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Application News

Shimadzu Energy Dispersive X-Ray Fluorescence Spectrometer EDX-8000/8100

Quantitative Analysis of Fluorine by EDXRF: Powder and Fluorine-Containing Film

H. Moriya

User Benefits

- Although complicated sample preparation such as dissolution or cutting is necessary when using ion chromatograph or SEM-EDS, EDX allows direct analysis.
- Quantitative analysis of fluorine in samples containing less than 1 % is possible regardless of the sample form including solids, powders, and films.
- Operation of the instrument is simple, and analyses can be carried out immediately, even by inexperienced personnel.

■ Introduction

Fluoride compounds have various properties such as a flame retardancy, water repellence, antifouling property, and heat resistance. They are used in a wide range of fields from daily necessities to semiconductors. The ion chromatograph and SEM-EDS are mainly used for the analyses of fluoride compounds, but complicated sample preparation is necessary for them. On the other hand, the feature of the energy dispersive X-ray fluorescence spectrometer (EDXRF) is that it can perform analysis without chemical pretreatment. Fluorine, which is generally difficult to analyze, can be quantified with EDX-8000/8100, which has high sensitivity for light elements.

This article introduces the following two analysis examples.

1. Quantitative analysis of fluorine in powder samples (limit of detection, repeatability)
2. Analysis of the coating weight of a fluororesin coating agent (quantitation of coating weight by fundamental parameter (FP) method, limit of detection, repeatability)

1. Quantitative Analysis of Fluorine in Powder Samples

■ Standard Samples

Standard samples with 3 fluorine (F) concentration levels were prepared by adding lithium fluoride (LiF) powder to cellulose powder, thoroughly mixing the material, and forming briquettes (Fig. 1) by compression molding. Table 1 shows the F contents of the standard samples.

Fig. 1 Appearance of Standard Sample Briquette

Table 1 F Contents of Standard Samples

[ppm]

Standard sample	F content
①	0
②	2500
③	5000

■ Qualitative Profile of F

Fig. 2 shows the overlay of the profiles of the 3 standard samples.

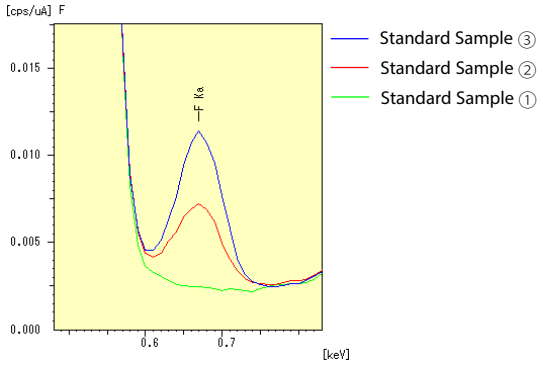

Fig. 2 Overlay of FKα Profiles

■ Calibration Curve

Fig. 3 shows the calibration curve of F prepared using the 3 standard samples (n = 3). Accuracy is 55 [ppm] at an integral time of 300 [s], the theoretical limit of detection is 203 [ppm]*, and quantitation is possible at concentrations of 1 % or less.

* Without film and under vacuum

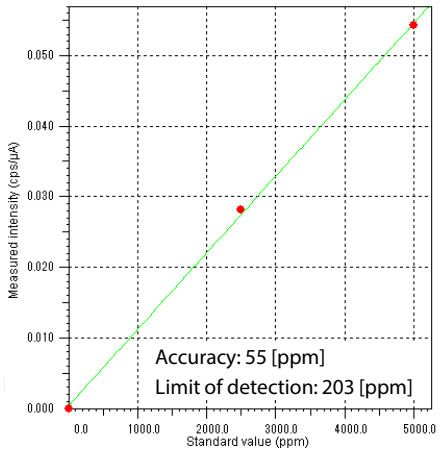

Fig. 3 Calibration Curve of F in Cellulose Powder

■ Repeatability

Table 2 shows the results of a simple repeatability test (n = 10) of the 5000 ppm standard sample ③.

Table 2 Results of Repeatability Test

Average value	5019 [ppm]
Standard deviation	125.0 [ppm]
Coefficient of variation	2.5 [%]

2. Analysis of Coating Film Weight of Fluororesin Coating Agent

■ Samples

Samples were prepared by spraying a spray-type fluororesin (PTFE; CF_2) coating agent on glass plates, and a quantitative analysis of the coating film weight of the coating agent was conducted. Fig. 4 shows the appearance of 3 samples with different coating weights.

