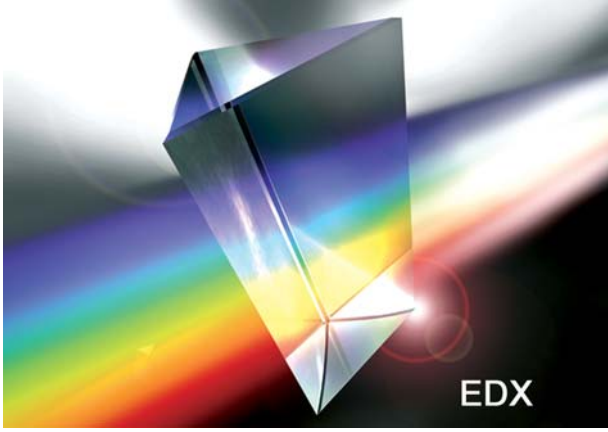
Application Note



EDXRF Analysis of Cd and Pb

Electrical and electronic equipment, Environmental, Recycling

Since the concerns regarding harmful heavy metals increase in numerous fields, improvement in the detection sensitivity of XRF analysis and the quantitative accuracy in non-standard-size samples is required. Shimadzu has approached these improvements in two ways. First, the detection sensitivity has been increased by a factor of 2 to 3 compared to conventional machines, thanks to changing the primary filter. Second, the improvement of the quantitative accuracy, regardless of the thickness, form, and size of the sample, using the BG (background) internal standard correction method[1)2)] has been examined. The results of this research show the utility and strength of XRF analysis as maximizing high throughput & non-destructive analysis. This system is very effective for use in various regulation compliance checks, such as the WEEE & RoHS directives and the ELV directive in the EU.

<Increased Sensitivity to Cd and Pb>

The detection limits of Cd and Pb in polymer resins have been improved. The new lower limit of detection (LLD) is now down to about 1/2 the previous LLD attained with conventional methods for Cd and 1/3 of that for Pb. This is achieved with two changes. One is the improvement in S/N ratio by changing the primary filter to Mo (for Cd, Tc-Ba) and Ni (for Pb, Ga-Mo, Hg-U). The other is doubling the power of the X-ray tube.

■ Samples

Cd:PVC (polyvinyl chloride) 0, 24, 48, 94, 190, and 300 ppm

Pb:PVC (polyvinyl chloride) 0, 24, 67, 230, and 500 ppm

■ Qualitative result and Lower Limits of Detection

(1) Cd 24 ppm

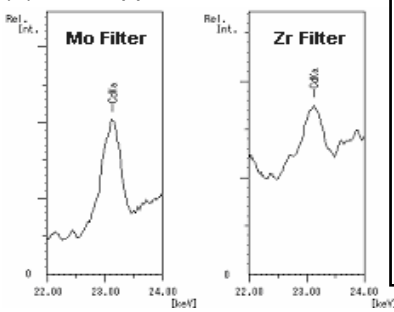


Table 1
L.L.D. of Cd in PVC
Mo filter
3. 7 ppm (300 sec)
1.9 ppm in polyethylene

(2) Pb 24 ppm

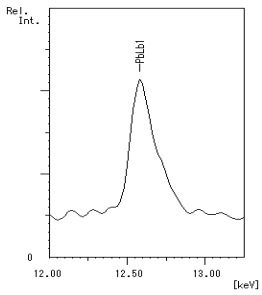
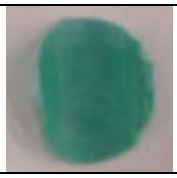


Table 2
L.L.D. of Pb in PVC
Nickel filter
8. 4 ppm (300 sec)
3.7 ppm in polyethylene

For actual samples, since additive agents such as pigments and stabilizers may be present, the LLD may differ.

<Improvement in the quantitative accuracy by the BG internal standard correction>

■ Sample: Standard sample: PE (polyethylene) standard sample, molded BCR-680, 681, and PVC
Evaluation sample: Each form of BCR-680 (Refer to photographs below)

Molds	Multiple Pellets	One pellet	Films	Curved Parts
				

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Quantitative Results

(1) Form, quantity, thickness, position, etc. were investigated. The results are shown in Table 3.

