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Application News

No.X248

X-ray Analysis

Quantitative Analysis of Antimony (Sb) in Plastics by EDXRF

In EDX analyses, antimony (Sb) compound, which is used as flame retardant promoter of plastics, is recently required to analyze as same as the elements (Cd, Pb, Cr, Hg, Br) subject to restriction in electrical and electronics equipment in the RoHS directive. Apart from this restriction, analysis of chlorine (Cl) and bromine (Br) in some electronic parts is recently needed to meet the new requirement for halogen-free materials.[1), 2)] As background, in the midst of the momentum that is building worldwide for increased protection of the environment, individual companies are now establishing their own regulations in addition to those currently enforced as public regulations.
Here we present the results of sensitivity evaluation testing of commercially available antimony-spiked PE (polyethylene) plastic standards using the EDX-720/GP.
In addition, since quick screening evaluation analysis of these restricted elements is often judged by the OK/Gray/NG method using a dedicated instrument, an example of this analysis is also presented here.

Samples

Sb standard plastic produced by Sumika Chemical Analysis Service (4 levels) PE-1E4

sample	Sb Content [ppm]
(1)	0
(2)	310
(3)	630
(4)	1100

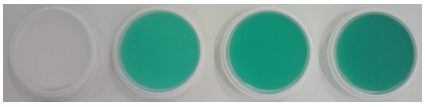

Fig. 1 Plastic Standards for Sb—PE-1E4

Calibration Curve and Detection Limit

The 4-point (four samples) Sb internal-standard-corrected calibration curve is shown in Fig. 2, and the intensity profile is shown in Fig. 3. With an integration time of 100 sec, accuracy was excellent at 0.8 ppm and the theoretical limit of detection was 9.8 ppm, which clearly demonstrated quantitative analysis at the ppm level.
<Internal-Standard-Corrected Calibration Curve and Detection Limit >
Sample density, shape, and some other properties can be corrected using the internal standard correction method, in which the intensity ratio is expressed as NET Intensity (X-ray fluorescence) ÷ BG (background, scattered X-rays) Intensity.[3)] The detection limit with this method is equivalent to that obtained using NET intensity if the calibration curve passes near the origin without interference lines overlapping. Also, with an integration time of 300 sec, the theoretical limit of detection[4)] is 5.7 ppm, which is comparable to that of heavy metals including Cd and Pb.[5)]

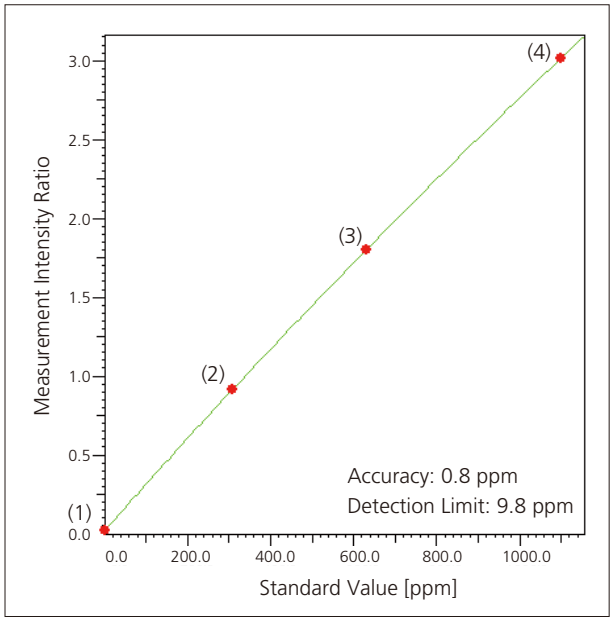

Fig. 2 Calibration Curve for Sb in Plastics

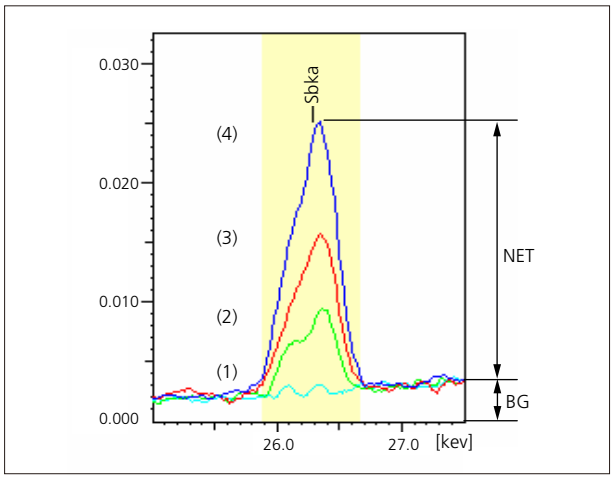

Fig. 3 Profile of SbKα

Repeatability

By using the internal standard correction calibration curve method described above, the 630 ppm sample (3) was measured 10 times in succession. The results of this repeatability testing are shown in Table 1.

