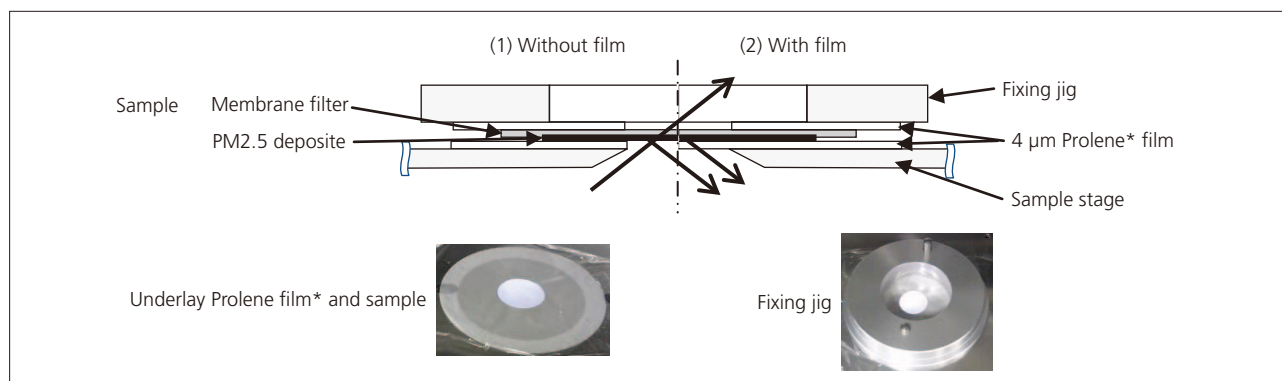


Fig. 1 Sample Preparation and Placement

Qualitative and Quantitative Analysis

A comparison of the qualitative analysis results for ¹¹Na-⁹²U using the pretreatment method described in (1) and results obtained using a blank filter is shown in Fig. 2. An optimum primary X-ray filter is mounted for detection of each of the trace elements. Next, a comparison of the quantitative analysis result values obtained using the FP method and standard values is shown in Table 1.

Theoretical Lower Limits of Detection (L.L.D.)

The theoretical lower limits of detection calculated using the following formula from the intensity (NET, BG) of the qualitative analysis results and the standard values are shown in Table 2.

$$L.L.D._{[ng/cm^2]} = \frac{3 \times C_{[ng/cm^2]}}{NET_{[cps/\mu A]}} \sqrt{\frac{BG_{[cps/\mu A]}}{A_{[\mu A]} \cdot T_{[sec]}}}$$

(C: standard value, A: X-ray tube current, T: Integration time)

