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Application News

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X-ray Analysis

Quantitative Analysis of Elements in Small Quantity of Organic Matter by EDXRF - New Feature of Background FP Method –

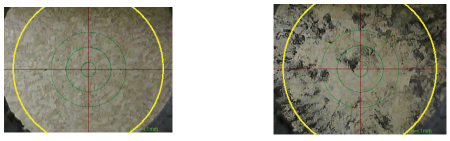
In X-ray fluorescence analysis, the fundamental parameter method (FP method) is often used for conducing quantitative analysis. If organic matter such as food, plant matter or resin is the principal component, the principal compounds are assumed to be CH_2O and CH_2, etc., and quantitative analysis is conducted regarding these components as balance components without conducting measurement. This is because measurement and accurate quantitation of carbon, hydrogen, oxygen and nitrogen, etc. is difficult using X-ray fluorescence.
But when a resin sample is of indeterminate form or the quantity of food or plant matter is small, even if the presence or absence of elements can be determined, obtaining stable quantitative values can sometimes be problematic due to fluctuation of the X-ray fluorescence intensity.
Therefore, taking into account these shape-related effects, a new feature of the background FP (BG-FP) method effectively provides stable quantitative values in analysis of such samples. Here we introduce an example of quantitative analysis of a small amount of hijiki (a type of seaweed) using the BG-FP method.

Sample

NMIJ*-certified reference material (powder)
CRM 7405-a No. 99 hijiki powder
* National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology

Preparation, Sample Volume

A small quantity of sample powder is placed on polypropylene film (thickness: 5 µm) which is spread over the sample container. For small volumes, the sample should be spread thinly.



(a) Sufficient Volume (b) Small (thin) Volume

Fig. 1 CCD Image of Sample

Quantitative Results

Quantitative analysis was conducted by the regular FP method using a sufficient quantity of sample, and by the FP method and BG-FP method using only a small amount of sample. Balance settings were made assuming the principal component to be $C_6H_{12}O_6$ in all of these.

The quantitation values are shown in Table 1, and a comparative graph of the quantitation values is shown in Fig. 2. Also, the qualitative profiles of the quantitative elements are shown in Fig. 3.

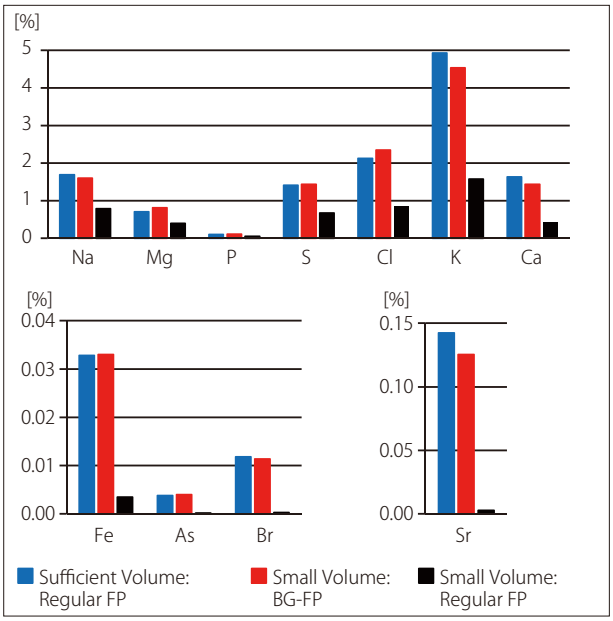


Fig. 2 Comparison Graph of Quantitative Values (from Table 1)

The quantitation values by the regular method showed a ratio of one-half to one-quarter the quantitation value for the light elements Na – Ca with respect to a small volume versus an adequate quantity of sample, and ratios of one-tenth to one-fiftieth for the heavy elements Fe – Sr, indicating a large difference in quantitation values. With a small sample quantity, the quantitative values will be correspondingly small when there are balance components because the X-ray intensity decreases. And, because X-rays of heavy elements in particular show strong transmission, the sample thickness can have a significant effect. However, with this new feature of the BG-FP method which can correct for the effects of shape, even for Mg with the largest error of 16 %, a quantitative value equivalent to that obtained with a sufficient volume of sample can be obtained even with a small amount of sample.

Table 1 Quantitative Results by Regular FP Method and BG-FP Method – Differences Due to Sample Volume –

[%]

		Na	Mg	P	S	Cl	K	Ca	Fe	As	Br	Sr	$C_6H_{12}O_6$
Sufficient Volume		1.69	0.70	0.10	1.41	2.13	4.92	1.64	0.033	0.0038	0.012	0.14	87.21
Small Volume	Background FP method	1.60	0.82	0.11	1.43	2.35	4.53	1.43	0.033	0.0040	0.011	0.13	87.54
	Relative Error	-5.5 %	16 %	2.7 %	1.7 %	10 %	-8.0 %	-12 %	0.7 %	3.9 %	-3.8 %	-12 %	0.4 %
	Regular FP Method	0.79	0.39	0.054	0.68	0.86	1.58	0.42	0.0035	0.0001	0.0003	0.0027	95.23
	Relative Error	-54 %	-44 %	-48 %	-52 %	-60 %	-68 %	-74 %	-89 %	-97 %	-98 %	-98 %	9 %

Balance components set assuming $C_6H_{12}O_6$ is the principal component.

