Screening Analysis for Hazardous Heavy Metals in Foods and Food Additives using Energy Dispersive X-ray Fluorescence Spectrometer

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1. Introduction

Control of hazardous heavy metals contained in foods and food additives is required in order to protect human health and safety.

From the viewpoint of sensitivity, the main technique used in analyses of toxic heavy metals is atomic absorption spectrophotometry. However, as disadvantages of this method, powder and solid samples must be dissolved in an acid such as nitric acid or hydrochloric acid, and advanced technology and know-how are required in the actual analysis. In contrast, fluorescent X-ray spectroscopy offers excellent convenience because analysis is possible as-is, without dissolving the specimens.

Shimadzu's new product, the ALTRACE, energy dispersive X-ray fluorescence spectrometer (Fig. 1), makes it possible to analyze toxic heavy metals with high sensitivity thanks to the increased output of the X-ray tube and optimization of the optical design. As an additional advantage, continuous analysis of a maximum of 48 samples is possible, contributing to improved analysis throughput.

This poster article introduces the following:

1. Analysis of cadmium (Cd) in rice
2. Analysis of cadmium (Cd) , arsenic (As) and lead (Pb) in milk
3. Analysis of arsenic (As) and lead (Pb) in food additives

Fig. 1 ALTRACE™

The equipment used in this experiment has unparalleled sensitivity compared to conventional equipment. The detection limits of the equipment used and the conventional equipment are shown in Fig. 2. This study implements batch elemental analysis from ppm to percent levels, with screening analysis ranging from sub-ppm to percent levels. The detection limits for Ni, Pb, Rn, and Cd are lower than 0.1 ppm.

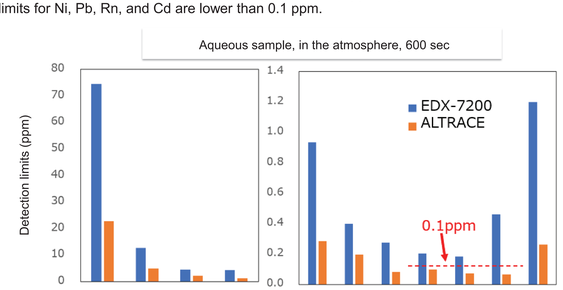

Fig. 2 Comparison of detection limits

2. Methods

■Analysis Conditions

The analysis conditions are shown in Table 1.

Table 1 Analysis Conditions

Instrument	: ALTRACE
Elements	: Cd, As, Pb
Analysis group	: Quantitative analysis
Analysis method	: Calibration curve method
Detector	: SDD
X-ray tube	: Rh target
Tube voltage	: 50 [kV] (As, Pb) 65 [kV] (Cd)
Tube current	: Auto [μA]
Primary filter	: #1 (Cd), #5 (As, Pb)
Atmosphere	: Air
Accumulation time	: 300 [s]
Dead time	: Max. 40 %

■Calibration Curves

Calibration curves were prepared for cadmium (Cd), arsenic (As), and lead (Pb) using standard solutions for atomic absorption spectrophotometry adjusted to the four concentration levels shown below. Fig. 3 shows the calibration curves.

Here, correction of the sample shape and matrix was done with scattered X-ray. In addition, correction for overlap of As by Pb was also carried out (coexisting element correction, dj method).

Concentrations of calibration curve standard solutions: 0 (blank), 0.5, 1, 5 μg/g

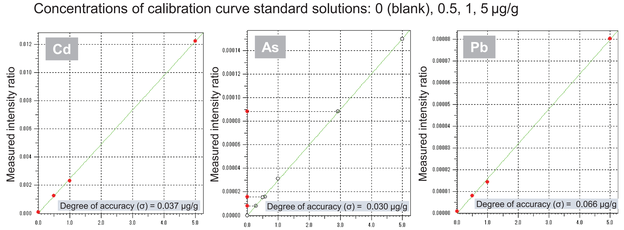

Fig. 3 Calibration Curves

■Lower Limit of Detection

Table 2 shows the lower limits of detection of each element calculated from the theoretical statistical variation of the calibration curves.

Table 2 Lower Limits of Detection

[μg/g]

Element	Cd	As	Pb
Analytical line	CdKα	AsKα	PbLβ1
Lower limit of detection	0.08	0.08	0.10

3. Results

3-1. Analysis of Cadmium in Rice

■Sample

White rice powder, certified reference material NMIJ CRM 7502-a

Fig. 4 Image of Sample

■Sample Preparation

The sample was set in a sample cell lined with polypropylene film (thickness: 5 μm) and subjected to simple compression. Fig. 4 shows an image of the sample.

■Cd Profile

Fig. 5 shows the profile of CdKα. A peak can be observed clearly, even with a trace amount of cadmium (0.548 μg/g).

■Results of Repeatability Test

Table 3 shows the results of a 10-time repeatability test.

Fig. 5 CdKα Profile

Table 3 Results of Repeatability Test

[μg/g]

Element	Cd
Standard value	0.548
Average value	0.532
Standard deviation	0.050
Coefficient of variation [%]	9.4

3-2. Analysis of Cd, As and Pb in Milk

■Sample

Milk

Fig. 6 Image of Sample

■Sample Preparation

The sample was prepared by placing 8 mL of milk into a sample cell lined with polypropylene film (thickness: 5 μm). Fig. 6 shows an image of the sample.

■Results of Quantitative Analysis

Table 4 shows the results of the quantitative analysis. All elements were below the lower limit of quantitation.

Table 4 Results of Quantitative Analysis*

[μg/g]

Element	Cd	As	Pb
Milk	<0.21	<0.28	<0.23

*The symbol "<" indicates that the result is below the lower limit of quantitation.
The lower limit of quantitation is the theoretical 10 σ value.

3-3. Analysis of Arsenic and Lead in Food Additive

■Sample

- Adipic acid
- L(+)-ascorbic acid (vitamin C)
- Citric acid

■Sample Preparation

The sample were set in a sample cell lined with polypropylene film (thickness: 5 μm) and subjected to simple compression. Due to the large grain shape of the citric acid, the sample was crushed with a crushing machine.

■Results of Quantitative Analysis

Table 5 shows the results of the quantitative analysis. Both arsenic and lead were below the lower limit of quantitation. Because the lower limit of quantitation is much lower than 1 μg/g, it can be understood that this analysis is effective for screening analysis of the organic samples listed in Japan's Specifications and Standards for Food Additives.

Table 5 Results of Quantitative Analysis*

[μg/g]

Element	As	Pb
Adipic acid	<0.21	<0.19
L(+)-ascorbic acid (vitamin C)	<0.28	<0.17
Citric acid	<0.28	<0.25

*The symbol "<" indicates that the result is below the lower limit of quantitation.
The lower limit of quantitation is the theoretical 10 σ value.

4. Conclusions

- The analytical sensitivity of the new Shimadzu ALTRACE was greatly improved by increasing the power of the X-ray tube and optimization of the optical design.
- With improved performance and ease of sample preparation, it has the potential to become an alternative to atomic absorption spectrometry or other analytical methods.
- In addition, because a large number of samples can be analyzed in a short time, also contributes to improved analytical throughput for the customer.

<References>
(1) Standards and criteria for food and food additives, etc. (1959, Ministry of Health and Welfare notification No. 370)
(2) Public Health Bureau, Food Safety Standards and Evaluation Division notification No.0308-1, dated March 8, 2024
(3) Japan's Specifications and Standards for Food Additives, 10th Edition
(4) CODEX GENERAL STANDARD FOR CONTAMINANTS AND TOXINS IN FOOD AND FEED (CODEX STAN 193-1995)

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