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Application News

No.X260

X-ray Analysis

Screening Analysis of Trace Heavy Elements in Powdered Milk by EDXRF

One of the methods used for testing for heavy metals in foods is the color reaction method, but since this method does not provide for attribution of metals (elements) or is influenced by sample components, elemental analysis such as AA (atomic absorption spectrophotometry) is used.
But due to the laborious sample preparations, such as component extraction and acid decomposition, etc., that are required, in addition to subjective variation in colorimetric determination, these methods have become a problem in the manufacturing process and in quality control.
Therefore, we investigated the use of the EDX method, which enables convenient analysis from sample pretreatment to measurement and finally to determination in the examination of powdered milk.
Generally, quantitation by EDX is difficult at concentrations below 1 ppm, as the lower limits of quantitation indicate in Table 1. However, in the case of powdered milk, since this standard value is multiplied by about 7.7 times by using the powdered state prior to dissolution in hot water, use of the EDX, which permits quantitation of powder as is makes it possible to conduct screening assays to determine whether the quantitative value is less or greater than the reference value.

Table 1 Tolerance of Heavy Metals*1, etc. in Baby Food (Unit: ppm)

Arsenic	Total Mercury	Lead	Cadmium	Tin
Less than 0.5*2	Less than 0.1*3	Less than 0.3	Less than 0.2	Less than 10

*1: Concentration represents the value obtained when prepared according to the method indicated on the product.
*2: Limit is less than 1.0 for items including seaweed and seafood.
*3: Limited to those contained in seaweed and seafood.
Japan Baby Food Conference (Quoted from the self-imposed standards)

Elements

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

Standard Samples

Atomic absorption standard solution was added to powdered milk so as to prepare mixtures having the following seven concentration levels.
• Each element: 0 (blank), 0.1, 0.2, 0.5, 1, 5, 10 (µg/g (ppm))
Also, in the case of As, due to overlapping with the Pb spectrum, the following 5 levels were also added to correct for coexisting elements.
• As/Pb: 0/15, 0.2/10, 1/5, 5/1, 10/0 (µg/g (ppm))

Sample Preparation

Twelve standard samples, each in the powdered state, were loaded at least 13 mm deep into sample containers covered with 5 µm-thick stretched polypropylene film. These were set in the turret, and measured continuously and automatically (Fig. 1).

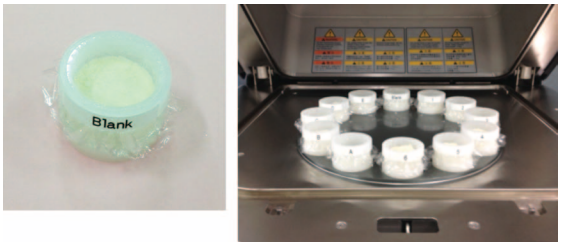

Fig. 1 Samples Set in the Turret

Calibration Curves

The calibration curves are shown in Fig. 2, and the accuracies in Table 2. The As value was corrected based on weight (matricies correction, dj method). Also, correction of the scattered X-rays internal standard was conducted to mitigate any X-ray intensity fluctuation which might occur due to such factors as the manner in which sample is loaded, sample particle size, etc. The calibration curves of Fig. 2 demonstrate excellent accuracy of less than 0.2 ppm.

