Application Brief

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SEA no.35 Measuring Controlled Substances in Halogen Using Fluorescent X-Ray Analysis

2008.7

1. Introduction

It is well known that the disposal and incineration of halogens releases organic halogen gases such as dioxin, which have a negative impact on the environment. Starting with the approval of the German Dioxin Ordinance, there has been a movement, particularly in the E.U, to limit the use of halogen in electrical products. In general, the focus has been on reducing the halogen content of fire retardants and additives on printed circuit boards (PCB).

The International Electrotechnical Commission (IEC) (in the document 61249-2-21) and the Japan Printed Circuit Association (JCPA) have defined "halogen-free" PCBs in the following manner. Both the chlorine and bromine content must be 900 parts per million or less and the total halogen content must be 1500 parts per million or less. The regulation of halogens continues to spread as an extension of the Restriction of Hazardous Substances Directive (RoHS). This application brief introduces methods for measuring halogens.

2. Samples and Testing Methods

Since it falls under the regulation of the RoHS directive, bromine has been tested in many forms and a correction method has been established. On the other hand, chlorine detection has been difficult because the analysis line appears in the low energy region, which makes it necessary to prepare the sample.

Figure 1 shows the relationship of polyethylene thickness and the theoretical intensity of chlorine. We can see that the chlorine intensity was close to saturation thickness at about 0.2 mm. In other words, when there is a concentration difference within a sample, it means that only surface data is being obtained. If there is a concentration difference between the interior and surface of the sample, this effect is very large.

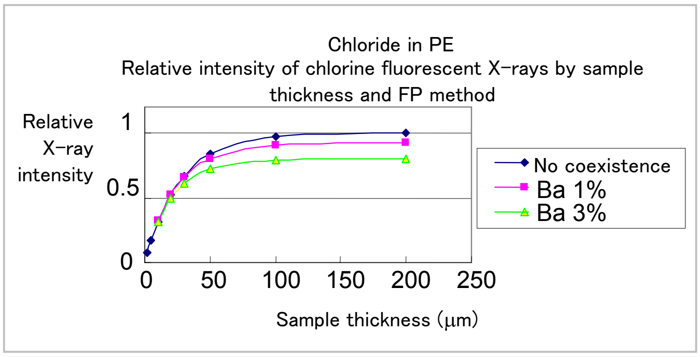

Figure 1 – Relative intensity of chlorine fluorescent X-rays by sample thickness and FP method

One method to standardize non-uniform samples is milling. A sample surface can be created by milling the sample and then compressing it. Low density powder samples in particular should be compressed.

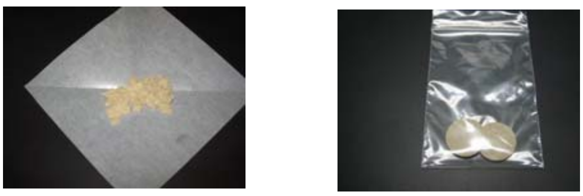

Figure 2 – A milled sample and milled and compressed samples

Measurement device:

Fluorescent X-ray analysis apparatus: SEA1200VX

Measurement conditions: See Table 1

Table 1 – SEA1200VX Measurement Conditions

	Measurement condition1
Model	SEA1200VX
Measurement time (seconds)	100
Dead time (%)	16
X-ray tube voltage (kV)	50
Tube current (uA)	500
Filter	For Cl
Sample environment	Vacuum and air
Collimator	φ8.0m
Picking time	1 μsec

Chlorine X-rays appear as an analysis line in the low energy range so the air absorbs chlorine rays and decays them. To combat this problem, Hitachi High-Tech Science optimized the detector and optical layout of the X-ray tube on the SEA1200VX so that they are closer to the sample. This improvement reduces the decay of the chloride rays to the extent that it is now possible to perform accurate measurements in air.

The unit can also measure chlorine at a high level of sensitivity when the sample is in a vacuum. This environment eliminates the interference of the adjacent argon peaks created by air.

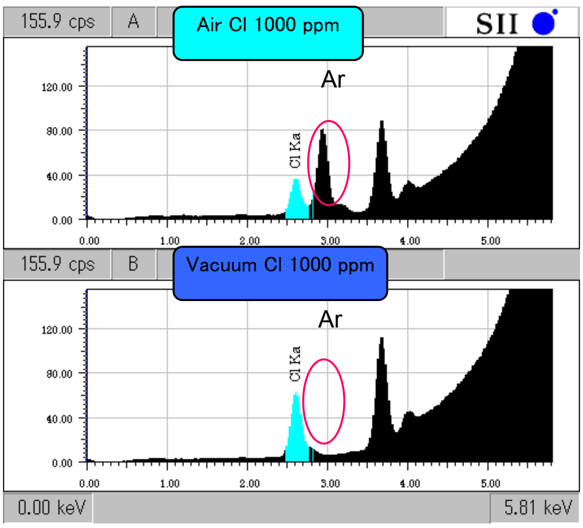

Figure 3 – Chlorine in air and vacuum environments

Features of the SEA1200VX

(1) Equipped with a chlorine filter

(2) Can measure chlorine in both vacuum and air and can measure chlorine in liquids and powders in air