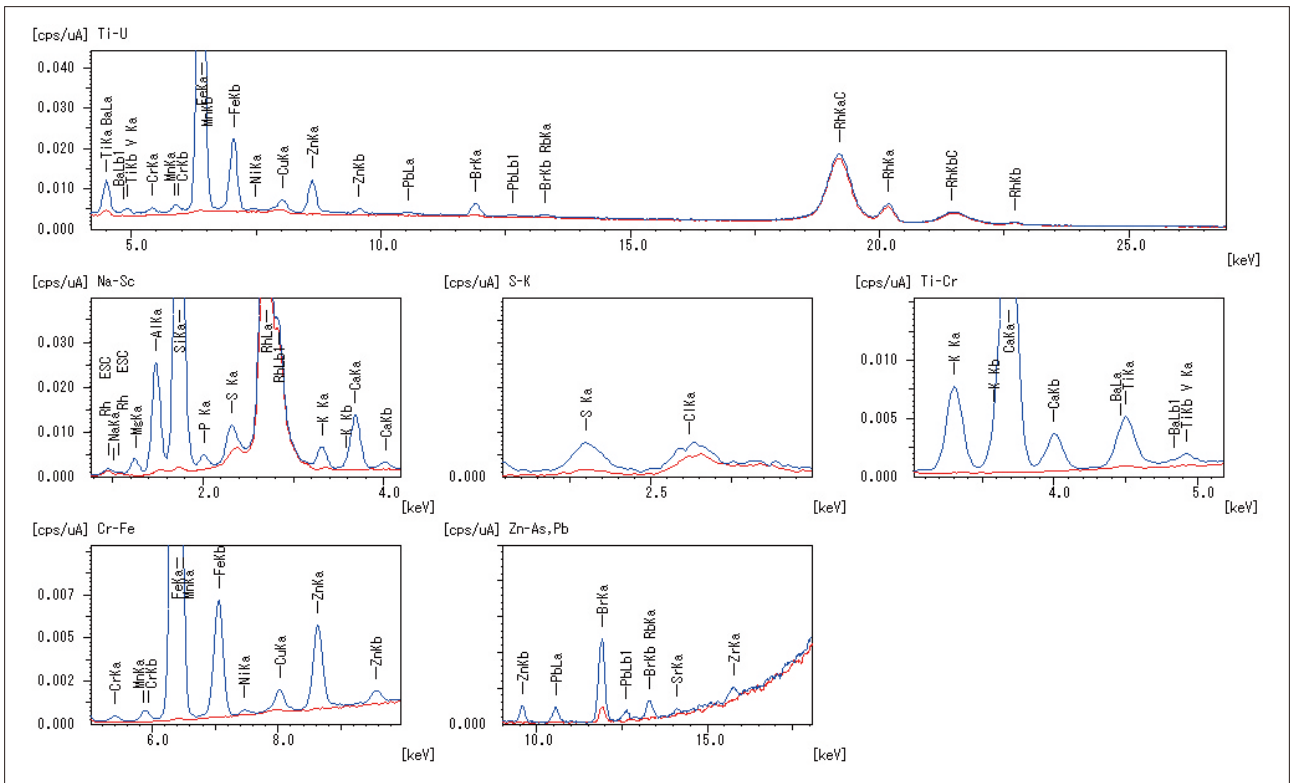


Fig. 2 Qualitative Analysis Results for NIST2783 Air Particulate on Filter Media Blue: #2408; Red: Blank

Table 1 Quantitative Analysis Results for NIST2783 by FP Method

Quantitative Value	Standard Value**	Ratio (Quant/Std)	[ng/cm ²]
11 Na	94.2	186.7	0.50
12 Mg	542	865.5	0.63
13 Al	1826	2330	0.78
14 Si	5028	<i>5884</i>	0.85
16 S	215	<i>105.4</i>	2.04
19 K	583	530.1	1.10
20 Ca	1177	1325	0.89
21 Sc	-	<i>0.36</i>	
22 Ti	138	149.6	0.92
23 V	3.2	4.9	0.66
24 Cr	17.7	13.6	1.31
25 Mn	30.6	32.1	0.95
26 Fe	2576	2660	0.97
27 Co	-	0.77	
28 Ni	6.5	6.8	0.95
29 Cu	44.7	40.6	1.10
30 Zn	174	179.7	0.97
33 As	-	1.2	
37 Rb	2.4	<i>2.4</i>	1.00
51 Sb	-	7.2	
56 Ba	30.2	33.6	0.90
58 Ce	-	<i>2.3</i>	
62 Sm	-	<i>0.2</i>	
74 W	-	<i>0.5</i>	
82 Pb	26.4	31.8	0.83
90 Th	-	<i>0.3</i>	
92 U	-	<i>0.1</i>	

**Calculated Value[ng/cm²] of Mass Loadings[ng] divided by Area[cm²]

Table 2 Theoretical Lower Limits of Detection

	[ng/cm ² /600 sec]
11 Na	60
12 Mg	25
13 Al	9.4
14 Si	9.4
16 S	5.7
19 K	4.8
20 Ca	3.8
22 Ti	2.9
23 V	3.7
24 Cr	1.9
25 Mn	2.5
26 Fe	2.7
28 Ni	1.9
29 Cu	1.7
30 Zn	3.1
37 Rb	1.2
56 Ba	6.0
82 Pb	8.2

Note:
"-": Not detected
Red italics: Reference values

■ Considerations Regarding Quantitative Analysis

The results indicate that the quantitation values are roughly one half to two times the standard values, indicating that this is an effective way to easily obtain an approximate value without conducting pretreatment. The elements are considered separately below.

- (1) Regarding K, Ca and the heavy elements above Ti, extremely good correlation was obtained at 10–30 %, except with regard to V, present at very trace levels.
- (2) S is twice as great with a quantitation value of 82.5 (ng/cm²), even being detected from the blank filter (data not shown).
- (3) The light elements Na, Mg, Al, and Si show ratios in sequence from lower to higher values, at 50 %, 63 %, 78 % and 85 %. One reason for this might be because this sample consists of a mixture of various substances, and the sample homogeneity in the region of X-ray fluorescence analysis may have been insufficient, resulting in the lack of a constant intensity with metals and compounds, etc. Then, in this non-homogeneous state, it is reasonable to assume that the effect was large because the lighter the element, the weaker becomes the X-ray fluorescence intensity.

