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Application News

No.X249

X-ray Analysis

Quantitative Analysis of Fluorine ($_9$F) by EDXRF

Fluorine compounds possess a wide range of properties, including flame retardance, water repellency, anti-fouling property, and heat resistance, and are therefore used in a wide range of fields from articles for everyday use to semiconductors. However, since the 1980s, the problems of global warming and ozone depletion in addition to the potential for bioaccumulation have led to strengthened legislation and self-regulation.
In response to these environmental problems and associated safety concerns, many of today's companies are beginning to use CFC substitutes and develop and promote products for reducing the adverse effects of anti-perfluorooctanoic acid (PFOA).
Here we introduce two examples of analysis of these products and test specimens using the EDX-800HS.
(1) Quantitation of fluorine-containing water repellent in fabric
(2) Lower limit of detection of F in powder, representative of resin, food, and drug products, and quantitative precision

(1) Quantitation of Fluorine-Containing Water Repellent in Fabric

Sample

The sample, a piece of fabric treated with fluorine-containing water repellent (hereinafter referred to as water repellent), is shown in Fig. 1. The treatment quantity is 100 g/m^2, and post-treatment adhesion quantity is 5.3 g/m^2. (film thickness is about 1 – 1.3 µm: observation by laser microscopy)
The water repellent concentrations in the standard samples are shown in Table 1. In addition quantitative analysis was conducted for unknown sample A.

Fig. 1 Fabric Treated with F-Containing Water Repellent

Table 1 Content of Water Repellent

Standard Sample	Concentration (%)
1	0
2	3
3	7
4	14

Qualitative Profile of F

The overlaid qualitative profiles of the standard samples and unknown sample A are shown in Fig. 2. The peak detected in the vicinity of 0.5 keV results from oxygen (OKα) contained in the water repellant or in the fabric.

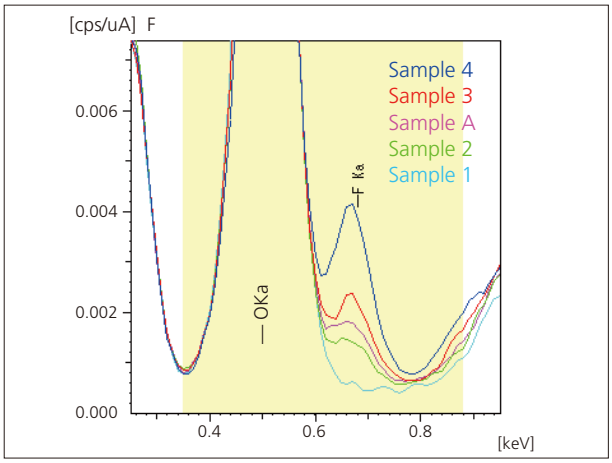

Fig. 2 Profile of F Kα

Quantitative Analysis by Calibration Curve

Fig. 3 shows the calibration curve for F generated using four standard samples. The accuracy using a 400 sec integration time is 0.052 %.
The quantitative analysis results for the unknown using this calibration curve method are shown in Fig. 4. With a 4.68 % concentration of water repellent, accurate measurement was possible, resulting in a 0.15 % standard deviation (3.2 % coefficient of variation).

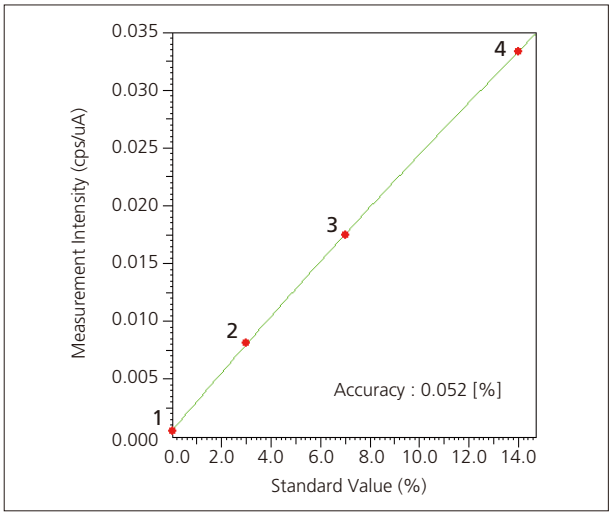

Fig. 3 Calibration Curve for F-Containing Water Repellent

Analyte	Result		(Std. Dev.)	Proc.-Calc.	Line	
F	4.682	%	(0.148)	Quant.-EC	F Ka	0.0121

Fig. 4 Quantitative Results for Sample A

Quantitative Analysis of Fluorine Resin Film

The lower limit of detection and upper limit of quantitation for the thickness of fluorine resin film (CF_2) are shown in Table 2 (using BG-FP theoretical intensity calculation). Also, Fig. 5 shows the relationship between the X-ray intensity and film thickness.

