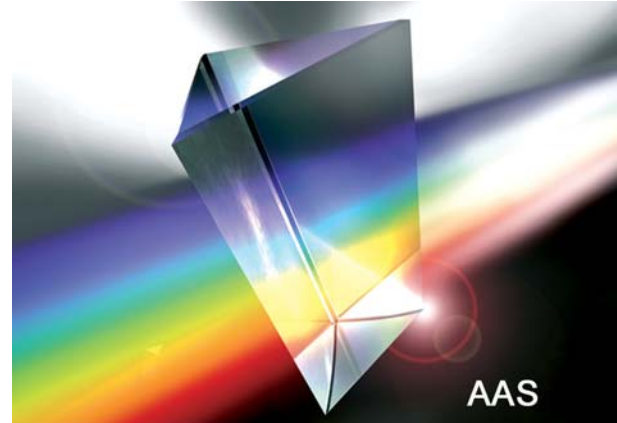


Application Note



The Determination of Hazardous Substances According to RoHS and WEEE Directives

Abstract

1st July 2006 is an important deadline for the electro- and electronics industries. This date bans hazardous substances like lead, cadmium, mercury, hexavalent chromium and polybrominated biphenyls and diphenyl ethers from electro- and electronic equipment. This restriction, even though in discussion since 1991, has become more and more important from year to year because of tons of electronic waste releasing toxic substances which are accumulated in the environment, the food chain and all human beings. In order to enforce the substances ban and the limitation or substitution of hazardous components, elemental analysis is obviously the most important control measure for monitoring limiting values. This requires precise analytical systems such as X-ray fluorescence, ICP- and atomic absorption spectrometers. These instruments are able to detect trace concentrations of hazardous compounds – for example cadmium, using an atomic absorption spectrometer in the flame atomisation mode up to 0.1 mg/L, or using the digital graphite furnace technique for electrothermal atomisation even up to 0.1 µg/L. For the determination of hexavalent chromium, UV-VIS spectrometry is the method of choice and can be carried out quickly and easily using a UVmini-1240 in routine analyses. Polybrominated biphenyls as well as polybrominated diphenyl ethers are analysed using FTIR spectrometers such as the IRPrestige-21 or GCMS systems (QP2010). The development of routine analytical methods for the accurate determination of all hazardous components will be explained and advantages of flexible system configurations will be discussed.

Introduction

In Summer 2000, the EU commission approved drafts of the guidelines for waste electrical and electronic equipment (WEEE) [1] and the guidelines for the restriction of the use of certain

hazardous substances in electrical and electronic equipment (RoHS) [2]. These were subsequently presented to the European Parliament and the Member States for discussion and decision-making. Meantime, the German Mediation Committee between the Houses of Parliament accepted the papers. On 13 February 2003, the WEEE and RoHS guidelines were ratified, and finally in January 2005, they have been adapted into the national legislature.

The guidelines establish that consumers can return waste electrical and electronic equipment to the manufacturers free of charge. Manufacturers and importers will, at the end of a transition period, finance the treatment, reuse and environmentally safe disposal of waste equipment. For waste equipment already purchased before adoption of the guidelines, all manufacturers will share responsibility. Bilateral agreements can be made for capital goods.

The minimum weight for collection is four kilograms per inhabitant per year. For reuse and recycling the minimum weight applies. This regulation applies to electrical household equipment, electrical tools, consumer electronics, IT and telecommunication equipment, lamps and lights, toys, medical equipment, monitoring and control instruments as well as slot or vending machines. As of July 2006, lead, mercury, cadmium, chromium (VI), polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) are prohibited. Exceptions are provided for certain applications

System configurations for determination of hazardous substances

In order to enforce the substances ban and the limitation or substitution of hazardous substances such as mercury, cadmium and lead, elemental analysis is obviously the most important control measure for monitoring limiting values. This

requires precise analytical systems such as X-ray fluorescence, ICP and atomic absorption spectrometers. These instruments are able to detect trace concentrations of hazardous substances – for example cadmium, using an atomic absorption spectrometer in the flame atomisation mode up to 0.1 mg/L, or using the digital graphite furnace for electrothermal atomisation even up to 0.1 µg/L.

