Application note

X-ray fluorescence

Analysis of plastics and polymers for RoHS/WEE compliance by EDXRF

ARL QUANT'X Energy Dispersive X-Ray Fluorescence Spectrometer

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Introduction

Heavy metals have been used for many years in the production of plastics. Plastics, in turn, have become pervasive materials in the production packaging of goods. Electrical equipment and consumer electronics, for example, are often made with plastics containing hazardous elements. However, the destruction or recycling of plastics and goods which contain them has led to the potential release of these heavy metals as toxins into the environment.

In recognition of these potentially toxic effects and the large scale of plastic-related waste streams, several countries and regions are stepping up attempts to prevent the release of hazardous substances by enforcing new regulations for monitoring the level of hazardous substances in the manufacture, recycling and destruction of products that include plastic.

RoHS stands for the European Union (EU) Directive on the Restriction of Hazardous Substances, which restricts the use of hazardous substances in electrical and electronic equipment to protect the environment and public health.

WEEE stands for the European Union (EU) Directive on Waste Electrical and Electronic Equipment. This directive establishes a set of rules for treating waste electrical and electronic equipment, in order to contribute to a circular economy.

Elements and compounds

Elements and compounds covered under these WEEE/RoHS directives are lead (Pb), cadmium (Cd), mercury (Hg), hexavalent chromium (Cr (VI)), polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), bis(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), dibutyl phthalate (DBP) and diisobutyl phthalate (DIBP).

These directives are introduced to reduce the damage both to the environment in terms of pollution and to human health from occupational exposure and exposure following disposal.

The allowed limits of concentrations for each element/compound are listed in Table 1.

Compound	Symbol	Conc., ppm
Lead	Pb	1000
Mercury	Hg	1000
Cadmium	Cd	100
Hexavalent chromium	Cr (VI)	1000
Polybromobiphenyls	PBB	1000
Polybromodiphenylethers	PBDE	1000

Table 1: Allowed limits of concentrations for each element/compound.

Regulations outside the European Union (EU)

Other countries and regions have similar legislation and guidelines. In this respect, it is worth mentioning ASTM F2617-08, the international standard test method for identification and quantification of Cr, Br, Cd, Hg, and Pb in polymeric material using energy dispersive X-ray spectrometry.

ARL QUANT'X and its capabilities to meet WEEE/RoHS compliance

Energy Dispersive X-ray spectrometry is the ideal analytical technique to meet WEEE/RoHS compliance. It is easy to use, non-destructive and requires little or no sample preparation.

While XRF is an elemental technique and is not compound specific, it provides results on total Pb, Cd, Hg, Cr and Br levels. Additional testing must be done to determine the specific levels of hexavalent Cr (VI) as well as PBB and PBDE.

The Thermo Scientific™ ARL™ QUANT'X is a high-performance benchtop Energy Dispersive XRF system. It is equipped with a 50 Watt X-ray tube which features a Rh or Ag anode. A large area silicon drift detector (SDD) covers detection of all elements with atomic number 11 (Na) to 95 (Am) when fitted with a Be window and down to atomic number 6 (C) with a graphene instead of Be window.

With its high count rate capability and excellent resolution, the ARL QUANT'X EDXRF measures solid and liquid samples, bulk samples, or thin films, and it is capable of handling multi-matrix and multiple elements with a wide dynamic range going from lower ppm to %.

The ARL QUANT'X EDXRF is accompanied by an outstanding analytical software allowing for multiple calibration options such as theoretical and empirical models, pure element standards, type or custom standards. In addition, a semi-quantitative, standardless analysis option is also available.

Polyethylene and polyvinylchloride standards

Thermo Fisher Scientific provides a set of polymer standards to calibrate and validate the ARL QUANT'X EDXRF to meet RoHS requirements. The set consist of three polyethylene (PE) and three polyvinylchloride (PVC) standards. For each type of polymer there are a blank and two concentration levels as shown in the table below.

