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Application News

No.**X247A**

X-ray Analysis

Qualitative and Quantitative Analysis of Seafood by EDXRF

X-ray fluorescence analysis, in addition to its effectiveness in analysis of inorganic materials such as metals and ceramics, is also effective for the detection and quantitative analysis of minerals and heavy metals in foods. Not only can samples be analyzed directly without conducting time-consuming pretreatment, sensitive and accurate measurement is also possible using simple preparation measures, such as pressure forming. Quantitative analysis by XRF does not necessarily require a standard sample, as approximate quantitative results can easily be obtained even when the principal components are organic matter. Here we introduce these preparation methods and our investigation of their respective differences in quantitation values and detection limits.
Furthermore, we also examined the differences attributable to instrument model, as well as the use of iodine and cesium.
(Regarding the analysis of radioactive elements, we cannot guarantee that the detector or electronic equipment will not be susceptible to adverse effects. Thus, in this investigation, we used stable isotopes.)

■ Standard Samples

NMIJ certified reference material (powder)
(1) CRM 7405-a No. 99 (Powdered hijiki seaweed)
    Trace Elements and Arsenic Compounds in Seaweed (Hijiki)
(2) CRM 7403-a No. 52 (Powdered swordfish)
    Trace Elements Arsenobetaine and Methylmercury in Swordfish Tissue
NMIJ: National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology

Fig. 1 Standard Samples (NMIJ)
(1) Seaweed; (2) Swordfish Tissue

■ Sample Preparation

Samples were prepared in two different ways, as described below.
(1) Pressure Forming (Fig. 2)
    The sample is pressed into a 25 mmɸ vinyl chloride ring, and pressure forming is conducted using 50 kN for 20 seconds.

(2) Easy Press (Fig. 3)
    1) 4 µm thick PROLENE[*1] film is spread over the surface of the sample cup, and the layer of powdered sample is then placed over the film at a thickness greater than 5 mm.
    2) A small hole is then made in the film to allow the escape of air from the sample cup.

Fig. 2 Machine-Formed Briquette of Swordfish Tissue

Fig. 3 Seaweed Hand-Pressed (Easy Press) into Cup

■ Qualitative and Quantitative Analysis

The qualitative and quantitative analysis results for powdered seaweed and powdered swordfish tissue are shown in Fig. 4, Table 1, and Fig. 5, Table 2, respectively. The principle components are assumed to be organic material overall and are represented with the chemical composition CH_2O[*2], and the balance (remaining content) was quantified by the FP method.
The error (quantitative value versus standard value) is determined using a quick and easy quantitative method, in which it is:
1) within about 30 % for non-sodium elements present at greater than 0.1 %
2) within about 50 % for sodium present at less than 1 %
3) within about twice the value for trace elements present at less than 0.1 %
Regarding the differences due to the sample preparation method, it is clear from Fig. 4 and Fig. 5 that since pressure forming resulted in better sensitivity for Na – Ca, this method is effective when the detection of light elements is important.