For reference, micrographic images of this sample are shown in Fig. 3. A variety of particles as small as a few micrometers can be observed, colored black, white, brown, etc.

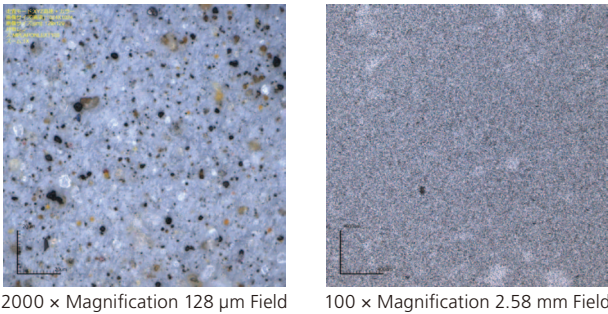


Fig. 3 Optical Microscopic Images of NIST2783 #2048

■ Detection of Sodium

For substances such as organic materials and soil, consisting mainly of light elements such as carbon, silica, and alumina, a large amount of scattered rays of the tube target Rh material are generated, and their escape peaks¹⁾ are detected. Since these Rh escape peaks are located right in the vicinity of Na, detection of Na becomes difficult. Those energy values are shown below.

- RhL α ESC 0.96 (keV)
- NaK α 1.04 (keV)
- RhL β1 ESC 1.09 (keV)

Since it is likely that this sample is composed mainly of carbon, silicon and their compounds, Na is not detected as a clear peak in the spectrum. However, as shown in Fig. 4, comparison with the blank filter and its difference spectrum (blank correction feature) clearly reveals the difference peak as Na.

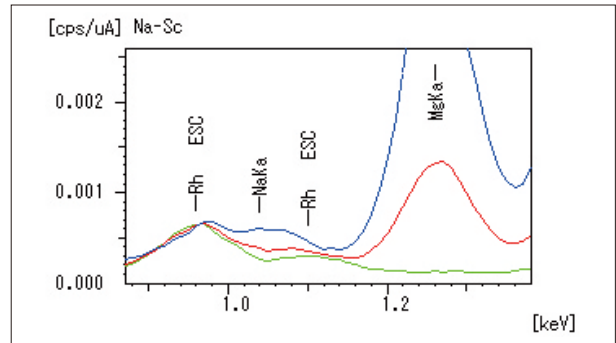


Fig. 4 Spectra of NaKα and RhL-Escape
Blue: Subtraction Blank from #2048; Red: #2048; Green: Blank (Normalized at 0.96 (keV))

■ Quantitative Analysis Conditions with the FP Method

Because collected dust, paper and film are thin, they are considered as thin film with respect to the FP method, and the detected constituents are quantitated as deposit quantity (unit: mg/cm², etc.). Since the principle constituents were considered to be a mixture of substances including carbon, organic material and oxides, they were all assumed to be cellulose (C₆H₁₀O₅), and were treated as balance (balance setting). When thin film is treated as balance, since the total adhering quantity must be known, a standard value was used. Because this is an unknown value in the case of an unknown sample, the adhering quantity is calculated from the weight and adhesion area, and is considered as known. In addition, since the substrate membrane filter has little effect on the quantitative calculation, it was omitted. An example of the above settings and the results are shown in Fig. 5.

Layer Info	Analyte	Result	[3-sigma]	Proc.-Calc.	Line	Intensity
1 Layer1						
1 Layer	Layer1	48.690 ug/cm2	[-----]	Fix	-----	-----
1 Elem.	Si	5027.556 ng/cm2	[17.020]	Quant.-FP	SiKa	1.2718
1 Elem.	Fe	2576.279 ng/cm2	[13.375]	Quant.-FP	FeKa	0.4915
	⋮	⋮				
1 Elem.	C6H10O5	35.935 ug/cm2	[-----]	Balance	-----	-----

Fig. 5 Example of Quantitative Analysis Conditions Using the FP Method

■ Absorption by Film Beneath Sample

Fig. 6 shows a clear comparison of typical samples, such as reagent, using preparation method 1) and 2). A big difference is seen with regard to Na and Mg, but the results are the same with elements higher than K.

