Application Brief

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SEA no.34 Measuring Controlled Substances in Toys Using Fluorescent X-Ray Analysis

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1. Introduction

Fluorescent X-ray analysis is often used as a screening tool for the Restriction of Hazardous Substances Directive (RoHS) adopted by the European Union (EU). One feature of this analysis is that it can be used for on-site product inspection because it is non-destructive and quick.

The EU document EN71 regulates the safety of toys for children 6 years and younger. Part 3 specifically deals with the ingestion of heavy metals from licking or swallowing toy parts and components. This regulation stipulates that test samples must be pre-treated with hydrochloric acid to simulate the effects if a child puts a toy in their mouth and heavy metals migrate into the body.

This pre-treatment process makes the inspection of many samples very time and labor intensive. Fluorescent X-ray analysis has received a lot of attention recently because it is non-destructive and quick. This application brief provides an example of this analysis.

2. Samples and testing methods

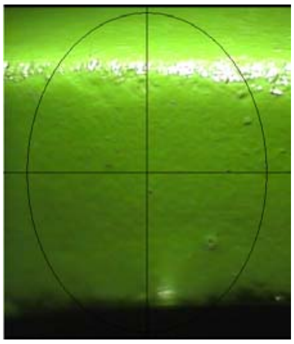
Fluorescent X-ray analysis can also be performed by filling the sample cup with elulate. However, the pre-treatment process takes considerable time and effort. In many cases, the concentration of the eluate is less than the concentration in the actual sample because the sample was only partially dissolved.

The lead concentration of toys was measured using non-destructive fluorescent X-ray analysis. These results were then compared to the concentration of dissolved samples.

Test materials:

1. Wooden
2. Rubber
3. Plastic
4. Synthetic leather

1. Wood



2. Rubber

3. Plastic

4. Synthetic leather

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Pre-treatment

Optical emission spectrometry (ICP-OES)

Sample: A sample was cut to an appropriate size (approximately 0.5 g).

Solvent: HCl 0.07mol/l, 25ml

Dissolution method: Agitated for one hour at 37°C ±0.2°C and then left to stand for one hour at 37°C ±0.2°C

Fluorescent X-ray analysis

Sample: No pre-treatment

Equipment

Fluorescent X-ray analysis:

SEA1000A or SEA1200VX

Emission spectrometry: SPS5520

Measurement conditions of the fluorescent X-ray analysis (SEA1200VX)

	Condition 1	Condition 2	Condition 3
Model		SEA1200VX	
Measurement time (seconds)	100	100	100
Dead time (%)	16	8	11
X-ray tube voltage (kV)	50	50	15
Tube current (uA)	1000	1000	1000
Filter	For Pb	For Cd	For Cr
Environment		Air	
Collimator		φ8.0 mm	

Measurement

A calibration curve for plastic was used for fluorescent X-ray analysis. As with measurements compliant with the RoHS directive, shape correction was performed using scattered X-rays.

For the emission spectrochemical analysis, a standard solution for atomic absorption analysis was diluted to create a standard solution for a calibration curve and the calibration curve method was used for measurements.

3. Results

Table 1 shows the threshold limit values for toy safety listed in EN71- part3.

Tables 2 and 3 show the results for fluorescent X-ray analysis and emission spectrochemical analysis, respectively. The fluorescent X-ray analysis confirmed the presence of Ba and other elements thought to be components of paint and Cd and other elements in plastic. Some of these items exceeded the concentration limits in EN71. On the other hand, the emission spectrochemical analysis found values much lower than those found by fluorescent X-ray analysis. These values were also lower than the EN71 standards. This comparison shows that fluorescent X-ray analysis tends to produces higher values.

Table 4 shows a comparison of the fluorescent X-ray analysis and emission spectrochemical analysis for synthetic leather. Although the samples were easily saturated by the solvent and showed a comparatively high migration quantity in emission spectrochemical analysis, the fluorescent X-ray analysis values reflected the content and detected high concentrations.

These results show that the dissolved quantity is only part of the actual sample content. To learn the true concentration, the dissolvability of the sample must be fully understood.

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Table 1 – Element migration limits from toys (from BS EN71-3) (unit: ppm)

	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Molding clay and finger paint	60	25	250	50	25	90	25	500
Other toy material	60	25	1000	75	60	90	60	500

Table 2 – Fluorescent X-ray analysis results (SEA1200VX) (unit: ppm)

	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Wood	-	-	4900	-	-	-	-	-
Rubber	-	-	99	-	-	3.9	-	-
Plastic	-	-	940	15	-	730	-	-

– : Not detected

Table 3 – SPS5520 results (unit: ppm)

	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Wood	-	-	2.5	-	-	-	-	-
Rubber	-	-	0.014	-	0.016	0.013	-	-
Plastic	-	-	-	-	-	0.009	-	-

– : Not detected

Table 4 – Fluorescent X-ray analysis (SEA1000A) and emission spectrochemical analysis (SPS5520) for synthetic leather (unit: ppm)

	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
X-ray	-	-	2000	19	-	860	-	-
ICP-OES	-	-	217	2.2	0.2	43	-	-

– : Not detected

4. Conclusion

While the results of emission spectrochemical analysis of dissolved samples and direct non-destructive X-ray measurement do not always match, fluorescent X-ray analysis precisely detects the presence of controlled substances in samples. While the material content is small, it does migrate out so the concentration must be investigated.

In cases where many samples need to be measured, it is necessary to have a screening method that can quickly calculate concentrations and detect the presence of controlled substances. Suspicious samples can then be more precisely analyzed.

These results in this application brief confirm that fluorescent X-ray analysis can easily measure the danger of migration and is an effective screening method.

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