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Application News

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Inductively Coupled Plasma Atomic Emission Spectrometry

Precision Analysis of Toxic Elements in Plastic by ICPE-9800 Series

Introduction

In response to various environmental regulations, including RoHS/ELV, measurement of toxic elements (Cd, Pb, etc.) in plastics that are used in a wide range of materials and components is required. Analysis of such toxic elements can be conducted quickly and accurately using an ICP atomic emission spectrometer (ICP-AES). However, conducting analysis by ICP-AES requires that the sample be placed in solution, so the selection of a suitable pretreatment method is important to ensure that accurate results are not jeopardized due to shortcomings of specific digestion pretreatment methods.

Here, we conducted analysis of a polyethylene standard material using the Shimadzu ICPE-9800 series multi-type ICP atomic emission spectrometer, while using 3 different methods of digestion, including the dry ashing method, the wet decomposition method, and the microwave sample digestion method. The ICPE-9800 series, an instrument equipped with a newly designed CCD detector, and which features reduced gas combustion, offers high-throughput, accurate and low-cost analysis.

Sample

BCR680, 681 (polyethylene standard substance)

Sample Preparation

The sample was placed in solution using the following 3 methods.

(1) Dry ashing method

First, 0.2 g of sample is weighed out in a quartz crucible. After adding enough sulfuric acid to just cover the sample, the crucible is placed on a hot plate and heated until thin white fumes of SO_3 are generated, after which the crucible is placed in an oven at 450 °C until ashing is completed. After ashing, 5 mL of hydrochloric acid (1 + 2) is added to the residue, and the liquid is permitted to evaporate to dryness on a water bath. Then, 10 mL of 1 mol/L nitric acid is added, and the mixture is placed on a hot plate until the residue is dissolved. After cooling, the digest solution volume is adjusted to 20 mL.

(2) Wet digestion method

First, 0.2 g of sample is weighed out in a Kjeldahl flask. After adding sulfuric acid, nitric acid, and hydrogen peroxide, thermal digestion is conducted on a heating mantle (about 300 °C). The contents turns to black ash, and white SO_3 smoke is generated. After the liquid content is charred black, nitric acid and hydrogen peroxide are added, and heating is continued (at about 350 °C). This process is repeated until the content of the flask turns a pale yellow color. After cooling the flask, the digest solution volume is adjusted to 20 mL. (Reference: BS EN1122 Method A: 2001)

(3) Microwave sample digestion method

First, 0.2 g of sample is weighed out into a digestion vessel. After adding nitric acid and hydrogen peroxide, the vessel is sealed. Digestion is accomplished in the microwave sample preparation system. After the digestion vessel cools down, the digest solution volume is adjusted to 20 mL.

Note: For samples that contain large quantities of additives and coexisting components, a small amount of hydrofluoric acid is used. (Reference: US EPA SW-846 Method 3052)

Instrument and Analytical Conditions

For measurement, the Shimadzu ICPE-9800 series multi-type ICP atomic emission spectrometer was used. The measurement conditions were as shown in Table 1. The ICPE-9800 series adopts a CCD detector, thereby permitting measurement of a single sample to be completed in about 2.5 minutes (n = 3), regardless of the number of elements or wavelengths. In addition, the mini torch with its reduced consumption of plasma gas, the Eco mode, which reduces gas and electric power consumption while in the standby mode, and finally, the reduced consumption of gas by adopting a vacuum spectrometer, which eliminates the need for purge gas, are all enhancements that greatly reduce running costs as compared with conventional ICP-AES systems.

Table 1 Analytical Conditions

Instrument	: ICPE-9800 series
Radio frequency power	: 1.2 kW
Plasma gas Flowrate	: 10 L/min
Auxiliary gas Flowrate	: 0.6 L/min
Carrier gas Flowrate	: 0.7 L/min
Sample introduction	: Nebulizer 10
Misting chamber	: Cyclone chamber
Plasma torch	: Mini Torch
Observation	: Axial (AX)
Measurement time	: 2.5 min/sample (Including rinse time)

Analysis

Quantitative analysis of Cd, Pb, Cr, and Hg was conducted using the calibration curve method.