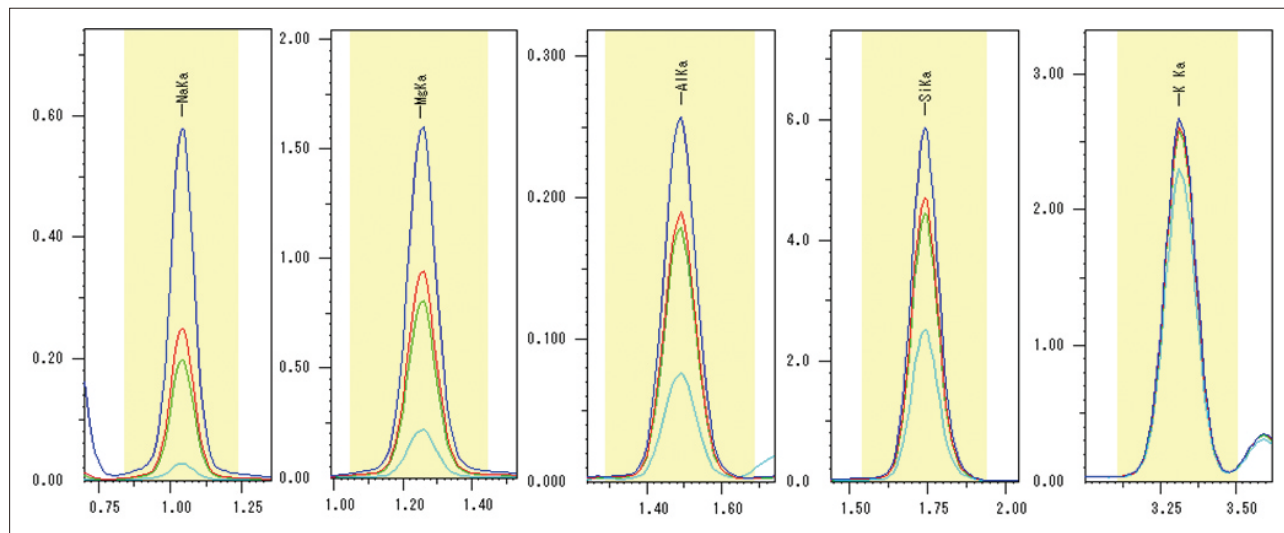


Fig. 6 Effect of Absorption by Film Intensity: a.without film > b. Prolene* 4 μm > c. Polypropylene 5 μm > d. Mylar*** 6 μm

■ Analytical Conditions

Instrument	: EDX-720
X-Ray Tube	: Rh target
Filter	: Without (Na - P) #1 (S - V, Cs - Pr) #2 (Cr - Zn, Nd - Os) #3 (Ge - Mo, Ir - U, #5 (Rh - I)
Tube Voltage	: 15 [kV] (Na - Cl) 50 [kV] (K - U)
Tube Current	: 1000 [μA] (Auto)
Atmosphere	: Vacuum
Measurement Diameter	: 10 [mm]
Measurement Time	: 600 [sec] × 5 ch
Dead Time	: Max 40 [%]

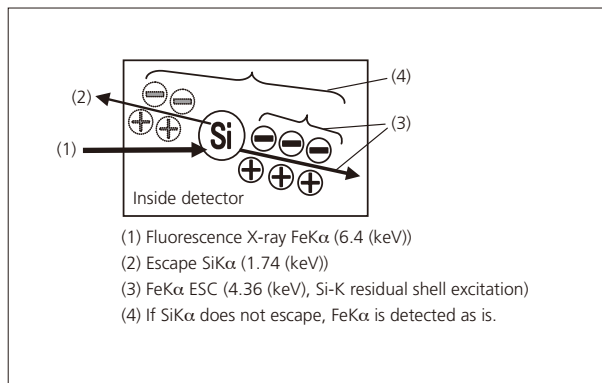


Fig. 7 Principal of Detection of Escape Peak

1) Escape Peak

The principle on which escape peaks are generated is shown in Fig. 7. The EDX detector is a semiconductor detector that is mainly composed of silicon, and it calculates energy based on the amount of charge proportional to the X-ray ionization energy. At this time, some X-rays will raise the SiKα inside the detector to excite the K-shell of silicon atoms. If this SiKα is consumed once again inside the detector due to ionization, that is measured as X-ray energy, but if it escapes the detector, it is measured as a small peak at an energy equal to that of the original energy minus the energy of the SiKα. This is referred to as a parent X-ray escape peak. Although escape peaks are small proportionally, they are detected as a peak in the case of strong intensity fluorescence X-rays of the principle constituent or Rh scattering.

* Prolene is a registered trademark of CHEMPLEX INDUSTRIES, INC.
*** Mylar is a registered trademark of DuPont Teijin Films U.S. Limited Partnership.