For the determination of hexavalent chromium, UV-VIS spectrometry is the method of choice and can be carried out quickly and easily using a routine spectrophotometer such as UVmini-1240. Polybrominated biphenyls as well as polybrominated diphenyl ethers are analysed using FTIR spectrometers such as the IRPrestige-21 or in the lower concentration range with GCMS systems (QP2010).

Energy-dispersive X-ray fluorescence spectrometry

The efficiency of X-ray fluorescence spectrometry as a fast screening method is demonstrated using the analysis of cadmium in Sicolen® following the directive for restriction of the use of hazardous substances in electrical and electronics equipment. Red, orange and also green polymers can contain organic cadmium compounds as pigments or stabilizer. In particular, "older" materials can include cadmium concentrations up to the percent range. Cadmium and other hazardous substances according to RoHS, as well as all elements from ${}^6\text{C}/{}_{11}\text{Na}$ to ${}_{92}\text{U}$ can be determined quantitatively using energy-dispersive X-ray fluorescence spectrometers such as Shimadzu's EDX series (EDX-700HS/ -800HS/ -900HS) in a fast and reliable way, often without any sample preparation. For the determination of heavy metals in plastic components such as cases or cable insulations down to the ppm range the samples are positioned directly in the large sample compartment as shown in figure 1.

The sample is irradiated from below with X-ray radiation. When this hits an atom with sufficient energy, an electron from one of the lowest energy levels of the K- or L-shell is expelled and leaves its former position. The resulting "hole" is filled immediately by an electron from a shell above to restore the original configuration. This process releases energy, known as secondary or X-ray fluorescence energy. The element-specific fluorescence radiation corresponds to the energy difference between the K and L shells and is called K(alpha)-fluorescence. Detecting the energy condition of each element allows

qualitative analysis and also, since the fluorescence radiation is proportional to the quantity of the element, quantitative analysis. Finally, the X-ray fluorescence emitted by an unknown sample, whether liquid or solid, is caught by the semiconductor detector and processed by the MCA (multi channel analyser).



Figure 1: Large sample compartment of EDX-700HS.

The entire system configuration is controlled with a desktop PC and the data processing software allows two different evaluation procedures. Using the qualitative analysis, the system computes all signals and assigns them to the appropriate elements. The concentration ranges from a few ppm up to 100% without changes in the measuring parameters.

Using the quantitative analysis, the system computes the accurate concentration of the elements which can be determined via the signal intensities and/or over a suitable calibration curve obtained with standard reference material.

The following experimental work on the investigation of cadmium-containing polymers demonstrates the efficiency of the EDX technique as a screening method according to the RoHS guidelines. Cadmium as a toxic heavy metal shows the most intensive fluorescence signal at Cd ($[\text{Kr}] 4d^{10} 5s^2$): K(alpha) = 23.106 KeV. Figure 2 shows a typical signal profile of the K(alpha)-line of cadmium. The X-axis represents characteristic energy in KeV (kilo electron volts) and the Y-axis, intensity of the signal in cps/µA (counts per second per microampere).

An ideal sample for EDX measurement is flat, has a smooth surface, is relatively thick (> 3 mm) and is larger than the beam diameter.

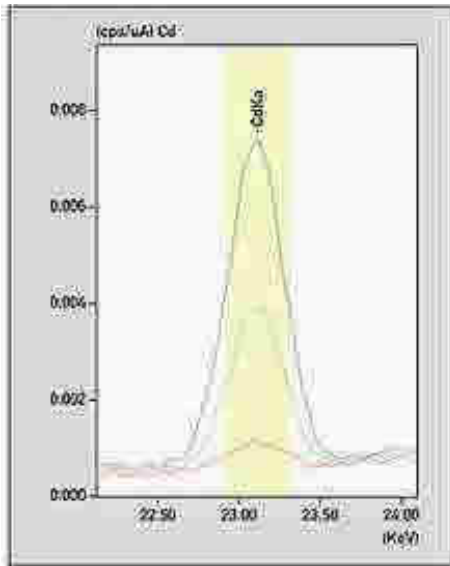


Figure 2: Cadmium peak profile in polymer.

