EDXRF for RoHS/WEEE Compliance Testing of Plastics

Energy Dispersive X-Ray Fluorescence (EDXRF) is a very powerful technique for measuring the concentration of elements in a sample. It is fast, non-destructive, requires no sample preparation, and can be carried out in the field or on a factory floor by operators with minimal training. It is a very important complement to other methods in analytical chemistry.

Amptek, Inc. provides components used in many EDXRF systems. Amptek is an OEM provider of X-ray detectors, preamplifiers, signal processing electronics, X-ray tubes, and analysis software to many of the companies providing turnkey EDXRF analyzers. These components are also used in custom systems, when the requirements not met by turnkey analyzers.

This note illustrates an application of Amptek's products: verifying compliance with RoHS/WEEE directives (measuring Cr, Br, Cd, Hg, and Pb at 100-1000 ppm) in polyvinyl chloride (PVC) and polyethylene (PE). A laboratory prototype was assembled, based on Amptek's "Experimenter's XRF Kit". Thirty second measurements gave a detection limit of 30 to 150 ppm.

This application is shown both because of the practical importance of RoHS/WEEE compliance and because it illustrates several important effects one must consider. The introduction provides an overview of the application, system, and results. This is followed by a section providing an overview of quantitative analysis with EDXRF, then a section discussing some key considerations: matrix effects, optimizing the excitation source, and optimizing count rates.

1   INTRODUCTION

The European Union has issued two directives, the Restriction of Hazardous Substances (RoHS) and Waste in Electronic and Electrical Equipments (WEEE) directives, which limit the use of lead, cadmium, mercury, hexavalent chromium, and brominated flame retardants in consumer electronics [i]. The RoHS limits are < 100 ppm for Cd and < 1000 ppm for Pb, Hg, Cr{6+}, and Br in each homogeneous component of a product, e.g. a molded plastic components or solder joints in a printed circuit board. A company selling consumer electronics in Europe must verify that their products are compliant with these directives. Similar requirements are found in many other companies.

EDXRF has emerged as the primary method for screening products for RoHS/WEEE compliance. EDXRF has some key advantages over other methods. First, it is non-destructive, causing no damage to the sample tested. This is very important for routine screening of products which must ship, permitting up to 100% screening. Second, it requires no sample

preparation. Third, it takes only tens of seconds per item. Finally, the measurement uncertainty of 10-50 ppm is sufficient to verify compliance with RoHS/WEEE. There are other methods used in chemical laboratories to analyze elemental concentration, some with far better accuracy. But these are destructive so cannot be used to screen items which will ship. They are also labor intensive, slow, and costly. EDXRF provides quick and non-destructive screening of many products, with other methods used to validate the EDXRF results.

PROTOTYPE ANALYZER DESCRIPTION

The laboratory prototype used here is shown in Figure 1. It is not packaged for commercial use but contains all of the components necessary to carry out EDXRF analysis and is fully functional. Everything except the mechanical fixture and radiation shielding are standard products from Amptek, Inc. It includes

1) An Amptek 25 mm^2 SDD X-ray detector, with a resolution of 128 eV at the Mn K$_\alpha$ line.

2) An Amptek X-123-SDD incorporating a DP5 digital pulse processor and PC5 power supplies, operated here at a peaking time of 9.6 μs (shaping time of 4 μs), output count rate of 8 kcps, dead time of 15%.

3) An Amptek Mini-X X-ray tube with a W anode, at 40 kVp and 50 μA, with a W/Al filter.

4) A mechanical fixture to hold the detector, tube, and sample, along with radiation shielding.

5) Amptek's ADMCA software for data acquisition and control of the signal processor and software to control the X-ray tube. Both use a USB interface.

6) Amptek's XRS-FP software for spectrum processing and quantitative analysis.

The system was not fully optimized for this application but demonstrates key considerations.