[References]

1) BS EN1122 Method A: 2001 (Plastics. Determination of Cadmium. Wet Decomposition Method)
2) US EPA SW-846 Method 3052 (Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices)

Analytical Results

Table 2 shows the analytical results. Fig. 1 shows the spectral profiles. The detection limits were lower than the maximum permissible RoHS values, demonstrating that analysis can be conducted with high sensitivity.

Comparison of pretreatment methods:
Good results that were consistent with the certified values were obtained for Cd and Pb using the dry ashing method, for Cd, Cr, Hg, and As by the wet digestion method (Kjeldahl method), and for all of the elements by the microwave sample digestion method. Low values are thought to have occurred due to the evaporation of Hg and As at high temperatures using the dry ashing method, and due to the precipitation of lead sulfate that occurs as a result of the reaction of Pb with the sulfuric acid used for digestion in the wet digestion method.

Conclusion

The microwave sample digestion pretreatment method can be used for accurate quantitation of all the regulated toxic metals. Although accurate analytical results can also be obtained using the other pretreatment methods, selection between these should be made according to the measurement target elements. Thus, toxic elements in plastics can be analyzed accurately, quickly and at low-cost using the ICPE-9800 series by selecting a pretreatment method suitable for the elements to be measured.

Table 2 Analytical Results of Polyethylene Resin (unit: mg/kg)

Element	RoHS Maximum Permissivle Value	Detection Limit (3σ)	BCR680 Preparation: Dry Ashing	BCR680 Preparation: Wet Decomposition	BCR680 Preparation: Microwave Decomposition	BCR680 Certified Value	BCR681 Preparation: Dry Ashing	BCR681 Preparation: Wet Decomposition	BCR681 Preparation: Microwave Decomposition	BCR681 Certified Value
Cd	100	0.02	140	140	141	140.8	21.1	21.3	21.6	21.7
Pb	1000	0.2	106	<	107	107.6	13.2	<	13.7	13.8
Cr	1000 *	0.03	106	112	115	114.6	16.1	17.3	17.9	17.7
Hg	1000	0.2	<	24.2	25.3	25.3	<	4.3	4.4	4.5
As	-	0.5	27	30	31	30.9	3	4	4	3.93

Detection limit: Detection limit when conducting pretreatment with sample dilution 0.2 g/20 mL
<: Below the detection limit
*: Cr^{6+} Maximum permissible value

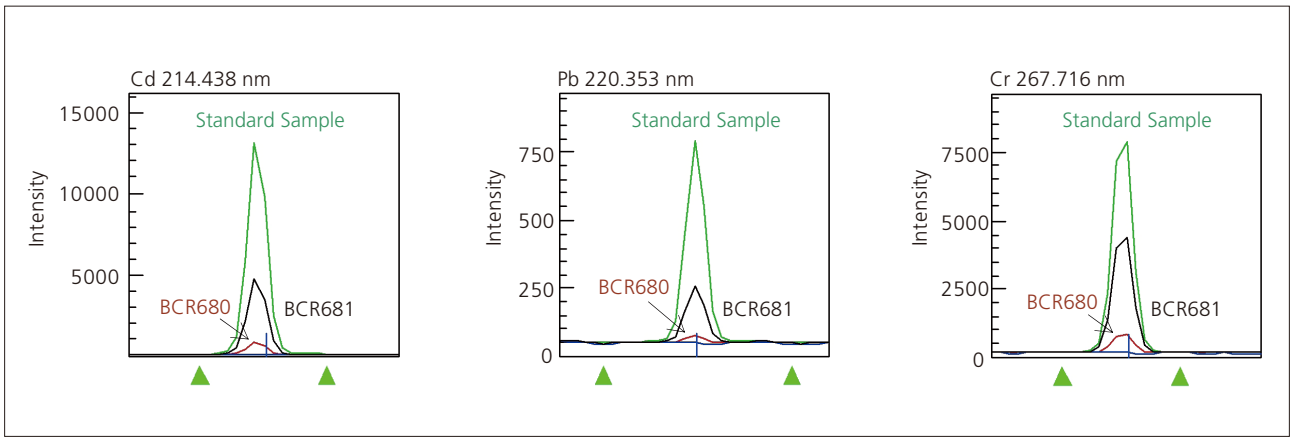

Fig. 1 Spectral Profiles of Polyethylene

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