SHIMADZU
Excellence in Science

Energy Dispersive X-ray Fluorescence Spectrometer ALTRACE™

Application News

Screening Analysis of Trace Heavy Metals in Powdered Milk

Yuki Tamura

User Benefits

- ALTRACE realizes the same analysis sensitivity as the conventional instrument (EDX-7000) in 1/10 the measurement time.
- Improved workability can be expected, as continuous analysis of up to 48 specimens is possible.
- Simple screening analysis of heavy metals without complex sample preparation is possible because it is only necessary to set the sample in the sample holder.

■ Introduction

One test method for heavy metals in food products is the color reaction (staining) method, but because that method cannot identify metals (elements) or is influenced by the sample components, AA (atomic absorption spectrophotometry), ICP-AES (inductively coupled plasma atomic emission spectrometry) or ICP-MS (inductively coupled plasma mass spectrometry) is used for elemental analysis. However, sample preparation for these test and analysis methods requires a lot of work, such as component extraction with reagents and acidic cleavage, and in the case of the staining method, individual differences in judgment have become an issue in production process and quality control. For this reason, we propose a method using energy dispersive X-ray fluorescence spectrometry (EDXRF), which enables simple analysis in the entire process from sample preparation to measurement and judgment.

In general, quantitation by EDXRF at levels below 1 ppm is difficult, as shown in Table 1, because these values are around or below the limit of quantitation. However, in the case of powdered milk, the standard values for the powder form before dissolution in hot water are about 7.7 times higher than the values shown in Table 1. This means that a screening analysis to determine whether the concentration is below the standard value or not is possible with EDXRF, which can analyze powders as-is.

Since the sensitivity of the ALTRACE for heavy metal elements was substantially improved in comparison with the conventional EDXRF (EDX-7000) by installing a high output X-ray tube, it is now possible to analyze samples with same sensitivity as the conventional instrument in only 1/10 the measurement time.

Table 1 Tolerances of Heavy Metals, Etc. in Voluntary Standards for Baby Food*1 [ppm]

Arsenic	Total mercury	Lead	Cadmium	Tin
0.5 or less *2	0.1 or less	0.3 or less	0.2 or less	10 or less

*1 The concentration shows the value when prepared according to the method shown on the product label.
*2 For products containing seaweed and seafoods, 1.0 or less.
Excerpted from the voluntary standards of the Japan Baby Food Council.

■ Elements

$_{33}As$, $_{48}Cd$, $_{50}Sn$, $_{80}Hg$, $_{82}Pb$

■ Standard Samples

After dripping an atomic absorption standard solution in powdered milk, the sample materials were frozen and crushed. Table 2 shows the concentrations of the standard samples. Certification of the samples was done by ICP-MS measurement. Sample 7 was included here for correction of overlap of Pb with As.

Table 2 Standard Samples [ppm]

Sample	As	Hg	Pb	Cd	Sn
1	ND*1	ND	ND	0.002	0.004
2	0.205	0.190	0.195	0.202	0.204
3	0.495	0.495	0.485	0.499	0.488
4	1.00	1.03	0.990	1.02	0.932
5	5.05	4.62	4.88	5.04	5.23
6	10.0	8.55	9.54	9.98	10.2
7	–*2	–	4.98	–	–

*1 ND: Below the limit of detection.
*2 – : Not measured.

■ Sample Preparation

The samples were introduced into sample containers lined with polypropylene film (thickness: 5 µm), and simple compression was applied. Fig. 1 shows an image of a sample.

Fig. 1 Image of Sample

■ Calibration Curves

Fig. 2 shows the calibration curves and Table 3 shows the calibration curve accuracy. For As, correction for overlap by Pb was applied (coexisting element correction, dj method), and to lessen the variations of the X-ray intensity, which are considered to be caused by the sample filling condition in sample preparation, the sample particle diameter, and other factors, correction was carried out using an internal standard for X-ray scattering.

Excellent results were obtained for the accuracy of the calibration curves in Fig. 2, as the results were 0.2 ppm or less in all cases (Table 3).