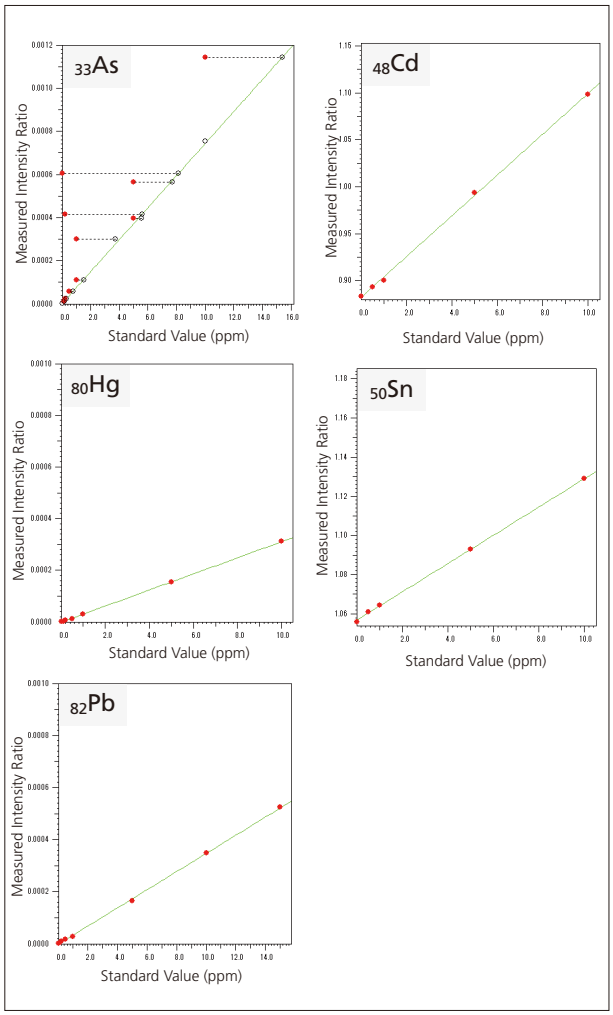

Fig. 2 Calibration Curves

Table 2 Calibration Curve Degree of Accuracy σ_c (ppm)

Element	$_{33}$As	$_{80}$Hg	$_{82}$Pb	$_{48}$Cd	$_{50}$Sn
Accuracy	0.13	0.040	0.12	0.11	0.08

X-Ray Fluorescence Spectra of Measured Elements

The X-ray fluorescence spectra obtained from analysis of a standard solution comprising As, Hg, Pb, and Cd at 1 ppm, and Sn at 5 ppm, in addition to a blank solution, are shown in Fig. 3. The peaks of As, Hg, Sn, and Pb are quite clear, and that of Cd can be verified by the difference with respect to the blank signal. A longer integration time is used for Cd to reduce the statistical fluctuation due to the scattered X-ray background.