The beam diameter can be reduced in four steps by the use of collimators from 10 mm to 0.3 mm, which significantly improves the analysis results of small samples. The use of energy-dispersive X-ray fluorescence spectrometers is suitable also for the analysis of thin, curved or small samples (< 3 mm), unlike wavelength dispersive systems. In these cases, the background intensity of the X-ray tube (Rhodium anode) and the fluorescence radiation of the sample itself are used to correct changes in the absolute intensity of the signals, caused by thickness or shape of the sample. This internal background correction can be used comfortably via the EDX software [3].

For experimental work, cadmium reference standard material has been used which has been prepared and certified by the Institute of Reference Materials and Measurements (IRMM), Geel, Belgium. These standards have been used for the cadmium calibration (figure 3) showing a very good linearity in the concentration range from 40.9 mg/kg up to 407 mg/kg. All measurements have been performed using a primary molybdenum filter (standard), 10 mm collimator and 300 seconds measurement time. In order to evaluate the calibration curve, another certified cadmium standard has been analysed using the same method.

Sicolen® orange (ref. no. 28/16494) containing 75.9 ± 2.1 mg/kg cadmium in Sicolen® has been measured in the same way as the standards. The quantitative analysis results in a concentration of 76.5 mg/kg (ppm) cadmium. The result is therefore within the certified tolerance – without

further sample preparation and after only 300 seconds of measurement time!

Energy-dispersive X-ray fluorescence spectrometry using the Shimadzu EDX-700HS is a fast and non-destructive method for quantitative determination of heavy metals in polymers. The experimental results of cadmium are also representative for other heavy elements such as lead, mercury, chromium and bromine. Depending on the system configuration, even measurement of the complete element range from ${}^6\text{C}/{}_{11}\text{Na}$ to ${}_{92}\text{U}$ is possible.

Atomic absorption spectrometry

For the quantitative analysis of heavy metals such as lead, cadmium, mercury and chromium according to the RoHS directive, atomic absorption spectrometry (AAS) is the method of choice. AAS is a relative measuring method for quantitation of element concentrations down to the ppt level of liquid or solid samples, using the relationship between concentration and absorbance according to Lambert-Beer's law. The measurement of unknown samples is performed against a calibration curve of aqueous standard samples. Unfortunately problems can emerge when the composition of standards and samples is different. Problems related to background absorption are classified as spectral interferences. Interferences which can be solved by background compensation methods include molecular absorption, particulate caused scattering and absorption line overlapping. During determination of heavy metals according to RoHS guideline, the spectral interferences by direct and indirect absorption line overlapping are to be expected for cadmium, lead and chromium [4]. Since the deuterium lamp method is not able to compensate for these interferences, the high speed self reversal method has been selected here as a universal technique covering the entire wavelength range from 190 nm to 900 nm in flame and furnace atomization and compensating interferences for both, direct and indirect line overlapping. All determinations have been performed using the Shimadzu atomic absorption spectrometer AA-6800 which is equipped with both deuterium lamp and high speed self reversal background compensation methods as a standard configuration, enabling proper compensation of all interferences. For electrothermal atomization the GFA-EX7 high sensitivity graphite furnace with digital control has been used in all cases [5]. In fully automatic measurement sequences the calibration curves have been prepared from multi-element stock standard solutions using the

autosampler ASC-6100 in combination with an ASK-6100 autodiluter.



Figure 1: Fullautomatic system AA-6800

The experimental results have been obtained from standard solutions, diluted samples and certified reference material. In contrast to the EDX screening method which does not require any sample preparation, the determination of heavy metals using AAS needs the digestion procedure to bring all samples into solution. The recommended sample preparation for polymers is a dry ashing method or a microwave acid digestion using nitric acid with hydrogen peroxide and hydrofluoric acid.

