



RoHS & WEEE Compliance: Analysis of PolyVinyl Chloride (PVC) and Acrylonitrile-Butadiene Styrene (ABS) Polymers

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XRF has emerged as an optimal solution for the screening of toxic heavy metals regulated by the EU Directives, RoHS (Restriction of Hazardous Substances) and WEEE (Waste Electronic and Electrical Equipment). The RoHS directive restricts the use of lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame-retardants in electrical and electronic equipment. Manufacturers of the many plastic components found in electronic devices will have to comply with the RoHS directive from July 2006. The MiniPal 4 RoHS WEEE – an energy-dispersive X-ray fluorescence spectrometer – provides a RoHS/WEEE screening function of the restricted elements. This datasheet describes a straightforward, robust method for the analysis of RoHS elements in two very different types of polymers (ABS and PVC) using a single calibration.

RoHS limits

The limits as set by the RoHS directive for the regulated substances are given in Table I.

Standards

The application was calibrated using two sets of standards, including both ABS and PVC polymer types (Analysis Center Co., Ltd., Japan). These standards covered concentration ranges of 0–1000 ppm for Cr, Cd, Br, Hg and Pb.

Table I: Limits for RoHS directive

| Element | Limit |
|-------------------------|----------|
| Pb, Hg, Cr6+, PBB, PBDE | 1000 ppm |
| Cd | 100 ppm |

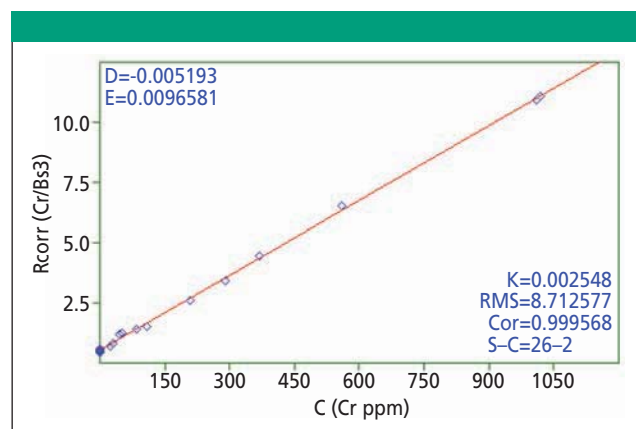


Figure 1: Calibration graph for Cr.

Instrumentation

Measurements were performed using a PANalytical MiniPal 4 RoHS WEEE EDXRF spectrometer, equipped with a 30 kV molybdenum anode tube, five filters, a helium purge facility, a high-resolution Silicon Drift Detector, a spinner and a 12-position removable sample changer.

Measurement procedure

Two different measurement conditions were used. Condition 1 to measure all RoHS elements, while condition 2 was used to measure the background scatter for applying matrix correction. These measurement conditions are given in Table II. The total measurement time per sample was 13 minutes.

Accurate calibration results

Figures 1–5 show calibration plots for Cr, Cd, Br, Hg and Pb, respectively. The calibration details are summarized in Table III. Matrix corrections were made for all five elements using a ratio channel. This matrix correction makes it possible to define a single calibration for the analysis of both PVC and ABS types of polymer.

Table II: Measurement conditions

| Condition | Elements | kV | μ A | Filter | Meas. Time (s) |
|-----------|--------------------|----|---------|--------|----------------|
| 1 | Cr, Cd, Br, Hg, Pb | 30 | 300 | Cu | 600 |
| 2 | Bg scatter | 30 | 40 | Al | 180 |

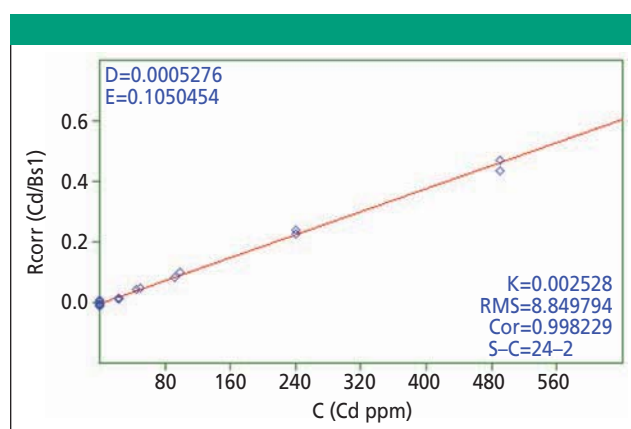


Figure 2: Calibration graph for Cd.