*1 PROLENE is a registered trademark of CHEMPLEX INDUSTRIES,INC.
*2 CH_2O in the FP method is equivalent to the composition expressed by the formula $C_6H_{12}O_6$.
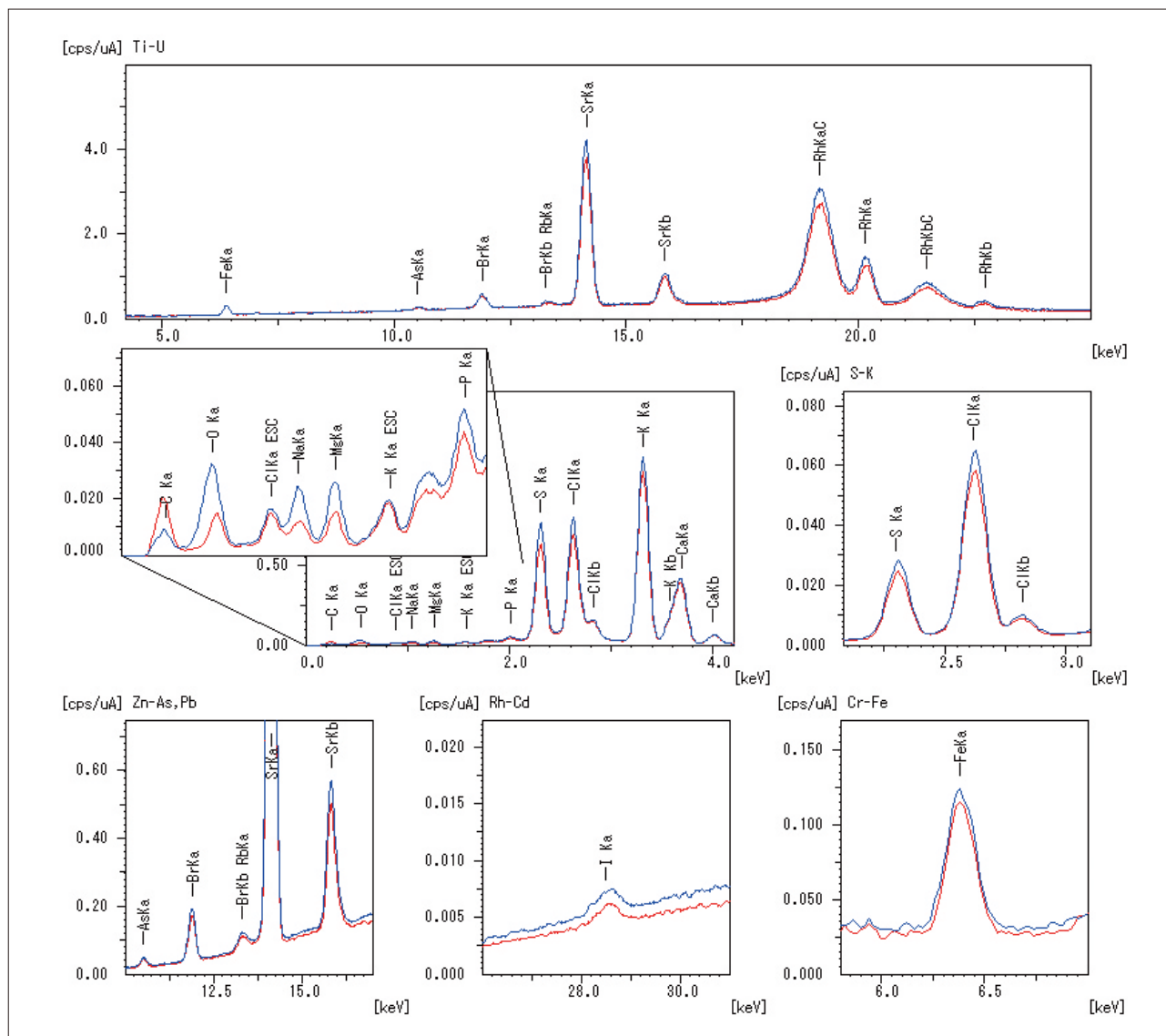
■ **Seaweed (Hijiki)**

Fig. 4 Qualitative Results for Seaweed Blue: Briquette Red: Easy Press

Table 1 Quantitative Results for Seaweed by FP Method

Element	Standard Value [mass%, (ppm)]*3	Quantitative Value [mass%, (ppm)]	
		Briquette	Easy Press
11 Na	1.62	1.59	2.05
12 Mg	0.679	0.54	0.54
15 P	0.101	0.091	0.085
16 S	–	1.40	1.31
17 Cl	–	2.03	1.93
19 K	4.75	4.60	4.33
20 Ca	1.52	1.28	1.26
26 Fe	311 [ppm]	315 [ppm]	287 [ppm]
33 As	35.8 [ppm]	27.5 [ppm]	24.4 [ppm]
35 Br	–	116 [ppm]	100 [ppm]
37 Rb	–	21.5 [ppm]	18.5 [ppm]
38 Sr	0.147	0.12	0.10
53 I	–	75.5 [ppm]	77.9 [ppm]
Balance CH_2O ($C_6H_{12}O_6$)	–	88.30	88.35