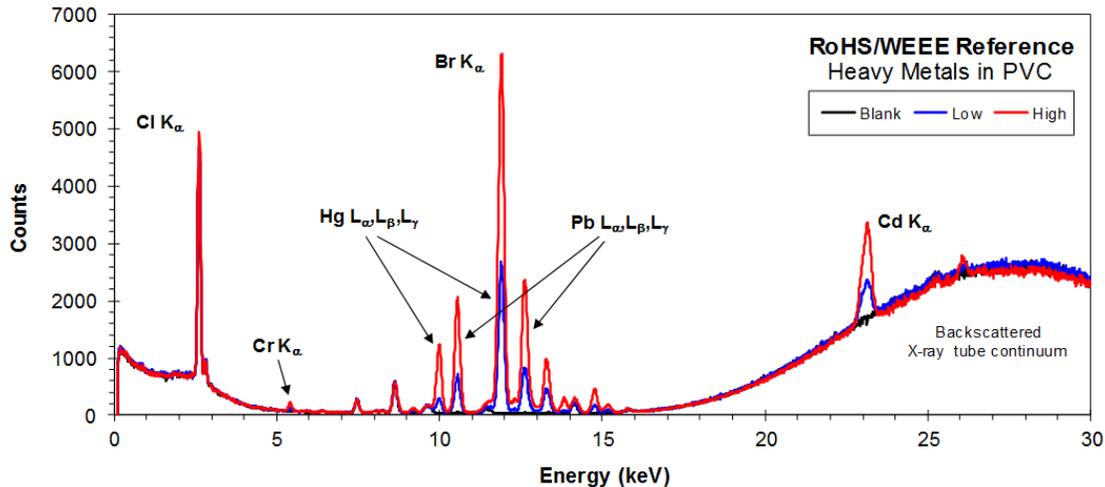Figure 1. Photograph of the prototype analyzer.

Figure 2. Spectra measured from three PVC reference standards, a blank (black trace), a standard with low levels of the RoHS elements (blue trace), and a standard with high levels of the RoHS elements (red trace).

SPECTRA

Figure 2 shows raw spectra taken on a set of reference samples[2], with the five RoHS elements in PVC matrices. There are three samples: a blank, one with low concentrations of the elements (100 to 500 ppm), and one with high concentrations (300 to 1000 ppm). Actual concentrations are shown in Table 1.

This spectrum shows how clearly the characteristic X-ray lines of the elements of interest can be seen. It also illustrates the key to quantitative analysis: the intensity of the characteristic X-ray lines increase with concentration. For example, in the Cd K_α peak at 23.2 keV, the 100 ppm measurement (the blue trace), is clearly distinguished from the background and its peak has ⅓rd the area of the 300 ppm result (the red trace).

These spectra also illustrate some key challenges in quantitative analysis. These include the large background on which the Cd peak is superimposed, the low intensity of the Cr peak, the presence of additional X-ray lines (such as the Cl line, due to the chlorine in the polyvinyl chloride matrix), and the overlapping Br K_α and Hg L_β photopeaks.

RESULTS

Once the system was setup and configured, calibration spectra were taken using the six samples (three concentration levels for both PVC and PE). These spectra were used to calibrate the XRS-FP analysis software, using a linear least-squares approach. A set of 50 spectra were then taken on each sample, with 30 second data acquisitions, and analyzed using the calibration values. Figure 3 and Table 1 shows the results of the analysis, comparing the measurement results to the certified values for these samples. In Table 1, the mean value of the measurements is shown along with the measured standard deviation of the results.
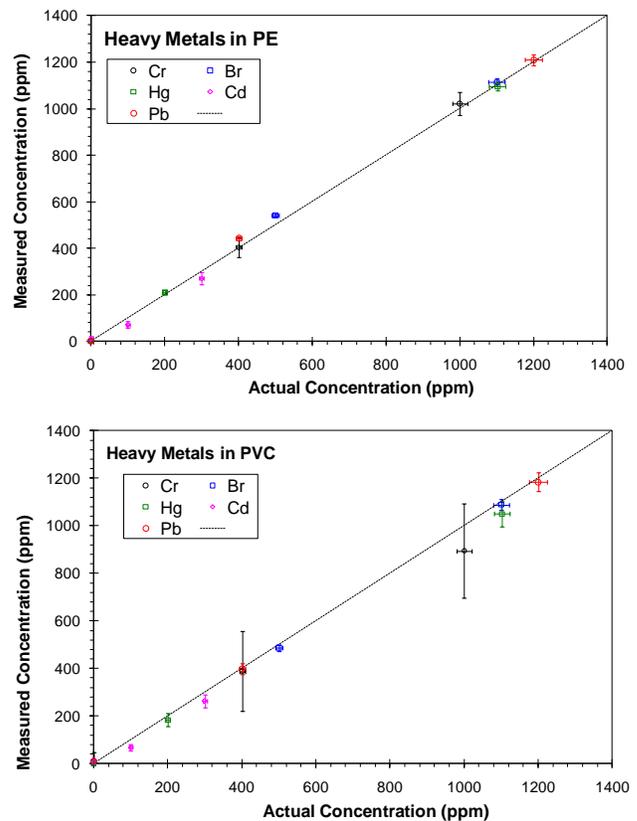

Figure 3. Plots comparing the measured concentration of the elements of interest to the certified values for PE (top) and PVC (bottom).

