SHIMADZU
Excellence in Science

Application News

No.A469A

Spectrophotometric Analysis

Measurement of Cadmium (Cd) and Lead (Pb) in Food Additives by Electrothermal Atomic Absorption Spectrometry (ETAAS)

Introduction

A food additive is defined in Japan's Food Sanitation Act as "an item to be used for the purpose of storage or processing of food, which is added to, mixed with, or diffused into food in any manner."
Food additives are used for a variety of purposes, as, for example, preservatives, sweeteners, coloring agents, and stabilizers. Test methods and component standards have been established for many of these, and have been published as a food additives compendium titled "Japan's Specifications and Standards for Food Additives." One of the purity test items is heavy metal testing (in terms of lead content), for which the eighth edition of the compendium adopts a colorimetric method using Nessler cylinders. However, in the ninth edition, a different test method is under review, in which the element lead is handled individually.
Here, we introduce an example of analysis of cadmium (Cd) and lead (Pb) in α-cyclodextrin (cyclic oligosaccharide), a substance used in functional foods, pharmaceuticals, cosmetics, etc. The analysis was conducted by electrothermal atomic absorption spectrometry (ETAAS) using the AA-7000 atomic absorption spectrophotometer.

Sample Preparation

Sample digestion was conducted using the ETHOS One microwave sample preparation system (Milestone Srl). Compared to pretreatment using dry ashing or an open system such as wet digestion, microwave digestion permits quick digestion of the sample, making it unlikely that contamination or volatilization of the measurement element will occur. The digestion process flow is shown in Fig. 1.
For validity assessment of the pretreatment and measurement, the same process was conducted on a sample spiked with standard solution prior to digestion. Preparation was conducted so that the spiked solid concentrations were 0.05 µg/g of Cd and 0.5 µg/g of Pb.

Transfer 0.5 g sample to digestion container.
↓
Add small amount of distilled water and 8 mL nitric acid, then mix.
↓
Seal container, set in ETHOS One, digest for approx. 1 hour.
↓
After cooling, transfer to a vessel, add distilled water to a volume of 50 mL.
↓
Measure the sample by electrothermal atomic absorption spectrometry.

Fig. 1 Flowchart of Sample Decomposition

Analysis Method and Conditions

The standard solutions for atomic absorption analysis were prepared by diluting a 1000 mg/L standard solution to obtain 1 µg/L of cadmium and 10 µg/L of lead, respectively. The calibration curves were generated using an autosampler to adjust the injection volumes of standard solution in a stepwise manner. In addition, 5 µL of a palladium nitrate solution (50 mg/L palladium content) was added as a matrix modifier to all of the samples. The main conditions that were used for the spectrometer and atomization are shown in Tables 1 and 2.

Table 1 Optics Parameters

	Cd	Pb
Analytical wavelength	228.8 nm	283.3 nm
Slit width	0.7 nm	
Ignition mode	BGC-D2	

Table 2 Atomizing Conditions

	Cd	Pb
Ashing temperature	700 ℃	800 ℃
Atomizing temperature	2200 ℃	
Standard solution concentration (ppb)	0.2, 0.5, 1.0	2.5, 5, 10
Tube type	Platform	
Sample injection volume	20 µL	
Matrix modifier	5 µL of 50 ppm palladium nitrate	None

With the microwave digestion method, since much of the acid that is added remains, it is not uncommon for the acid concentration in the sample solution to be more than 10 %. High acid concentration is a factor that can lead to a decrease in repeatability and sensitivity. The platform tube used for this measurement (see Fig. 2) is resistant to the effects of acidity and coexisting substances in the matrix because the sample is injected into a plate having a recess (platform) that is mounted in the tube and then uniformly heated by radiant heat from the outer wall. Fig. 3 shows the changes in absorbance of a lead standard solution caused by varying the nitric acid concentration. A fairly constant absorbance was found to be obtained up to a nitric acid concentration of 20 %.

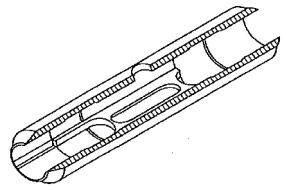

Fig. 2 Sectional View of Platform Tube

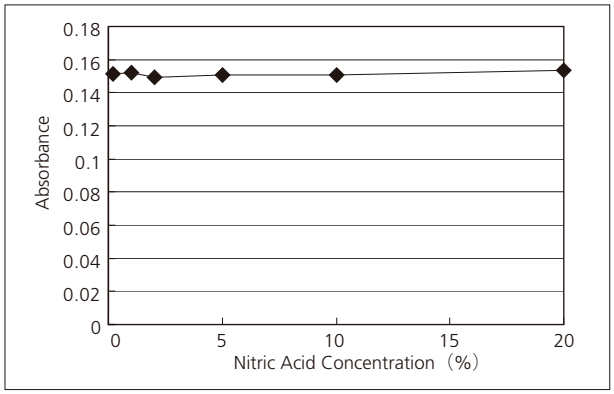

Fig. 3 Sensitivity Variation of Pb 10 µg/L Standard Solution Due to Changes in Nitric Acid Concentration When Using a Platform Tube