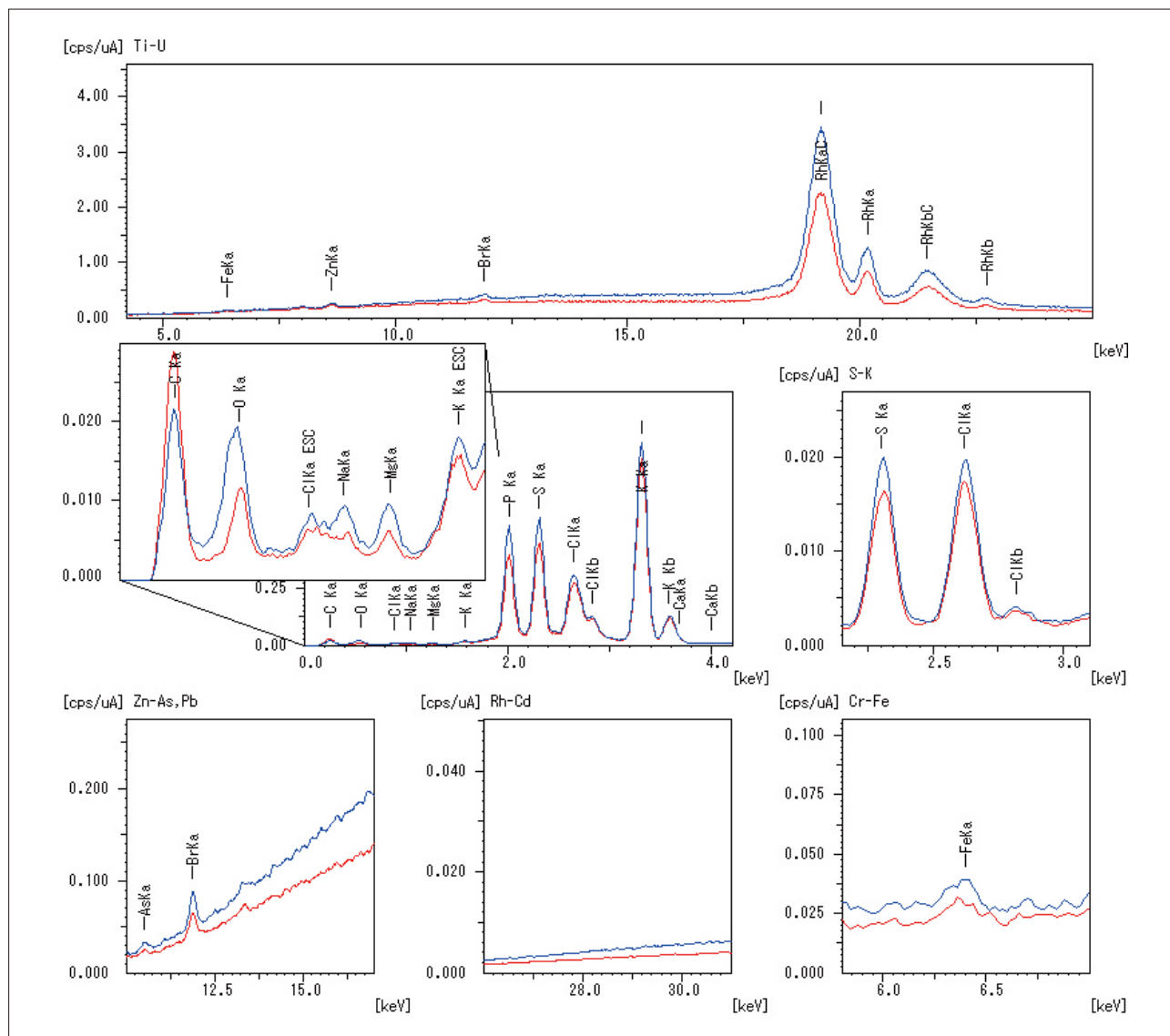*3 g/kg expresses 1/10 mass%, and mg/kg expresses ppm.

■ **Swordfish Tissue**

Fig. 5 Qualitative Results for Swordfish Tissue Blue: Briquette Red: Easy Press

Table 2 Quantitative Results for Swordfish Tissue by FP Method

Element	Standard Value [mass%, (ppm)][*3]	Quantitative Value [mass%, (ppm)]	
		Briquette	Easy Press
11 Na	0.357	0.47	0.54
12 Mg	0.158	0.14	0.14
15 P	1.45	1.62	1.50
16 S	–	0.95	0.88
17 Cl	–	0.52	0.49
19 K	2.63	2.97	2.76
20 Ca	0.0189	0.035	Not detected
26 Fe	13.1 [ppm]	26.9 [ppm]	22.0 [ppm]
30 Zn	33.6 [ppm]	31.6 [ppm]	19.1 [ppm]
33 As	6.62 [ppm]	6.7 [ppm]	4.0 [ppm]
35 Br	–	21.2 [ppm]	14.9 [ppm]
Balance CH_2O ($C_6H_{12}O_6$)	–	93.28	93.69

*3 g/kg expresses 1/10 mass%, and mg/kg expresses ppm.

Qualitative Analysis of Iodine and Cesium

Powdered swordfish was spiked with I (iodine) and Cs (cesium), and the results of qualitative analysis of this sample using the 2 instruments, EDX-720 and EDX-800HS, were compared. The sample was homogenized by mixing, and then pressure-formed into a briquette. The overlaid qualitative analysis results are shown in