Table 2 Lower Limit of Detection and Upper Limit of Quantitation of Fluorine Resin Film Thickness

Lower Detection Limit	2.0 [µm]
Upper Quantitation Limit	2.7 [µm]

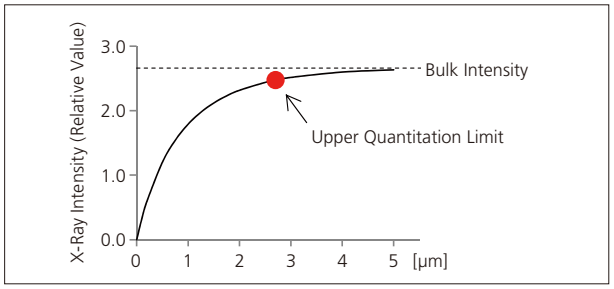

Fig. 5 Correlation Between X-Ray Intensity and Film Thickness [µm]

(2) Lower Limit of Detection and Precision for Fluorine in Powder

Standard Samples

After adding lithium fluoride (LiF) powder to cellulose powder and mixing thoroughly, the mixture was pressure-molded to form briquettes. The three levels of F content are shown in Table 3.

Fig. 6 Briquette of Cellulose Powder

Table 3 Standard Samples

No.	F Content [ppm]
1	0
2	2,500
3	5,000

Qualitative Profile of F

The profiles of the three standard samples are shown overlaid in Fig. 7.

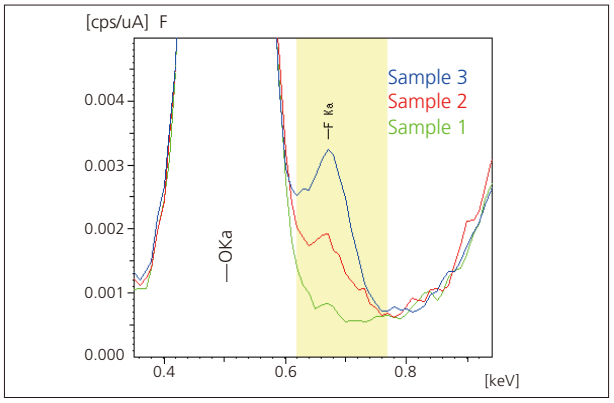

Fig. 7 Profile of F Kα

Calibration Curve

Fig. 8 shows the three-point calibration curve generated using the standard samples. The accuracy using a 300 sec integration time is 84 ppm, with a theoretical detection limit of 500 ppm, demonstrating quantitation at a concentration of 1 % or less.

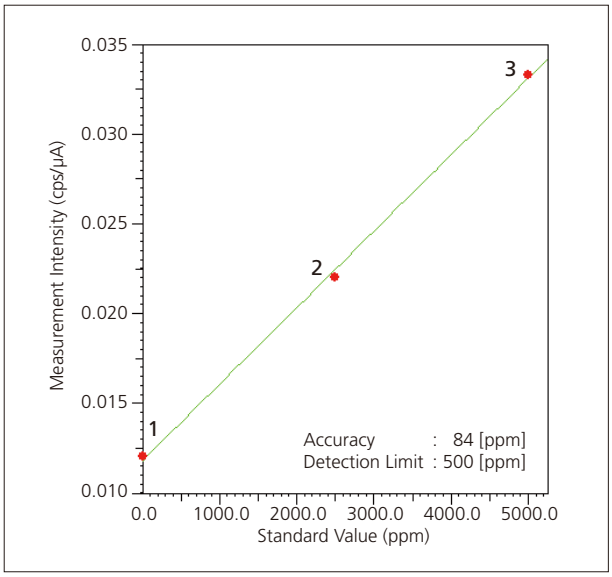

Fig. 8 Calibration Curve for F in Cellulose Powder

Repeatability

Table 4 shows the results of repeatability testing obtained from ten repeat measurements of Sample 3 at 5000 ppm.

Table 4 Repeatability

Average	5,066 [ppm]
Standard Deviation	182.6 [ppm]
Coefficient of Variation	3.6 [%]

Conclusion

Light elements such as fluorine are typically considered to be difficult to analyze by EDX. In quantitative analysis, however, fluorine content can be measured even at concentrations less than 1 % (although this is sometimes difficult when the matrix includes heavy elements). Also, in the quantitative analysis of a thin film consisting of a fluorine compound, its content can be measured with sufficient sensitivity because in such a compound, fluorine is often the principal component.

Analytical Conditions

Instrument	: EDX-800HS
Elements	: F (Kα)
Analytical Group	: Working Curve
X-ray Tube	: Rh target
Tube Voltage-Current	: 15 [kV]-Auto [µA]
Primary Filter	: Without
Collimator	: 10 [mmϕ]
Atmosphere	: Vacuum
Detector	: Si (Li)
Integration Time	: (1)400/ (2)300 [sec]
Dead Time	: Max 25 [%]

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