Except for Cr in PVC, the measurement uncertainty for the blank is about 10 ppm, which implies a detection limit of 30 ppm. Even the Cr in PVC has an uncertainty of <50 ppm, for a detection limit of 150 ppm. Since the regulatory limits are 100 ppm (for Cd) and 1000 ppm for the other elements, this prototype demonstrates the ability to meet the measurement requirement.

		Certified		Measured PE		Measured PVC	
High	Cr	1000	± 20	1022	± 50	895	± 198
	Br	1100	± 22	1114	± 17	1089	± 23
	Cd	300	± 6	270	± 25	264	± 28
	Hg	1100	± 22	1096	± 19	1050	± 53
	Pb	1200	± 24	1210	± 23	1184	± 39
Low	Cr	401	± 8	404	± 41	388	± 167
	Br	500	± 10	541	± 7	487	± 13
	Cd	100	± 5	72	± 15	68	± 13
	Hg	200	± 5	209	± 9	183	± 27
	Pb	400	± 8	442	± 11	398	± 23
Blank	Cr	0	± 5	2	± 9	7	± 40
	Br	0	± 5	0	± 0	1	± 2
	Cd	0	± 5	11	± 10	9	± 10
	Hg	0	± 5	0	± 0	0	± 0
	Pb	0	± 5	0	± 0	10	± 9

Table 1. Summary of measurement results, in ppm.

2   DISCUSSION

MATRIX EFFECTS

Matrix effects are very important in EDXRF analysis and are clearly demonstrated in the data taken here. Figure 4 shows two spectra, both taken with "high" standards so they have the same concentration of the analytes (Cr, Br, Hg, Pb, and Cd), and under the same conditions (beam energy, filtering, etc) but using the PVC and PE plastics.

Note that the characteristic X-ray lines are less intense with the PVC than with PE. The chlorine in the PVC attenuates the characteristic X-rays much more strongly than the hydrocarbons in PE. This attenuation depends strongly on the energy: the Cd peak is of comparable intensity in the two samples, while the Cr peak is very weak with the PVC. Table 2 shows that the Cr photopeak intensity is seven time higher in PE than PVC.

	Intensity		Ratio
	Cts/sec/ppm		
	PE	PVC	PE/PVC
Cr	0.019	0.003	7.0
Br	0.559	0.127	4.4
Cd	0.385	0.259	1.5
Hg	0.165	0.029	5.7
Pb	0.205	0.044	4.7

Table 2. Photopeak intensities in PVC and PE.

This matrix effect has two important consequences. First, if one were to calibrate the software with one plastic, then measure with another, the error can be a factor of seven! This is quite significant. Second, the count rate from Cr is much lower in PVC than PE, therefore the precision of the Cr measurement is much worse in PVC. This is why the measurement uncertainty is so much worse for the Cr in PVC than in PE. In general, the measurement uncertainty shown in Table 1 is larger for the PVC than for the PE.
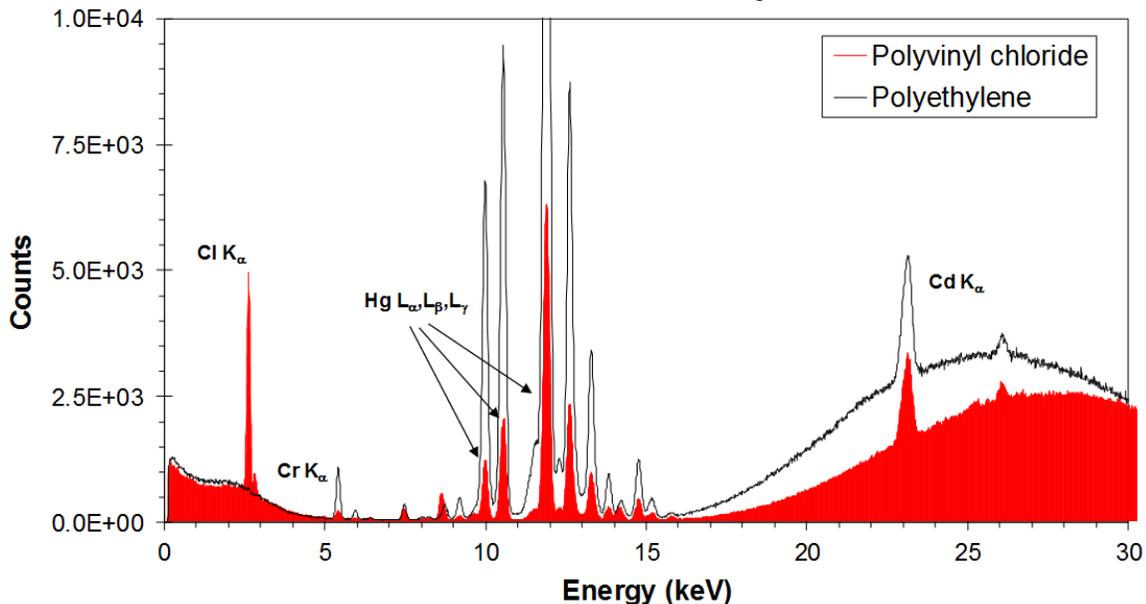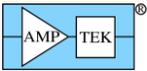