(3) Has the following lower detection limits for chlorine in PE (300-second measurement time)

Air: 200 ppm Vacuum: 6 ppm

3. Results

3-1. Chlorine

Measurement was performed in a vacuum because chlorine X-rays are in an energy region that is absorbed by air. The following figures are the measured spectrum of a PCB and the chlorine calibration curve, respectively.

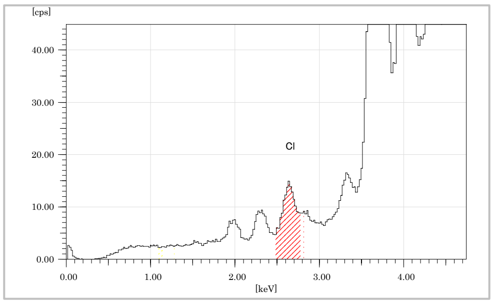

Figure 4 – Spectrum of a PCB in a vacuum

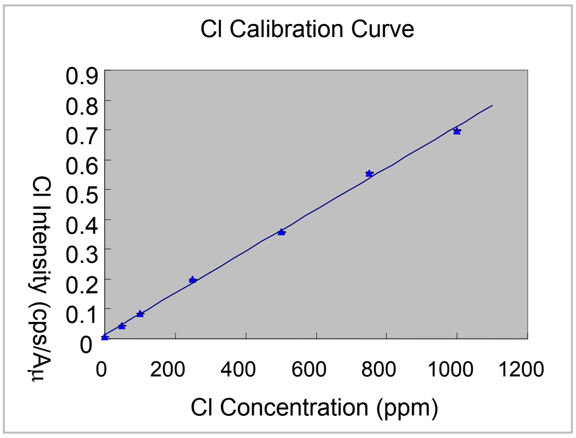

Figure 5 – Calibration curve for chlorine in a vacuum

PCBs have several layers of boards and printed surfaces. As mentioned previously, chlorine X-rays data can only be obtained from near the surface so it is necessary to divide samples and measure each section individually. The following chart shows the results of measurement of a low concentration of chlorine in an epoxy-resin PCB.

Table 2 – Measurement results of an epoxy-resin PCB

	Chlorine concentration (ppm)
Readings	10 times
Avg.	66.9 ppm
Range	7 ppm
Standard deviation	2.4 ppm
CV value (%)	3.6 %

Repeated measurements of a chlorine concentration of less than 100 ppm had a coefficient variation of 3.6 %, indicating good repeatability.

When measuring chlorine, it is difficult to correct data using scattered rays so X-ray intensity errors may occur with samples with complex shapes. When calibration curves are used, the sample surface must be flat and the irradiation areas must be uniform.

3-2. Bromine

Bromine measurements have been well-investigated for RoHS directive compliance measurements. When measuring bromine in plastic, the data must be corrected because sample shape and thickness alter X-ray intensity. The SEA unit series uses scattered X-ray correction, which was introduced in Application Brief SEA No.27.

A comparison of measurement results of a thin sample like a flexible PCB is shown below.

Table 3 – Thickness and quantity (ppm) of bromine in PCB material

No. of sample layers	Sample 1	Sample 2
1	1829	4025
4	1997	4589
8		4395
16	1692	3987
32		3956

(The thickness of one sample layer is approximately 0.05 mm)

Table 4 shows the results when the same sample was combusted, melted and then measured by either emission spectrophotometer (ICP-OES) or ion chromatography. The samples were divided in two pieces and then both pieces were measured.

Table 4 – ICP-OES/ Ion Chromatography Results for Bromine in PCB Material

Method	Sample 1	Sample 1
ICP-OES 1	1499	3669
ICP-OES 2	1517	3643
Ion chromatography 1	1670	4020
Ion chromatography 2	1628	4055

The results from the emission spectrophotometer and ion chromatography were roughly the same as those for fluorescent X-ray analysis. This suggests that to achieve the best results with fluorescent X-ray analysis, the sample thickness should be several millimeters but data correction is also effective with thinner samples.

4. Conclusion

Fluorescent X-ray analysis can measure bromine and chlorine in plastics with a high level of accuracy.