In the next sections we will show how these standards are used to calibrate the ARL QUANT'X EDXRF. An ARL QUANT'X with Ag target X-ray tube and SDD with Be window was used to measure the standards.

Excitation conditions

Table 3 below shows the excitation conditions used to determine the different elements. Since all elements covered by the RoHS directive emit characteristic X-rays of relatively high energy and therefore not absorbed by air, measurement in vacuum or helium isn't necessary. The current is adjusted automatically per condition and per sample, to achieve a dead time of 50%.

We use three conditions in total to optimize the excitation of all five elements. At the expense of some sensitivity, the number of conditions could be reduced to two by eliminating condition Mid Za and adding Cr to condition Mid Zc. Measurement time is set to 100 s live time per condition.

	Cr ppm	Br ppm	Cd ppm	Hg ppm	Pb ppm
PE-1	0	0	0	0	0
PE-2	500	500	50	500	500
PE-3	1000	1000	100	1000	1000
PVC-1	0	0	0	0	0
PVC-2	500	500	50	500	500
PVC-3	1000	1000	100	1000	1000

Table 2: Nominal concentration levels of polymer standards.

Condition	Filter	Voltage, kV	Current	Atmosphere	Live time, s	Elements
Mid Za	Thin Ag	16	Auto	Air	100	Cr
Mid Zc	Thick Ag	30	Auto	Air	100	Br, Hg, Pb
High Zb	Tick Cu	50	Auto	Air	100	Cd

Table 3: Excitation conditions.

Spectrum acquisition

As an example, Figure 1 below shows the spectrum of standard PE-2 obtained using condition High Zb labeling the most important element lines. Most of the element lines are well resolved. In case of spectral overlap, the software's spectrum deconvolution algorithm derives net background-corrected intensities for every element characteristic line.

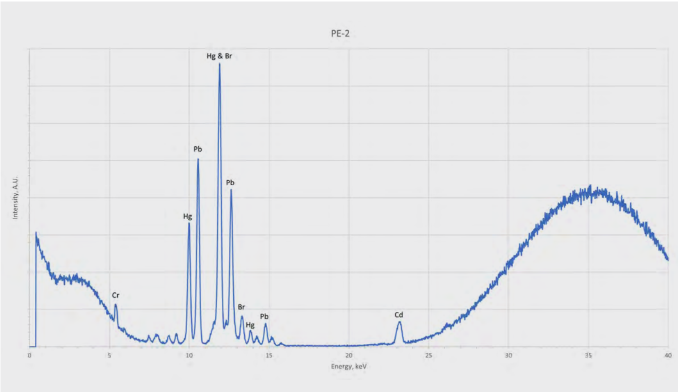


Figure 1: Spectrum of PE-2 obtained with condition High Zb.