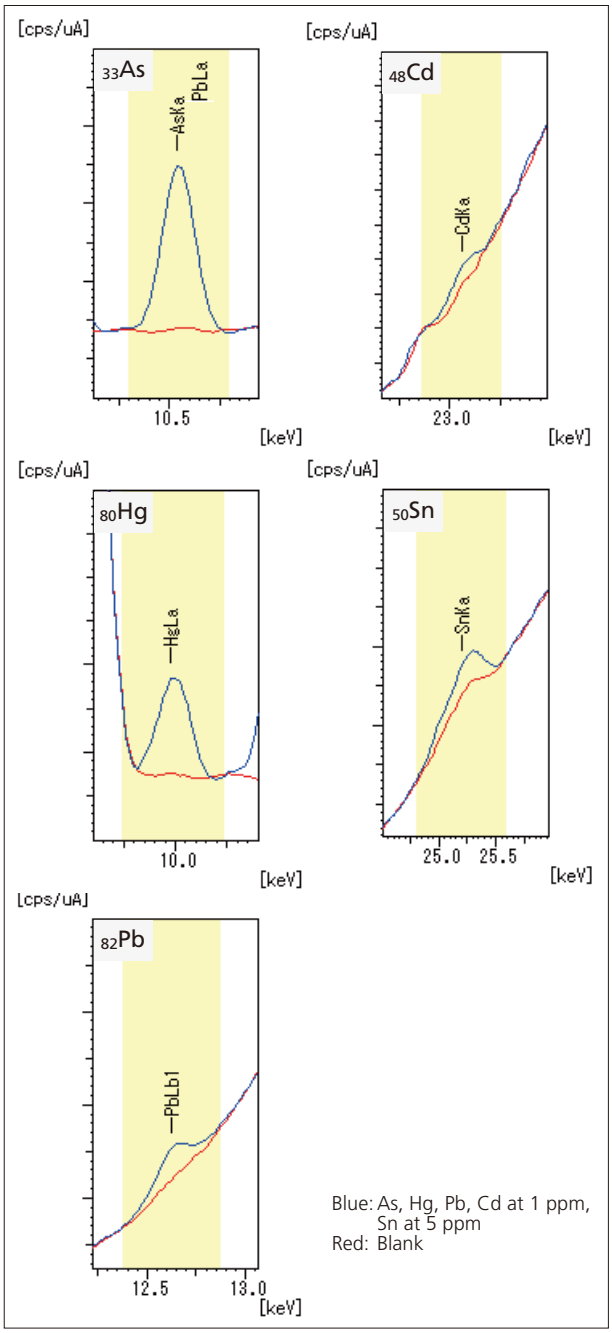

Fig. 3 X-Ray Fluorescence Spectra

Lower Limits of Detection

Using the calibration curve, ten repeat measurements of the blank were conducted, and the lower limits of detection were calculated at three times the standard deviation (Table 3).

Table 3 Repeatability of Blank and Lower Limits of Detection

(ppm)

Element	As	Hg	Pb	Cd	Sn
Standard Deviation of Blank	0.016	0.023	0.025	0.079	0.191
Lower Limit of Detection	0.047	0.069	0.074	0.23	0.57
Integration Time	3600 seconds			7200 seconds	

Screening Analysis Results

Considering a standard concentration of a powdered milk solution obtained by dissolving 13 g of the powdered milk in hot water, and adjusting the total weight to 100 g, the standard value as a powder is set to that obtained using the dilution factor 7.69 (100/13) based on the criteria of Table 1. If the value equivalent to the sum of the quantitation value and the error value (determination value) is less than the reference value, the determination is "OK."

The results of screening analysis of 1 ppm of standard sample are shown in Table 4. From this result, it is clear that this determination of about 1 ppm is sufficiently possible.

Table 4 Results of Screening Analysis of 1 ppm of Standard Sample

(ppm)

Heavy Metals, etc. (Analyte Elements)	Arsenic (As)	Total Mercury (Hg)	Lead (Pb)	Cadmium (Cd)	Tin (Sn)
Judgment	OK	Not OK	OK	OK	OK
(1) Quantitative Value	1.01	0.99	0.96	1.01	1.07
(2) Standard Deviation σ_m	0.037	0.025	0.043	0.135	0.308
(3) Calibration Curve Accuracy σ_c	0.13	0.040	0.12	0.11	0.080
(4) Error $2 \times \sqrt{(2)^2+(3)^2}$	0.27	0.094	0.255	0.348	0.636
(5) Determination Value (1) + (4)	1.28	1.08	1.21	1.36	1.7
(6) Reference Value	3.8	0.76	2.3	1.5	77

Note: The error value was obtained using the following expression[1), 2)].

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

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

Conclusion

In this analysis of powdered milk, good results were obtained with respect to both the calibration curve and the analytical results. Samples can be measured directly in the powdered state or following simple pretreatment, and with the simple handling of the instrument and excellent repeatability of results, enabling judgment with almost no variation due to individual differences among operators, this is an instrument that is useful in both the production process and quality control.

1) Codex standards, CAC/GL 54-2004 Guidelines on Measurement Uncertainty (in Japanese edition), CAC-GL 59-2006 Guidelines on Estimation of Uncertainty of Results, Ministry of Health, Labour and Welfare (Japan), "Expanded Uncertainty"
2) Toshimi Fujimori, "Bunsekigijustusya no tameno Toukeiteki Houhou (in Japanese)" Maruzen, 2008, p45
Meaning of the title: Statistical Analysis Method for Analysis Engineers

Analytical Conditions

Instruments	: EDX-7000/8000
Elements	: As, Hg, Pb, Cd, Sn
Analytical Group	: Calibration curve
Detector	: SDD
X-Ray Tube	: Rh target
Tube Voltage [kV]-Current [μA]	: 50-Auto
Collimator [mmø]	: 10
Primary Filter	: #1, #4
Atmosphere	: Air
Integration Time [sec]	: 3600 (As, Hg, Pb), 7200 (Cd, Sn)
Dead Time [%]	: Max. 30

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