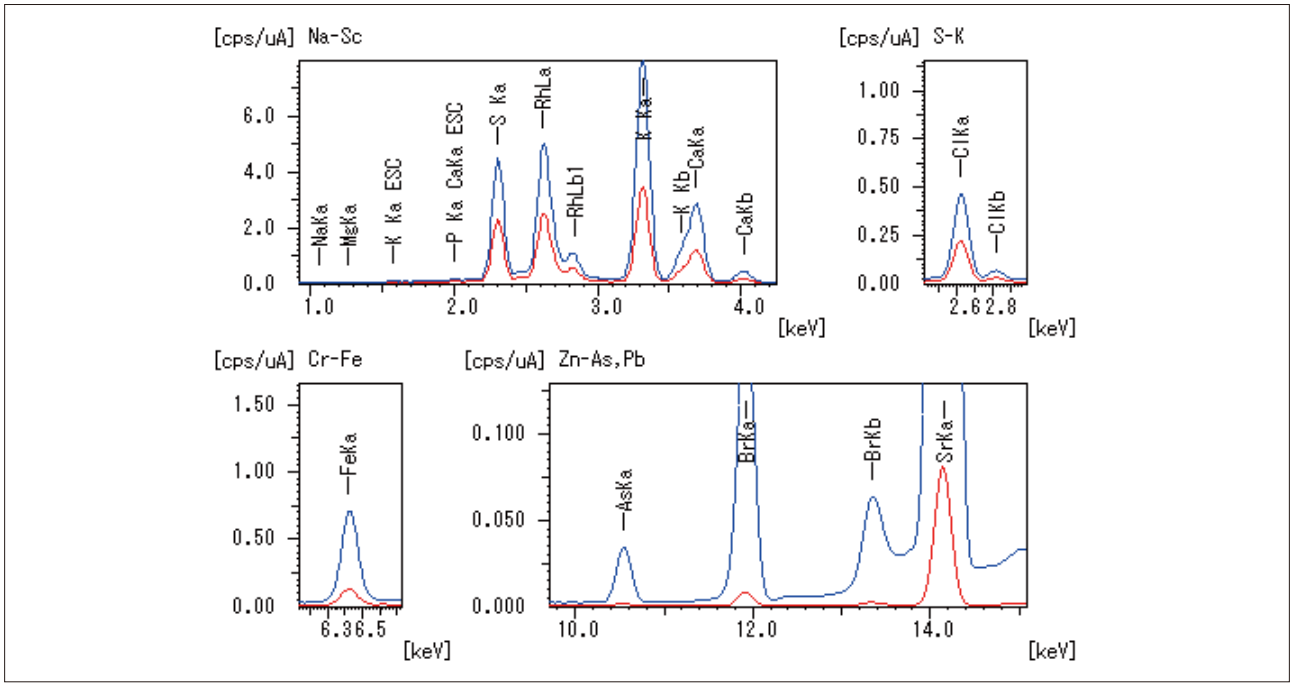


Fig. 3 Na-Sr Qualitative Profile Blue: Sufficient Volume; Red: Small Volume

New Feature of Background FP (BG-FP) method

The regular FP method[1] is used for quantitation of elements and compounds using only X-ray fluorescence intensity. In addition, the existing BG-FP method, which uses the background consisting of scattered X-rays, is used for determination of resin film thickness and elemental composition determination.[2]
On the other hand, the new feature of the BG-FP method also uses scattered X-rays to eliminate the effects of shape (or material).[3]
The above is summarized in Table 2.

[References]
1) Hirotomo Ochi, Hideo Okashita: Shimadzu Review, 45 (1-2), 51 (1988)
2) Shimadzu Application News X219
3) Hirotomo Ochi, Shinji Watanabe: Advances in X-ray Chemical Analysis, 37, 45 (2006)

Table 2 Types, Application and Usage of FP Methods

FP Method Type		Quantitative Analysis Target	Intensity Used in Quantitative Analysis
Regular FP Method		Inorganic component composition of fixed-shape sample	X-ray fluorescence [NET] (=Total X-rays[Total] – Scattered X-rays [BG])
BG FP Method	Existing	Resin film thickness and its inorganic component composition	X-ray fluorescence [NET] Characteristic X-rays (Rh, etc.), scattered X-rays
	New Feature	Inorganic component composition of amorphous samples	X-ray fluorescence [NET] Scattered X-rays [BG], characteristic X-ray scattered radiation

Conclusion

Accurate quantitative analysis using X-ray fluorescence generally involves the use of a sample of fixed shape or quantity. However, referring to RoHS screening analysis as a representative example, it has become common to conduct analysis of products of indeterminate form just as they are, without conducting sample pretreatment. In most of these cases, however, application of a calibration curve method such as internal standard correction was used, while use of the FP method was not possible.
Now, the new feature of the BG-FP method that makes this possible strengthens the current role of the FP method of permitting quantitative analysis without a standard sample, by also eliminating the influences of sample shape and quantity, thereby maximizing the ease and convenience of EDX. Further, it can also be effective in cases where there are other constraints, such as the availability of only a small quantity of sample for research or a small contaminant.

Analytical Conditions

Instrument	: EDX-7000
Elements	: Na-U
Analytical Group	: FP, BG-FP
X-ray Tube	: Rh target
Tube Voltage [kV]-Current [μA]	: 15-Auto, 50 kV-Auto
Primary Filter	: Without, #2, #3, #4
Collimator [mmϕ]	: 10
Atmosphere	: Vacuum
Detector	: SDD
Integration Time [sec]	: 100
Dead Time [%]	: Max. 30 %

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