Table 3 Comparison with and without using the BG internal standard correction.

Sample BCR-680		Cd				Pb			
		with correction		without		with correction		without	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Molding, STD		140.8	1.00	140.8	1.00	107.6	1.00	107.6	1.00
Pellet	Multiple Pellets	137.2	0.97	85.5	0.61	105.0	0.98	74.1	0.69
	One piece on center	151.9	1.08	15.5	0.11	111.9	1.04	17.3	0.16
	One on the side	174.5	1.24	26.6	0.19	109.9	1.02	(-8.5)	--
	One on back side	194.4	1.38	6.8	0.05	65.0	0.60	(-8.3)	--
	One on right side	224.7	1.60	6.7	0.05	90.6	0.84	(-8.2)	--
Film	One sheet	143.4	1.02	57.5	0.41	104.7	0.97	57.9	0.54
	Two sheets	135.1	0.96	99.1	0.70	103.3	0.96	90.6	0.84
	Three sheets	140.7	1.00	132.5	0.94	101.1	0.94	109.5	1.02
	Four sheets	134.5	0.96	138.6	0.98	104.8	0.97	114.5	1.06
Curved Surface		146.8	1.04	11.4	0.08	97.0	0.90	15.4	0.14

(a) Quantitative value, (b) Ratio against standard value

(2) The quantitative test of the PE samples was carried out to investigate the effect of different resins using the PVC calibration. The results are shown in Table 4.

Table 4 Comparison with and without using the BG internal standard correction.

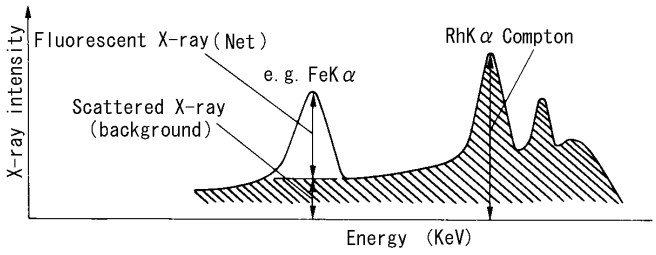
Sample BCR-	Cd				Pb			
	with correction		without		with correction		without	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
680(STD)	124.9 (140.8)	0.89	171.4 (140.8)	1.22	76.7 (107.6)	0.71	320.3 (107.6)	2.98
681(STD)	16.3 (21.7)	0.75	25.3 (21.7)	1.17	9.4 (21.7)	0.68	84.9 (21.7)	6.15

■ Conclusion

When the BG internal standard correction is performed, the errors caused by variation in form and thickness are within ±10 %, which is fairly effective compared with the ~90 % when not correcting for this. However, since this exceeds 10 % for one pellet when the measurement position is not in the center, it is necessary to use a CCD camera option for precise positioning. Moreover, even in different types of resins, this correction is quite effective for Pb, although not quite as accurate for Cd.

■ The BG-Internal standard correction method

The internal standard correction is a method of taking the fluorescent X-ray intensity and the scattered ray (BG), RhKa(primary X-ray target material), or the Compton scattered X-rays, in order to remove changes in absolute intensity due to variations in the density, form, or size of a sample. In addtion, X-rays from a matrix element or another component element may be used as an internal standard as a complement to the scattered rays.



References

1) Kimiko Seno, Hideo Ishizuka, Yoichi Motoyoshi and Kazuyuki Shiraishi, (2002): Quantitative chemical analyses of rocks with X-ray fluorescence analyzer: (3) Rare earth elements, Antarctic Record , Vol.46, No.1, 15-33
2) Hirotomo Ochi, Shinji Watanabe (2002): X-ray fluorescence analysis of minor heavy elements in soil and rock using theoretical intensity of X-ray scattering, Summaries of the 38th X-ray National annual discussion of the discussion group X-ray, 20