Results and Conclusion

The sample measurement results are shown in Table 3. Neither of the elements was detected in the sample. Calculation of the lower limit of quantitation as a concentration in a solid at an absorbance of 0.01 Abs yielded 0.003 µg/g for cadmium and 0.07 µg/g for lead. Good values were obtained in spike and recovery testing, and high-sensitivity analysis of heavy metals was possible using electrothermal atomic absorption spectrometry with a platform tube, without adverse effects from the acid concentration. The calibration curves are shown in Figs. 4 and 5, respectively, and the peak profiles are shown in Fig. 6.

The AA-7000 Series features a lineup that includes not only dedicated instruments for the flame method and electrothermal method, but also a dual-use instrument that offers automatic switching of the atomization method, thereby supporting a wide range of application requirements.

Regarding the α-cyclodextrin that was measured in this application, the eighth edition of the Specifications and Standards for Food Additives specifies a separate reference value for lead (1 µg/g or less). For pretreatment, after ashing 10 g of sample, nitric acid is added to bring the solution to a volume of 10 mL, and flame atomic absorption is specified as the measurement method. When the AA-7000 flame method is used to analyze the sample prepared in this manner, the expected detection limit of lead in a solid sample is about 0.2 µg/g.

Table 3 Measurement Results of Cd and Pb in α-Cyclodextrin

Element	Cd	Pb
Measured value	<0.003 µg/g	<0.07 µg/g
Spike and recovery rate	105 %	99 %

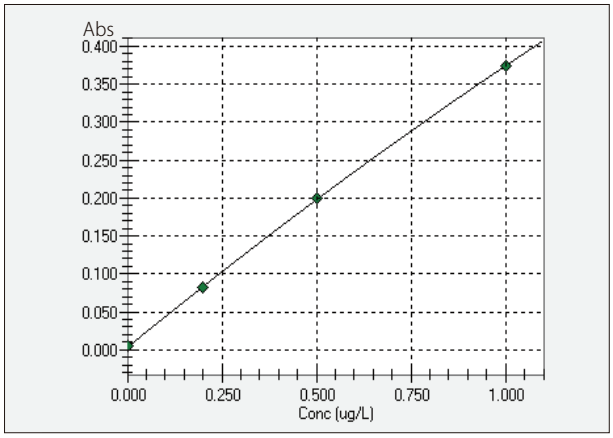

Fig. 4 Calibration Curve of Cd

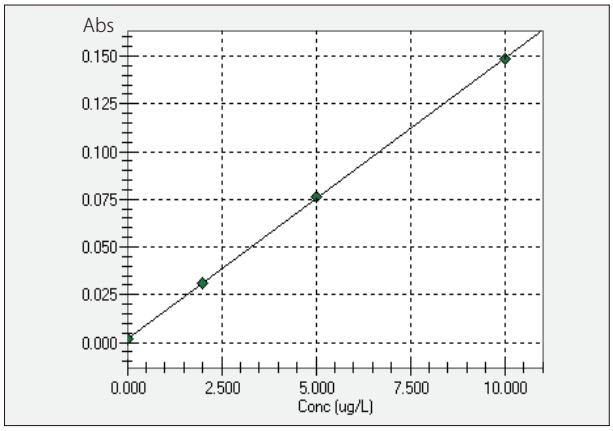

Fig. 5 Calibration Curve of Pb

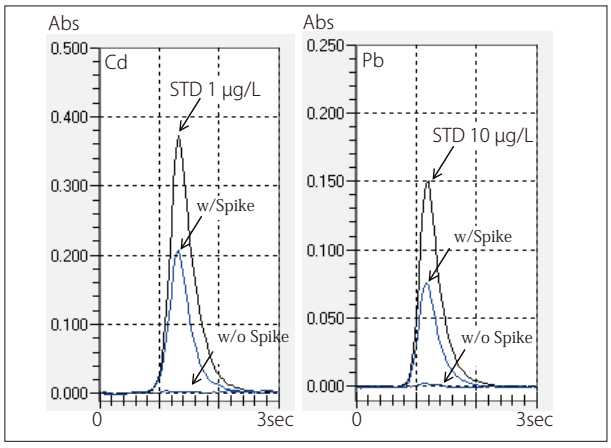

Fig. 6 Peak Profiles

First Edition: Aug. 2013

SHIMADZU

Shimadzu Corporation
www.shimadzu.com/an/