The determination of cadmium, lead and chromium has been carried out in the calibration range from 0.1 mg/L to 5 mg/L using flame atomisation, and 0.1 µg/L to 20 µg/L using electrothermal atomisation. Mercury determination is possible g/L and µg/L using electrothermal atomisation for concentrations from 5 µg/L to 100 down to 1 µg/L using the cold vapour method. The instrumental parameters for determination of cadmium, lead, and mercury are listed in table 2 including the lamp current for deuterium (D2 BGC) and self reversal (SR BGC) background compensation. A total volume of 5 µL palladium modifier solution with a Pd (NO₃)₂ concentration of 1000 mg/L has been added to the 20 µL injection volume of standards and sample solutions during the cadmium and lead analysis. This analytical procedure allows a precise and reliable determination of heavy metals such as cadmium, lead, mercury and chromium using atomic absorption spectrometry.

The determination of hexavalent chromium using UV-VIS spectrometry

X-ray fluorescence and atomic absorption spectrometry allow the determination of total

chromium concentration of a sample with or without sample preparation. Since the RoHS directive requires determination of hexavalent chromium, the photometric method using 1.5-diphenylcarbazide is used for this purpose. The method is suitable for the determination of hexavalent chromium which is used as a coating to protect metallic surfaces of electric and electronic equipment against corrosion. It is also used as a coating for screws, washers and fittings.

In the first stage the sample material has been eluated during a defined time in the reaction vessel, after which the blank value is measured and finally the reagent is added to the sample solution. The hexavalent chromium oxidates 1.5-diphenylcarbazide to 1.5-diphenylcarbazone, which forms a red-violet colored complex. The absorption of the color complex measured at a wavelength of 540 nm is directly related to the concentration of hexavalent chromium (figure 4).

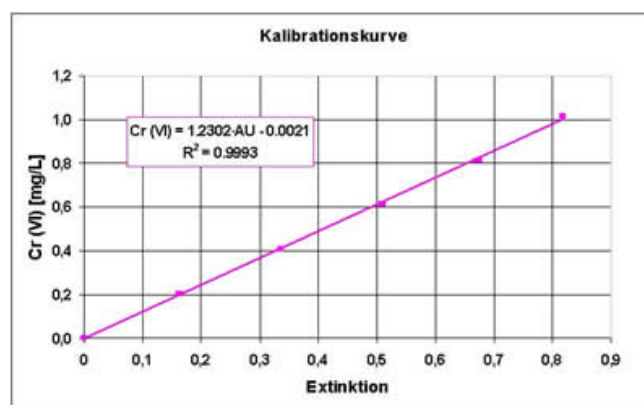


Figure 4: Chromium calibration.

The determination of PBB and PBDE using FTIR and GC/MS

The RoHS directive regulates the restriction of the use of brominated flame retardants in electrical and electronic equipment as of July 2006. Consequently, polybrominated biphenyls (PBB) and polybrominated diphenylethers (PBDE) can no longer be used as flame-retardants in polymers unless their concentrations are lower than 1,000 ppm. The objective of the RoHS directive is the assurance of human health and the environment from hazardous effects. During recycling of electronics waste, contamination by brominated compounds should therefore be reduced. Polybrominated biphenyls are classified as health hazards. PBB and PBDE are chemicals that have, in the past, been used as flame retardants in

polymers in concentrations of 5% up to 10%. RoHS restricts the use of compounds such as tetrabrominated biphenyl A (TBBA), brominated polystyrene and brominated aromatic triazine.

According to RoHS, the following compounds are considered as hazardous: pentabrominated diphenyl ether (PentaBDE) and octabrominated diphenyl ether (OctaBDE). OctaBDE has been used in polymers such as ABS and PS. Currently, decaBDE is largely being used as a flame retardant in PS, PE, ABS and polyester. DecaBDE has not yet been included in the RoHS directive. However, commercial decaBDE consists of a mixture of approximately 97% to 98% decaBDE and 0.3% up to 3% of other BDEs. Therefore, when a polymer contains 10% decaBDE (containing 1% contamination of other brominated BDEs), the PBDE content will exceed the RoHS threshold value of 1,000 ppm.

