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Application News

No.X251

X-ray Analysis

Quantitative Analysis of Tin (Sn) in Plastics by EDXRF

EDX analysis of controlled substances in electrical and electronic equipment currently includes the 5 RoHS elements (Cd, Pb, Cr, Hg, Br) and 2 halogens (Cl, Br). However, due the current restrictions and limitations placed on organic tin compounds, tin (Sn) is expected to be added to that list of controlled substances.
Although EDX cannot be used for the identification and quantitation of organotin compounds, their detection is possible based on the analysis of tin as an element.
As standard samples of PE (polyethylene) plastic spiked with tin are now commercially available, we are able to present the results of sensitivity evaluation in analyses conducted using the EDX-LE/GP (720).
Since dedicated instruments are often used for rapid OK / GRAY / NG screening analysis of these elements, here we present one such example of elemental analysis.

Samples

Sn-Containing Resin Standards (4 levels): Sumika Chemical Analysis Service, Ltd

Samples	Sn Content (ppm)
(1)	0
(2)	310
(3)	700
(4)	1100

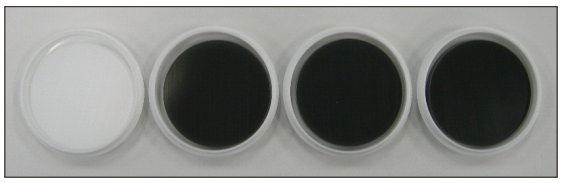

Fig. 1 Resin Standards with Sn

Calibration Curve, Lower Limit of Detection

Fig. 2 shows an Sn internal-standard-corrected calibration curve[*1] generated using the four samples, and Fig. 3 shows the corresponding intensity profiles. The calibration curve accuracy and lower limit of detection[*2] are shown in Table 1.

Table 1 Accuracy and Lower Limit of Detection for Sn

Instrument	EDX-LE	EDX-GP (720)
Calibration curve accuracy	1.4	1.0
Lower Limit of Detection	7.5	8.2

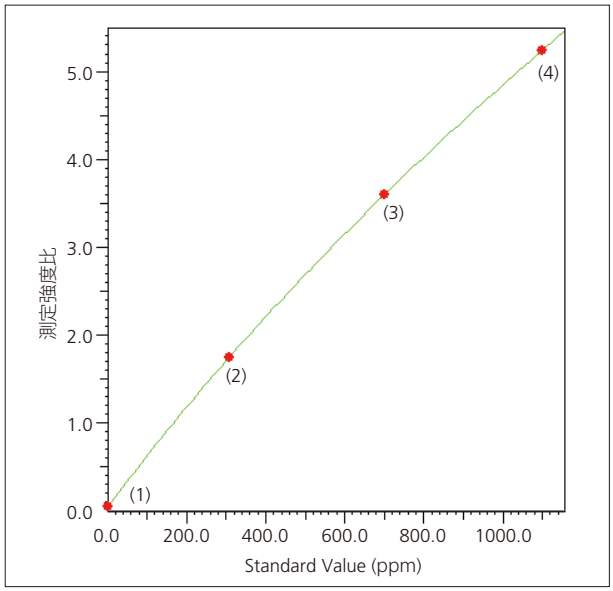

Fig. 2 Calibration Curve for Sn in Resin

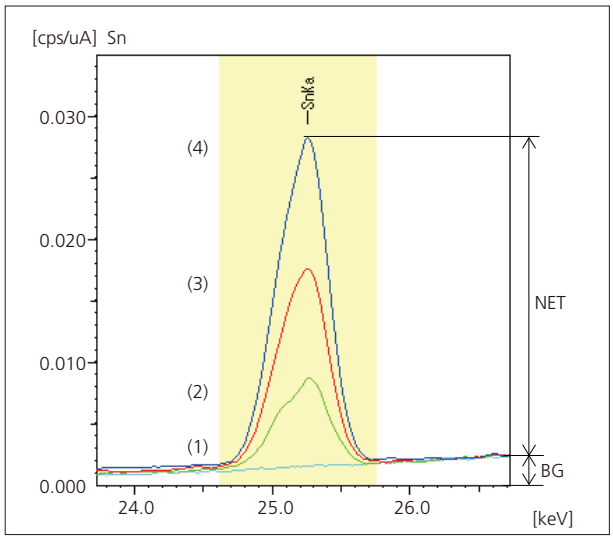

Fig. 3 Profile of SnKα

Repeatability

Using the above internal-standard-corrected calibration curve method, we conducted 10 repeat measurements using the above 700 ppm Sample (3). The repeatability test results are shown in Table 2.