Table 1 Repeatability

Average	630.9 ppm
Standard Deviation	14.0 ppm
Coefficient of Variation	2.2 %

Quantitative Analysis of Unknown Sample

After setting up analytical conditions for the seven elements—Sb, Cd, Pb, Cr, Hg, Br, Cl—quantitative analysis of a piece of plastic was conducted (Fig. 4). Fig. 5 shows an excerpt from the results report that includes the quantitative values and judgment results. Because the analytical conditions for Sb are the same as those for Cd, thus allowing these elements to be measured simultaneously, the total analysis time did not increase with the addition of Sb to the analysis.

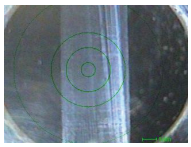

Fig. 4 Image of Plastic Fragment Sample

Element	Content	3σ	Unit	Judgment
Cd	132.0	9.3	ppm	GRAY
Pb	351.2	10.1	ppm	OK
Cr	116.4	7.3	ppm	OK
Hg	147.0	6.5	ppm	OK
Br	5.6	3.9	ppm	OK
Cl	97.4	30.7	ppm	OK
Sb	207.2	12.5	ppm	OK

Fig. 5 Excerpt from 7-Element Analysis Report

Screening Analysis

Currently, the five RoHS-controlled elements plus Cl are often analyzed using a screening method for various types of products and materials to quickly determine if they are in the intermediate gray zone.

Fig. 6 shows the screening analysis and judgment results for a piece of plastic analyzed on an EDX-GP after adjusting the pre-installed conditions to include Sb. Determination of the seven elements (Sb, Cd, Pb, Cr, Hg, Br, Cl) was completed in about 2 minutes, and the result for Sb was OK with the upper limit reference value set to 500 ppm.

Quantitation Value + 3σ = 242.3 + 26.1 = 268.4 < 500 => OK

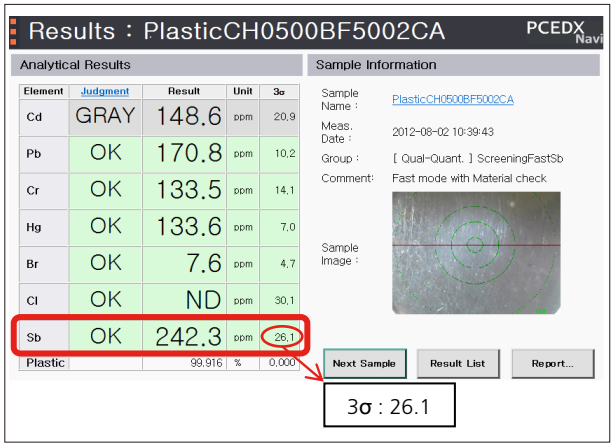

Fig. 6 Plastic Fragment Screening Results Window

Conclusion

The results show that the quantitative analysis can be conducted with good sensitivity to the ppm level for Sb just as for the elements Cd, Pb, Cr, Hg, and Br. Furthermore, Sb can be added to the series of RoHS regulated substance without affecting the throughput, as the analysis time remains unchanged. This extends the range of possible applications by merely adding to the existing analytical conditions.

Analytical Conditions

Instrument	: EDX-720, EDX-GP
Elements	: Sb(Kα)
Analytical Group	: Working Curve
X-ray Tube	: Rh target
Tube Voltage[kV]–Current[μA]	: 50–Auto
Primary Filter*	: #1*
Collimator [mmϕ]	: 10
Atmosphere	: Air
Detector	: Si(Li)
Integration Time [sec]	: 100
Dead Time [%]	: 40

[References and Note]

1) JPCA-ES02:Halogen-free copper-clad laminates for printed wiring boards-Paper base, phenolic resin JPCA(Japan Electronics Packaging Circuits Association)
2) IEC61249-2-21
3) Shimadzu Application News No.X222,X235
4) Shimadzu Application News No.X231:"Equation for Calculating Lower Limit of Detection"
5) Shimadzu Application News No.X224

* When adding Sb to the series of RoHS regulated substance for analysis, the primary filter is the same as that used for Cd. This allows simultaneous analysis, and therefore permits the total analysis to take the same time as though only Cd were being analyzed.

First Edition: Oct, 2012

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