SHIMADZU

Screening Analysis of Trace Heavy Metals in Powdered Milk

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1. Introduction

One method for detecting heavy metals in food products is the color reaction (staining) method. However, this approach cannot identify specific metals (elements) and can be affected by sample components. Therefore, techniques like AA (atomic absorption spectrophotometry), ICP-AES (inductively coupled plasma atomic emission spectrometry), or ICP-MS (inductively coupled plasma mass spectrometry) are used for elemental analysis. Nonetheless, preparing samples for these tests often involves labor-intensive steps such as reagent extraction and acidic digestion. In the case of staining, subjective judgment can vary, posing challenges in production and quality control.

To address this, we propose using energy dispersive X-ray fluorescence spectrometry (EDXRF), which offers a simple, seamless process from sample preparation to measurement and analysis. Generally, quantification by EDXRF below 1 ppm is challenging, as shown in Table 1, because these levels are near or below the quantitation limit. However, powdered milk provides a practical example: the standard values for the powder before dissolving in hot water are about 7.7 times higher than those listed in Table 1.

This indicates that EDXRF can reliably screen whether the heavy metal concentration is below the standard value since it can analyze powders directly. Additionally, the sensitivity of the ALTRACE instrument for heavy metals has been significantly improved compared to conventional EDXRF (EDX-7000) by installing a high-output X-ray tube, allowing analysis with the same sensitivity as older models but in only one-tenth of 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.

2. Analysis Conditions

Table 2 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 [%]

2. Elements, Standards and Samples

The following elements were studied: $_{33}$As, $_{48}$Cd, $_{50}$Sn, $_{80}$Hg, $_{82}$Pb

After spiking an atomic absorption standard solution into powdered milk, the samples were frozen and crushed. Table 3 displays the concentrations of the standard samples. Certification of the samples was performed using ICP-MS measurement. Sample 7 was included for correction of the overlap of Pb with As.

Table 3 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.

The samples were introduced into sample containers lined with polypropylene film (thickness: 5 μm), and simple compression was applied.

3. Results

Excellent results were obtained for the accuracy of the calibration curves in Fig. 1, as the results were 0.2 ppm or less in all cases. 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.

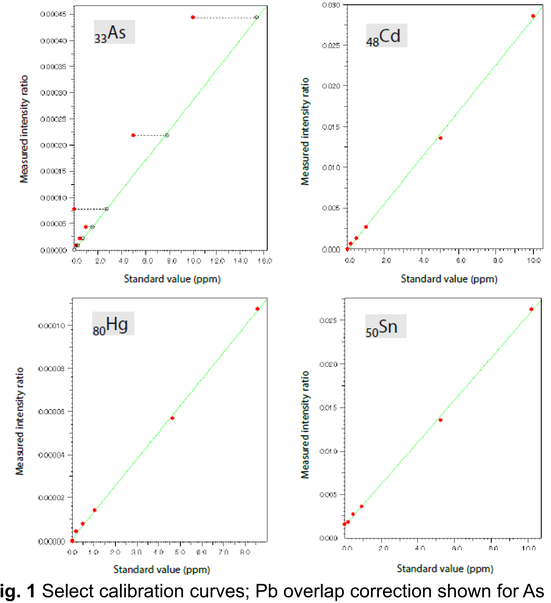

Fig. 1 Select calibration curves; Pb overlap correction shown for As

Table 4 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

Table 5 shows the limits of detection calculated from the theoretical statistical variation. The data for the EDX-7000 are excerpts from previous work in Application News No. 260. 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 one-tenth of the measurement time. Determination at the 1 ppm level is sufficiently possible with ALTRACE allowing for routine screening of As, Pb, Cd, and Sn.

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.

4. 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.