Table 2 Repeatability

Instrument	EDX-LE	EDX-GP (720)
Average (ppm)	704.0	697.9
Standard deviation (ppm)	13.8	9.7
Coefficient of variation (%)	2.0	1.4

Quantitative Analysis of Unknown Sample

After setting up revised analytical conditions for 7 elements including the original 5 RoHS elements, Cl, and finally Sn, we conducted quantitative analysis of a plastic sample (Fig. 4). Fig. 5 shows the excerpted portions of the results report pertaining to quantitation and determination. As the analytical conditions for Sn are the same as those for Cd, the total analysis time was no different from that in measurement of the original 5 elements, or the 6 elements.

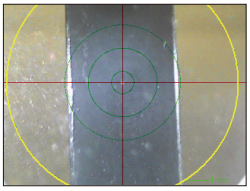

Fig. 4 Image of Plastic Sample

Element	Content	3σ	Unit	Judgement
Cd	21.8	3.2	ppm	OK
Pb	57.9	4.8	ppm	OK
Cr	56.9	5.3	ppm	OK
Hg	45.4	2.6	ppm	OK
Br	192.6	5.0	ppm	OK
Cl	ND	27.2	ppm	OK
Sn	290.3	15.5	ppm	OK

Fig. 5 Excerpt from Analysis Report for 7 Elements

Screening Analysis

Presently, the analysis of the RoHS 5 elements and Cl that is most often used is a screening analysis which can quickly determine whether or not the sample satisfies the reference value with respect to the product type and material, or whether the results fall into an intermediate area referred to as the gray zone.
Therefore, we set up screening analysis conditions in the EDX-LE that included 7 elements including Sn, and analyzed the plastic sample.
Fig. 6 shows the screening analysis determination results window. Determination was possible for all seven elements, Cd, Pb, Cr, Hg, Br, Cl and Sn. When the Sn determination threshold values were set to OK ≤ 700 ppm < GRAY < 1300 ppm ≤ NG, the determination result "OK" is generated.
Quantitation Value + 3 σ = 278.1 + 17.1 = 295.2 < 700 → OK

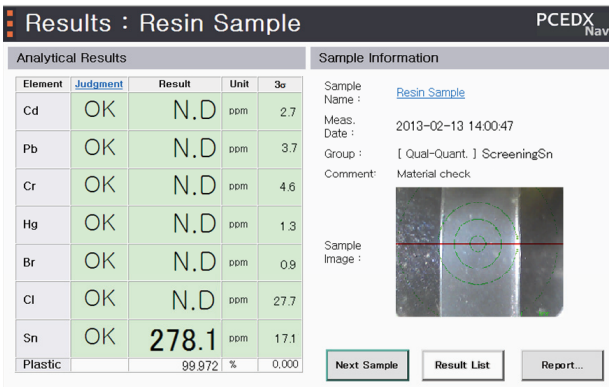

Fig. 6 Plastic Sample Screening Analysis – Determination Results Window

Conclusion

Quantitative analysis of Sn can be conducted at the ppm level using the EDX Series just as with the heavy elements including Cd, Pb, Cr, Hg, Br. Furthermore, throughput is the same as that with the conventional analysis using the RoHS analytical conditions, with no difference in the total analysis time. Thus, additions and changes to existing analytical conditions are fully supported, permitting a wide range of applications.

Analytical Conditions

Instrument	EDX-LE	EDX-GP (720)
Elements	Sn (Kα)	
Analytical Group	Working Curve	
X-ray Tube	Rh target	
Tube Voltage [kV] — Current [μA]	50–Auto	
Primary Filter*3	#1*3	#1 (#4) *3
Collimator [mmϕ]	10	
Atmosphere	Air	
Detector	Si-PIN	Si (Li)
Integration Time [sec]	100	
Dead Time [%]	40	

*1 Refer to Shimadzu Application News No. X248.
*2 Refer to "Equation for Calculating Lower Limit of Detection" described in Shimadzu Application News No. X231.
*3 When Sn is added to the analytical conditions for the 5 RoHS elements, since analysis for Sn is conducted using the same conditions as those for Cd, the total analysis time remains unchanged.

Note: If the EDX-LE is used, the additional function kit (optional) is required.

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