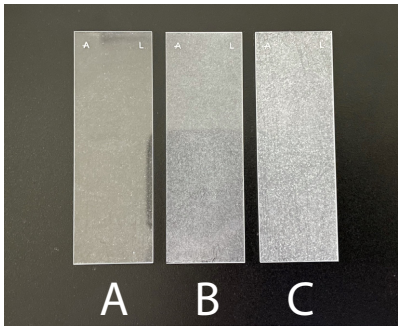

Fig. 4 Appearance of Samples
(From Left, Coating Film Weight in Order of A, B, C)

■ Qualitative Profiles of F

Fig. 5 shows the overlay of the profiles of the 3 samples coated with the fluororesin.

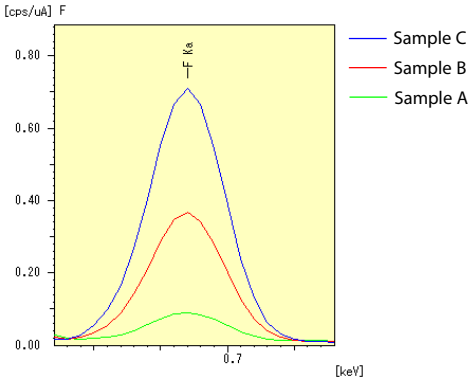

Fig. 5 Overlay of FKα Profiles

■ Quantitative Analysis of Coating Film Weight by FP Method

Table 3 summarizes the results of the quantitative analysis of the coating film weights of the 3 samples. These quantitation results are based on the assumption that the composition of the glass substrate is SiO_2 and all compositions of the fluororesin coating agent are PTFE (CF_2).

Table 3 Results of Quantitative Analysis of Coating Weight of Fluororesin (PTFE)

[μg/cm²]

Sample	PTFE coating film weight
A	10.4
B	52.6
C	127.5

■ Limit of Detection

A calibration curve (Fig. 6) including a blank was prepared using the quantitation values shown in Table 3 as a standard value and the limit of detection was calculated. It can be understood that the theoretical limit of detection is 0.13 [μg/cm²].

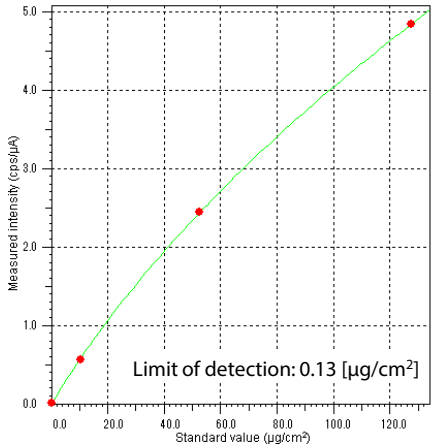

Fig. 6 Calibration Curve

■ Repeatability

Table 4 shows the results of a simple repeatability test (n = 10) of sample C.

Table 4 Results of Repeatability Test

Average value	126.6 [μg/cm²]
Standard deviation	0.47 [μg/cm²]
Coefficient of variation	0.37 [%]

■ Conclusion

It was found that EDXRF is effective for analysis of fluorine. The features are summarized below.

1. No chemical pretreatment required
   Measurement can be performed simply by placing the sample on the instrument without complicated pretreatment.
2. Analytical precision
   The lower limit of detection of F in powders and solids is about 200 ppm, and quantitative analysis of contents of 1 % or less is possible.

   In film thickness analysis, quantitation on the nm to μm order is possible in the case of PTFE, which can be expected to contribute to quality control.
3. User-friendliness
   Operation of the instrument is simple, and even inexperienced people can analyze samples easily.
4. Non-destructive analysis
   The sample after the measurement can be used for other analyses.

■ Measurement Conditions

Instrument	: EDX-8000/8100
Element	: ₉F
Analysis group	: Quantitative analysis
Analysis methods	: 1. Calibration curve method, 2. Film FP method
Detector	: SDD
X-ray tube	: Rh target
Tube voltage – current	: 15 [kV] – Auto [μA]
Collimator	: 10 [mmφ]
Primary filter	: None
Atmosphere	: Vacuum
Integral time	: 300 [s]
Dead time	: Max. 30 [%]

01-00164-EN First Edition: Sep. 2021

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