Figure 4.   Spectra taken from PVC and PE "high" samples under the same conditions and measurement times, illustrating the matrix effect and the importance of matrix corrections.

Correcting for the matrix effect

For purposes of this application note, we separately calibrated and measured the PVC and PE samples. We kept two sets of calibration constants and applied each to the known sample. For real world applications, one must use the correct calibration constants for the plastic to be measured. There are several different possible solutions:

1) Maintain separate calibration standards for each plastic matrix and to require an operator to select the correct matrix. This requires one to calibrate for each possible plastic matrix and requires operator input. In many applications, the operator will know what plastic is being tested.

2) Maintain separate calibration standards for each plastic matrix and estimate the matrix properties from the backscatter spectrum. In Figure 4, the backscatter peak has a lower intensity and a higher mean energy with PVC than with PE. The shape and intensity of the backscatter spectrum depend on the mean Z of the matrix so can be used to select calibration values.

3) Use the "Scattered Intensity Ratio" to estimate the mean Z and the calibration constants. This is discussed in more detail in a different Amptek Application Note. With an Ag anode X-ray tube, the Ag K_α lines undergo both Compton and Rayleigh scattering. X-rays scattered by the two processes have different energies, and the ratio of the intensity of the two lines depend on the mean Z of the matrix.

Linear Least-Squares Approach

In these samples, the intensity of each photopeak was found to directly proportional to the concentration of the corresponding element and independent of the concentration of the other elements. This permitted the use of a linear quantitative analysis method. This linearity is not a general property of EDXRF. In general, atoms in the sample will absorb X-rays from elements with higher energy lines, and this affects the intensity of both. For example, Cr in the plastic will absorb X-rays emitted by Hg, Pb, etc. The intensity of Hg, Pb, etc lines is thus reduced while the intensity of the Cr lines is enhanced. In the samples measured here, the concentration is low enough that the absorption and enhancement effects may be ignored. At higher concentrations, one must correct for these inter-element effects. In XRS-FP, the "fundamental parameters" analysis option carries out this correction.

EXCITATION SPECTRUM EFFECTS

The energy and filtering of the excitation source can have a very important impact on the measurement results. Figure 5 shows spectra measured from the PVC

high standard for three different X-ray tube configurations: (1) 40 kVp with a filter using 25 μm W and 1000 μm Al, (2) 35 kVp with 1000 μm Al, and (3) 35 kVp with no filter. The beam current was adjusted to give the same dead time in all cases.
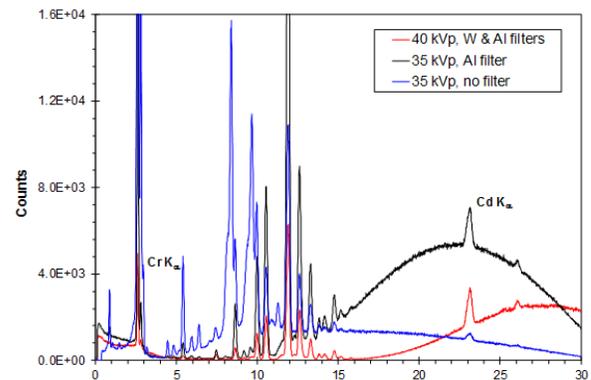

Figure 5. Plot showing spectra measured from the PVC high standard for three different tube energy and filter configurations.

It is interesting to compare the photopeak and background intensities for the lowest and highest energy photopeaks, for Cr and for Cd.