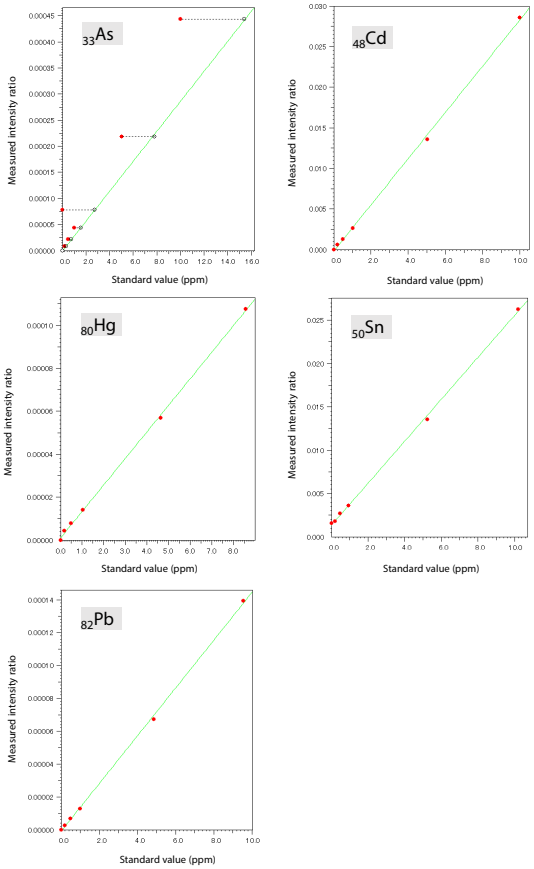

Fig. 2 Calibration Curves

Table 3 Accuracy of Calibration Curves [ppm]

Element	$_{33}$As	$_{80}$Hg	$_{82}$Pb	$_{48}$Cd	$_{50}$Sn
Accuracy	0.08	0.08	0.11	0.12	0.11

■ X-ray Fluorescence Spectra of Measured Elements

Fig. 3 shows a comparison of the X-ray fluorescence spectra of the 1 ppm standard sample and blanks of As and Cd acquired with ALTRACE and EDX-7000 (excerpted from Application News No. X260). In the case of As, a clear difference between the added samples and the blank can be detected by both instruments, but for Cd, only ALTRACE can detect a clear difference in the peaks. The greatly improved sensitivity of ALTRACE can be understood from the peak shape, particularly in the measurements of Cd, Sn and other high energy band elements.

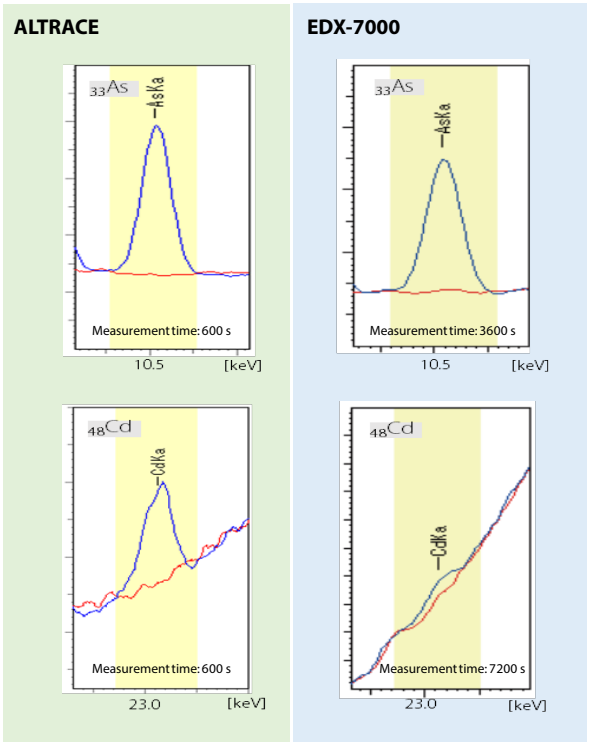

Fig. 3 X-ray Fluorescence Spectra (Blue: As, Cd 1 ppm, Red: Blank)
Measurement time: ALTRACE (As 600 s, Cd 600 s)
EDX-7000 (As 3600 s, Cd 7200 s)

■ Analysis Conditions

Table 4 shows the analysis conditions.