Calibration

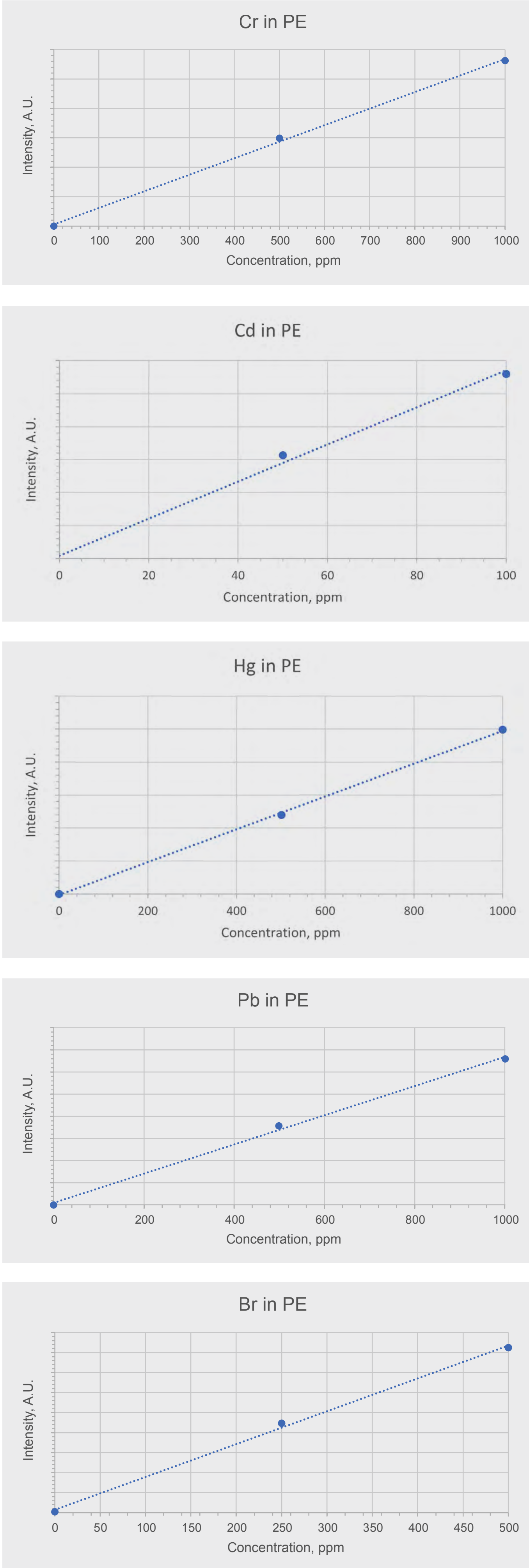
For the concentration ranges at hand, the relationship between element concentration and the element characteristic line intensity is a straight line. Quantitative analysis is straightforward when the matrix doesn't change. Whether the matrix is PE or PVC is verified by the absence or presence of an intense Cl peak. Figures 2a, 2b, 2c, 2d and 2e show the calibration curves to determine the elements in PE.

Limits of detection

Table 4 below shows the limits of detection for the different elements in both PE and PVC matrices, obtained using the conditions mentioned in the table. The detection limits were determined by analyzing the blank PE and PVC samples, 10 times in a row (10 repeats) and calculating the standard deviation for each series of determined concentrations. The limit of detection equals the standard deviation multiplied by three. For all elements except Cd, the limits of detection are around or below 1 ppm. The limit of detection for Cd is slightly higher at 2 to 3 ppm.

	Cr ppm	Br ppm	Cd ppm	Hg ppm	Pb ppm
PE	0.4	0.2	3.1	0.3	0.4
PVC	1.1	0.7	2.6	1.1	0.6

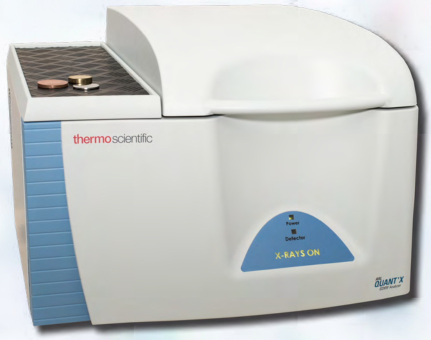
Table 4: EDXRF limits of detection.



Figures 2a, 2b, 2c, 2d, 2e: Calibration curves of specific elements in polyethylene (PE).

Conclusion

The ARL QUANT'X EDXRF Spectrometer is a high-performing and easy-to-use instrument for the determination of the concentrations of Cr, Cd, Hg, Pb and Br in polymers. A set of polymer standards allows for easy setup and calibration of this analytical tool. Sample preparation is straightforward and analysis in air, combined with short measurement times, allows for a cost-effective analytical solution. The limits of detection achievable with this instrument are largely sufficient to meet the quantification requirements of the RoHS directive.



ARL QUANT'X EDXRF Spectrometer.

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