In order to comply with the requirements of the RoHS directive, the total bromine content of a sample is first determined. If this exceeds 5% after the preliminary examination using the EDX systems, infrared spectroscopy is recommended as this will enable identification of compounds. This simple and non-destructive method quickly leads to useful results. Compound identification is possible as the flame retardants were present up to now in polymers in concentrations of higher than 5%. This level is still detectable in polymer mixtures using FTIR. However, concentrations approaching the detection limit must be measured using other analytical methods. In this case GC/MS is highly suitable as all brominated compounds can be separated and detected down to the trace level. GC/MS, on the other hand, is more time consuming with respect to sample preparation and data analysis. In general, it is recommended to carry out an overall pre-screening via energy-dispersive X-ray fluorescence (EDX). Using this analytical method the total concentration of elemental bromine in the sample is detected, although it is not possible to distinguish which compound actually contains bromine. When more than 5% of total bromine is detected, FTIR can be used for further identification of bromine compounds. When less than 5% bromine is detected, GC/MS analysis can be implemented for separation and identification.

Fast and straightforward IR-analysis of polymers is possible since brominated biphenyls exhibit very characteristic infrared spectra. The polystyrene example exhibits three spectra: DBDPE, PS with DBDPE and pure PS. The range in the IR fingerprint, where DBDPE in PS identification is possible, is clearly discernible.

Figure 5 shows polystyrene with different brominated flame retardant additives. The fingerprint region of $1,500\text{ cm}^{-1}$ to $1,000\text{ cm}^{-1}$ is important for the identification of brominated flame retardants, where clear differences between the spectra can be seen. Based on this information, an analytical method for fast identification of brominated flame retardants and polymers has been developed using Shimadzu's FTIR-8400S in combination with a single reflection accessory. In the present example, a diamond ATR unit with KRS-5 crystal was used as single reflection accessory. A diamond as sample surface is recommended as the polymer can be present in different hardness. The diamond sample surface enables the application of high pressures, ensuring tight positioning of the sample on the crystal so that optimum penetration of the sample by the IR beam is guaranteed. The beam penetrates the sample surface to a depth of approximately $2\text{ }\mu\text{m}$. As RoHS specifies a homogeneous sample material, this depth of penetration is sufficient in order to completely characterize the sample. Using this measuring configuration, the spectrum is acquired within a very short time interval (approximately 1 min.) and is evaluated automatically according to RoHS guidelines.

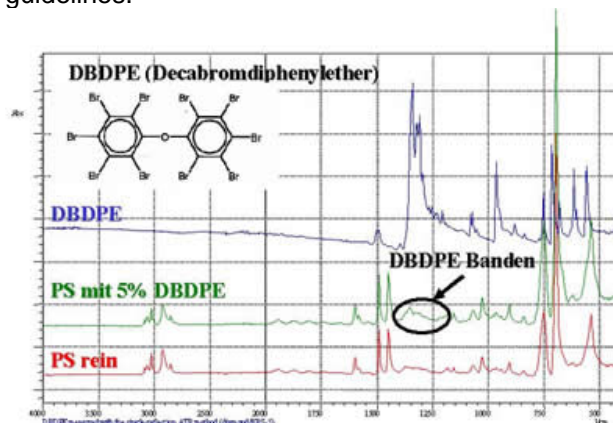


Figure 5: Infrared spectra of polystyrene with different flame retardants.

To validate analysis results, the spectrum is compared subsequently with a library of polymer spectra. For polymer identification, a data base already containing 41 polymers is used. This data base contains logical associations and the Distinction Software tests for plausibility, for instance by evaluation of signal ratios. The decision criterion includes warning messages that range from "Identification of the polymer not possible" to "Applied pressure not sufficient" and finally to the conclusion "O.K." or "Not O.K.". These FTIR analysis results may be considered to be unambiguous when combined with the pre-

analysis from the EDX system. Infrared spectrometry can therefore be regarded as a fast and simple alternative solution to the preselection of polymers. Minimal sample pretreatment is necessary and fast results are obtained via predefined methods.