Table III: Calibration details and detection limits

| Element | Cr | Cd | Br | Hg | Pb |
|-------------------------------|--------|--------|--------|--------|--------|
| Conc. range (ppm) | 0-1020 | 0-490 | 0-550 | 0-1250 | 0-1120 |
| RMS (ppm) | 8.7 | 8.8 | 7.6 | 16.7 | 18.5 |
| Correlation (r ²) | 0.9996 | 0.9982 | 0.9988 | 0.9988 | 0.9980 |
| LLD (ppm) | 2-4 | 15-18 | 1 | 1 | 1 |

Table IV: Repeatability measurements on a PVC sample (n=20)

| Element | Cr | Cd | Br | Hg | Pb |
|---------------------|-----|-----|-----|-----|-----|
| Average conc. (ppm) | 44 | 94 | 0.1 | 0 | 991 |
| Std. dev. (ppm) | 3 | 6 | 0.3 | 0.4 | 4 |
| Std. dev. (rel%) | 6.4 | 6.5 | n/a | n/a | 0.4 |

Limits of Detection

The estimated Limits of Detection (LLDs) for Cr, Cd, Br, Hg and Pb are also shown in Table III and are based on a 600 s measuring time. These limits are based on 3σ and are calculated from the standard deviation of twenty repeated measurements on blank PVC and ABS samples.

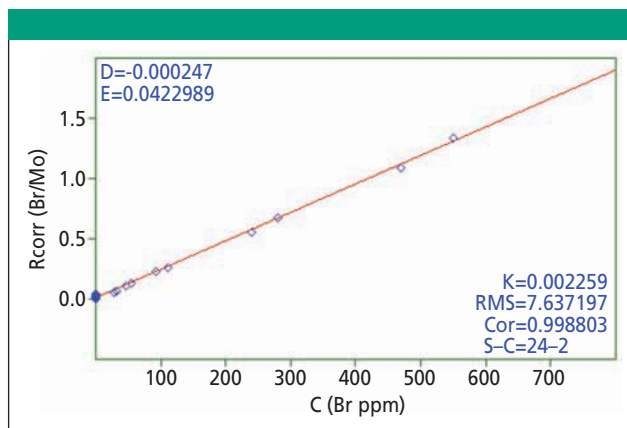
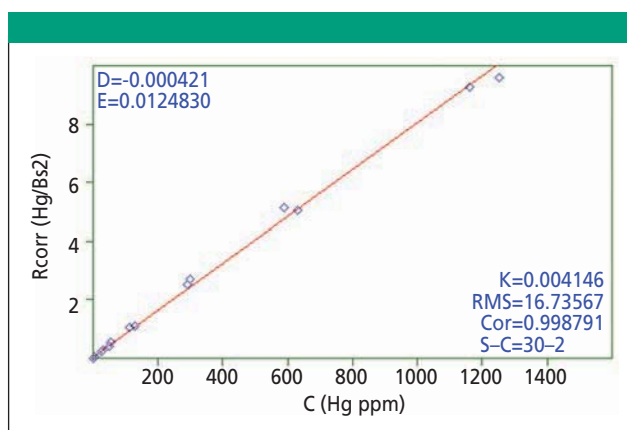
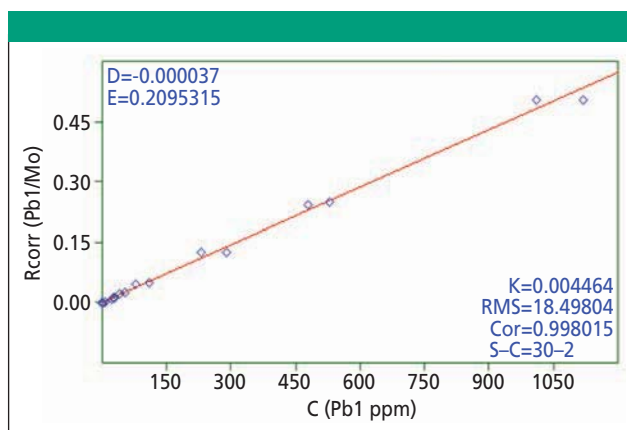
Precision results

To show the precision of the method, a PVC sample was measured 20 times consecutively. The results are presented in Table IV.

Summary

The results show that the MiniPal 4 RoHS WEEE analyzer is suitable for the screening of Cr, Cd, Br, Hg and Pb in plastics for RoHS/WEEE compliance.

Cadmium was analyzed using the $K\alpha$ line rather than the $L\alpha$ line. Even though this may result in lower sensitivity for Cd, the accuracy of the analysis is far better. The Cd $L\alpha$ line suffers from interferences by Cl (in PVC) and Ca (can be present in ABS). By using a Cu 75 μ m filter, optimum sensitivity and detection limits are obtained for Cd.

**Figure 3:** Calibration graph for Br.**Figure 4:** Calibration graph for Hg.**Figure 5:** Calibration graph for Pb.

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