Fig. 6. The L spectral lines of elements with close atomic numbers are adjacent to one another, but since the K spectral lines separate, when such elements are coexistent, it is effective to conduct measurement using the K spectral line.
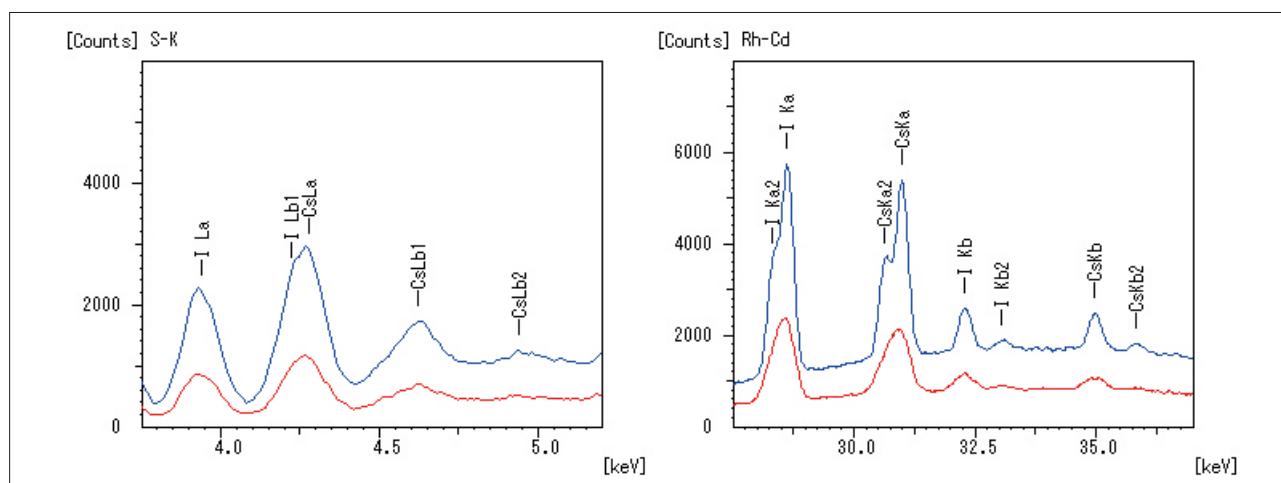

Fig. 6 Powdered Swordfish Spiked with I (1,000 ppm) and Cs (1,500 ppm) Blue: EDX-720 Red: EDX-800HS

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

(1) Comparison of the Lower Limits of Detection According to Sample Preparation Method
Table 3 shows the values for hijiki calculated from the qualitative and quantitative analysis results.

Table 3 L.L.D. - Comparison of Sample Preparation ([ppm], 300 sec)

Element	Briquette	Easy Press
11 Na	503	1,008
12 Mg	208	349
15 P	54	66
16 S	(31)	(32)
17 Cl	(89)	(90)
19 K	53	57
20 Ca	47	48
26 Fe	17	17
33 As	4.3	4.4
35 Br	(3.0)	(2.8)
37 Rb	(3.0)	(2.9)
38 Sr	3.9	4.1
53 I	(14)	(13)

Analysis line spectrum: Kα (Values in parentheses are reference values based on quantitated values)

(2) Comparison of the Lower Limits of Detection According to Instrument Used
1) Table 4 shows the values calculated from the qualitative analysis results (Fig. 6).

Table 4 L.L.D. - Comparison of Two Instruments ([ppm], 300 sec)

Element	Spectral Line	EDX-800HS	EDX-720
53 I	I Kα	11	6.0
53 Cs	CsKα	23	15

2) Relationship Between Concentration and Radioactivity
Taking for example the radioactivity of Cs (^{137}Cs), the level of radioactivity at the detection limit is calculated as follows. Assuming 1 g sample at 10 ppm (10 µg), approximately 32 MBq (32 million becquerel)
$$(= 7.29 \times 10^{-10} \cdot W \times 10^{-6} \cdot m \div 136.9 \cdot 6.02 \times 10^{23})$$

^{137}Cs decay constant	: 7.29×10^{-10} [1/s]
Concentration	: W [ppm]
Sample weight	: m [g]
Atomic weight	: 136.9 [g/mol]
Avogadro's number	: 6.02×10^{23} [particles/mol]

(Ref: 10 Bq/kg ≈ 0.003 ppt)

Analytical Conditions

Instrument	: EDX-800HS (C–U)	EDX-720 (Na–U)
X-ray Tube	: Rh target	Rh target
Filter	: Without (C, O, Na, Mg, P, S, K, Ca), Al (Cl, Cs), Ti (Fe), Ni (Zn, As, Br, Sr, Rb), Mo (I, Cs)	#1 (I, Cs L-line) #5 (I, Cs K-line)
Tube Voltage	: 15 [kV] (C–Ca), 50 [kV] (Ti–U)	15 [kV] (L-line), 50 [kV] (K-line)
Tube Current	: Auto	Auto
Atmosphere	: Vacuum	Vacuum
Measurement Diameter	: 10 [mmφ]	10 [mmφ]
Measurement Time	: 300 [sec] × 5 ch	300 [sec] × 2 ch
Dead Time	: Max 25 [%]	Max 40 [%]

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