The analysis of polybrominated flame retardants in concentrations of less than 5% down to the ppm range has been carried out using GC/MS. With GC/MS it is possible to quantitate and identify ultra low sample concentrations by comparison with standard substances according to their specific retention time and mass spectra. Here we have two possibilities. The first one is a screening of the samples using pyrolysis GC/MS. This method has the advantage of direct determination of the samples without any sample pretreatment. During pyrolysis a high temperature is applied to the samples. Shimadzu's system configuration consists of the Py-2020iD pyrolyzer with the so called "double-shot method". During this method the PBB and the PBDE are evaporated from the polymer at low temperatures from 300°C to 400°C (Thermodesorption). In the second stage at higher temperatures the polymers are pyrolyzed and identified. The final result yields not only information about the flame retardant, but also the composition of the polymer.

After evaporation from the polymer, the PBB and PBDE are separated with gas chromatography and detected in the mass spectrometer. Figure 6 shows a typical example of such a pyrolysis chromatogram. The masses 720 and 882 correspond to the 9 brominated isomere PBDE (Peaks B, C, D), the masses 800 and 960 correspond to 10 brominated PBDE (Peak E).

For a quantitative analysis of PBB and PBDE the samples first need to be prepared, starting with an extraction. For soluble polymers the samples are dissolved in the selected solvent, after which the polybrominated substances are extracted with liquid/ liquid- or Soxhlet-Extraction. For non-soluble polymers, Soxhlet-Extraction is applied directly. The extract is cleaned afterwards using solid phase extraction or GPC. Finally, the sample is prepared for GC/MS analysis with liquid injection. Figure 7 shows the quantitative determination of PBDE in a polystyrene sample. The FTIR method was not sensitive enough to determine the PBDE in this example.

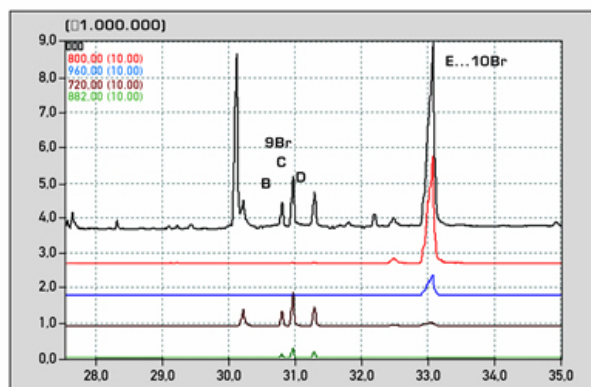


Figure 6: Determination of PBDE with pyrolysis GC/MS.

This system consisting of GCMS-QP2010 and the pyrolyzer Py-2020iD is an ideal configuration for a high sensitivity determination of flame retardants according to RoHS.

Conclusion

The system configurations and application examples have been used to demonstrate an actual overview of the state-of-the-art technology for determination of hazardous substances in electro- and electronic equipment as well as electronic waste according to the WEEE and RoHS guidelines. The maximum allowable concentration levels for lead, mercury, chromium, polybrominated biphenyls and polybrominated diphenylethers will probably be limited to a concentration of 1,000 mg/kg, for cadmium 100 mg/kg and correspond to the end of lifetime vehicles directive (ELV). The actual concentration level of single substances in the homogeneous sample is variable and, where sample preparation is needed, far lower than these concentration levels.

References

1. Guideline 2002/96/EC for Waste Electrical and Electronic Equipment (WEEE)
2. Guideline 2002/95/EC for the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS)
3. Hesper J, Oppermann U (2005) GIT Labor-Fachzeitschrift 113-115
4. Oppermann U, Schram J, Felkel D (2003) Spectrochim. Acta B 1567-1572
5. Oppermann U, (2002) GIT Labor-Fachzeitschrift 430-433