- The Cd K_α photopeak intensity is about the same for configurations (1) and (2) but is much lower for (3). The Cd K_α background is very high for configuratin (2). The Cd measurement will be best for configuration (1), with a high energy input spectrum: it gives a good photopeak intensity and low background.

- The Cr photopeak intensity is four times higher for (2) than for (1) and five times higher for (3) than for (2). Elements are most efficiently excited for incident X-rays just above their K edge. As the beam is filtered more strongly, the flux just above the Cr K edge is reduced, so the photopeak intensity is reduced. For the intermediate energy peaks, configurations (2) and (3) increase both the photopeak and background intensity.

The data shown in Figure 2, Figure 4, Table 1, and Table 2 were all taken with configuration (1),a 40 kVp beam filtered with 25 μm W and 1000 μm Al. This high energy beam provides a relatively good measurement for Cd (which has the lowest detection limit in the RoHS/WEEE regulations) but a degraded measurement for Cr.

The excitation energy and filtering are clearly important and the optimum configuration may be quite different for high and low energy elements. One often must compromise to find the best overall result for the measurement conditions. Some instruments utilize a filter wheel, with several filters which can be moved into the beam as needed. This adds complexity but permits better optimization.

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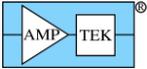
OPTIMIZING THE COUNT RATE

For this application note, we chose T_{peak}=9.6 μs, which gives the best energy resolution, and limited the beam current to keep the dead time to 15%. These were chosen because they yield very nice plots which show clearly the features of the spectrum. But they are generally do not yield the best analytical results.

For most applications, the best analytical results (i.e., the lowest detection limits, fastest measurements, and minimum measurement uncertainty) are obtained at high count rates, even if the energy resolution is degraded and the dead time and pile-up fraction are increased. The analytical software is very good at determining the peak area, even when the peak does not look as good to the eye. The statistical uncertainty scales as one over the square root of the counts. If one sets T_{peak}=2.4 μs, then with an SDD there is little loss of energy resolution (e.g. 145 vs 128 eV FWHM at the Mn K_α line) but, for the same dead time, a factor of two improvement in precision. And the processing software can easily correct for dead time fractions up to 50%.

Figure 6 shows three different spectra of the "Low" PE sample. The black trace was taken under the conditions used for this analysis. The blue trace was taken at a factor of four higher count rate, for 50% dead time. The red trace was taken at 2.4 μs peaking time, at the same count rate as the blue. If the X-ray tube had enough power, one could easily operate at 2.4 μs peaking time and 50% dead time with negligible change in the spectrum.
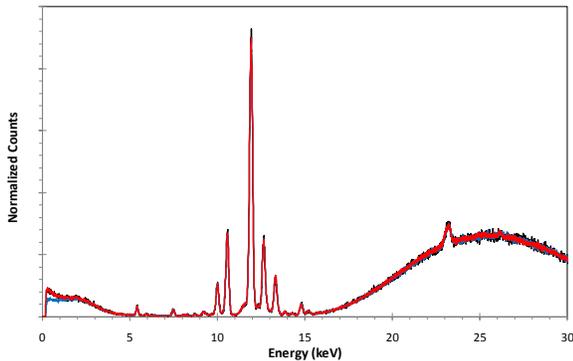

Figure 6. Spectra taken under different conditions.

The results in this note were found with thirty second data acquisitions, using the settings for the very best energy resolution. Similar results could be obtained four times as fast, e.g. 7 seconds, using the Amptek's Mini-X at maximum power. This is a compact X-ray tube, intended for portable instruments. With a higher power tube in a bench top instrument, the data could be acquired in 2 seconds. Users will often configure the system to give the best resolution, but much better results are often obtained by reducing the peaking time and increased the dead time fraction.

3 CONCLUSIONS

This note shows one possible application of Amptek's EDXRF equipment, verifying compliance with RoHS/WEEE directives. It shows how Amptek's "Experimenter's Kit" can be used and demonstrates a suitable detection limit, 10 to 150 ppm, in thirty second measurements.

This application also illustrates some interesting challenges in EDXRF. It shows how important matrix effects can be, it shows the trade-offs involved in selecting the energy and filtering of the excitation source, and it shows how to improve count rates to make these measurements in only a few seconds.

[i] Directive 2002/95/EC, "Restriction of certain Hazardous Substances Directive," and Directive 2002/96/EC, "Waste Electrical and Electronic Equipment," the European Union.

[2] Analytical Reference Materials, Inc., 700 Corporate Cr., Suite A, Golden, CO, 80501.