Table 4 Analysis Conditions

Instrument	ALTRACE
Elements	As, Cd, Sn, Hg, Pb
Analysis group	Calibration curve method
Detector	SDD
X-ray tube	Rh target
Tube voltage	50 [kV] (As, Hg, Pb) 65 [kV] (Cd, Sn)
Tube current	Auto [μA]
Primary filter	#5 (As, Hg, Pb), #1 (Cd, Sn)
Atmosphere	Air
Integration time	600 [s] x 2 Ch
Dead time	Max. 40 [%]

■ Limit of Detection

Table 5 shows the limits of detection calculated from the theoretical statistical variation. The data for the EDX-7000 are excerpts from Application News No. X260. Sensitivity equal to or higher than that of the EDX-7000 can be obtained with ALTRACE, even when the measurement time is greatly shortened to about 1/10 of the conventional level.

Table 5 Limits of Detection [ppm]

Element	$_{33}$As	$_{80}$Hg	$_{82}$Pb	$_{48}$Cd	$_{50}$Sn
Analytical line	AsKα	HgLα	PbLβ1	CdKα	SnKα
Instrument	ALTRACE				
LOD *1	0.029	0.069	0.059	0.075	0.131
Measurement time	600 s			600 s	
Instrument	EDX-7000				
LOD	0.047	0.069	0.074	0.237	0.573
Measurement time	3600 s			7200 s	

*1 LOD: Limit of detection; 3 times the theoretical statistical variation obtained from the calibration curve.

■ Results of Screening Analysis

Assuming a solution prepared by dissolving 13 g of powdered milk in hot water to make up a total of 100 g is used as the standard concentration when ingested, the value obtained by multiplying the standard values in Table 1 by the dilution factor of 7.69 (100÷13) is set as the reference value in the powder form. The result is "OK" if the total of the quantitative value and error (judgment value) is less than the reference value.

Table 6 shows the result of a screening analysis of sample 4 in Table 2. From this result, it can be understood that determination at the 1 ppm level is sufficiently possible with ALTRACE.

Table 6 Result of Screening Analysis of Standard Sample (1 ppm)

Heavy metal, etc. (analyte element)	Arsenic (As)	Total mercury (Hg)	Lead (Pb)	Cadmium (Cd)	Tin (Sn)
Judgment	OK	Not OK	OK	OK	OK
① Quantitative value	1.00	1.01	0.97	1.02	1.00
② Standard deviation σ_m	0.020	0.020	0.017	0.022	0.044
③ Calibration curve accuracy σ_c	0.08	0.08	0.11	0.12	0.11
④ Error $2\times\sqrt{(②^2+③^2)}$	0.158	0.162	0.215	0.237	0.232
⑤ Determination value ①+④	1.16	1.17	1.19	1.26	1.23
⑥ Reference value	3.8	0.76	2.3	1.5	77

Note: Error was obtained using the following expression:

$$\text{Error} = k \times \sqrt{\sigma_c^2 + \sigma_m^2}$$

k : With coverage factor set to 2
σ_c : Calibration curve accuracy
σ_m : Measurement repeatability (standard deviation)

■ Conclusion

Excellent results were obtained for both the calibration curves and the analysis results of powdered milk. EDXRF is useful for production process and quality control, as it is possible to measure samples directly in powder form or with only simple sample preparation, and thanks to its simple instrument handling and excellent repeatability, there are virtually no individual differences in results and judgments.

The sensitivity of ALTRACE for heavy metal elements was substantially improved by installing a high power X-ray tube, enabling highly accurate management in a shorter time, thereby contributing to improved throughput.

<Related Application News>

1. Screening Analysis of Trace Heavy Elements in Powdered Milk by EDXRF, Application News No.X260

01-00803-EN First Edition: Nov. 2024

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/