Lead in lead-free solder – E

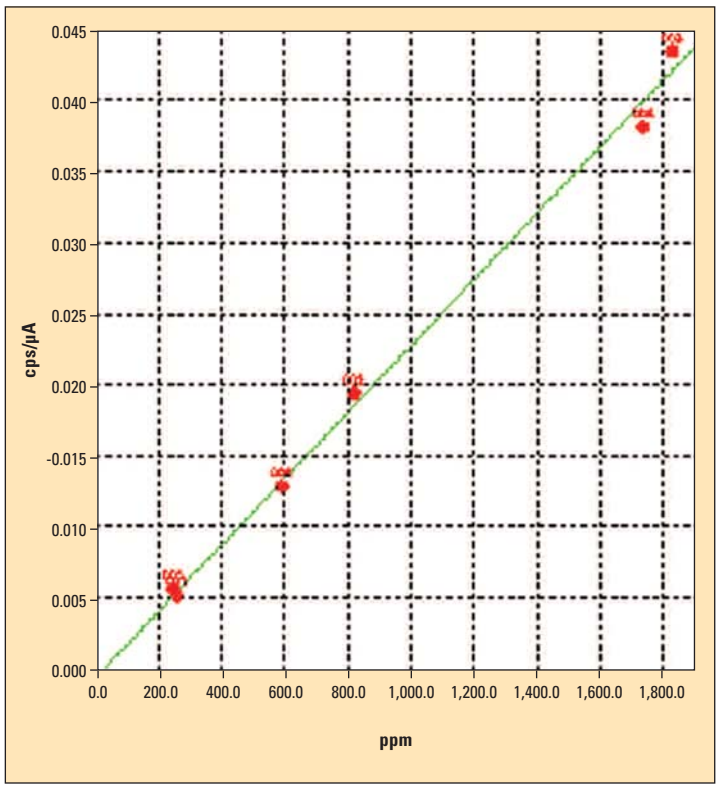

Figure 1: Calibration curve of the six lead-containing lead standards measured via the EDX-720

The EU directives WEEE and RoHS as well as the ElektroG (German Electrical and Electronic Equipment Act) regulation issued by the German Federal Government govern the return of used electrical and electronic equipment, their re-use or their recycling. These regulations also include a ban on hazardous substances including the elements lead, cadmium, chromium (VI) and mercury as well as polybrominated biphenyls and polybrominated diphenylethers (flame retardant in plastics) in the manufacture of electrical and electronic equipment.

Standard	Concentration (ppm) *
	Pb
74X-E	262
74X-HN	820
74X-TC	1830
74X-AM	1740
74X-HA	250
74X-HB	590

Table 1: Pb concentration of the certified standards.
*Obtained using ICP/MS

This article focusses especially on the heavy metal lead, which is still present in many so-called lead-free solders. In its directive of 21st October 2005, the European Commission specified additional exemption clauses for lead in the RoHS directive. The 2005/747/EG directive describes changes in subparagraphs 7 and 8 (cadmium) and includes the new subparagraphs 11 to 15.

Subparagraph 7 contains the following exemptions for lead:

- lead in high-melting solders (solders containing at least 85 % lead by mass)
- lead in solders used in servers, data storage systems and memory arrays as well as network infrastructure hardware for relaying, signal propagation, transmission and network management in the telecommunications sector
- lead in ceramic electronic components (for instance piezo-electronic components).

Subparagraphs 11 to 15 were added to the directive, specifying:

11. lead in press-in connectors with flexible zones
12. lead as coating material for C-rings in heat-conducting devices
13. lead in optical glasses and glass filters
14. lead in solders containing more then two elements with a lead content (mass percentage) of greater than 80 % and less than 85 %, used for connections between connector pins and microprocessor circuits
15. lead in solders which create a stable electrical connection between a semiconductor chip and a circuit board in integrated flip-chip circuits.

EDX-720 – twice the detection sensitivity

For the required monitoring of the use of lead, Shimadzu has developed an improved EDX system. The EDX-720 features sensitivity to lead (Pb) and cadmium (Cd) of more than twice the level of previous models. Based on the measurement of lead-containing solder standards, the sensitivity and reproducibility of acquired data are presented and discussed below.

Standards

The data on lead concentrations of the reference materials listed in Table 1 is supplied by MBH Analytical Ltd., Barnet, England. Tin (Sn) is the main component of the standards followed by Cu, Ag and Sb etc. in order of decreasing concentration.

In order to determine the lower limit of detection (LLD) a calibration curve was obtained via the PbL_{b1} line of lead. Although the PbL_{α} line is more intense, it can lead to inaccurate results due to line overlap phenomena. Therefore, the PbL_{α} line should not be used without prior testing. Based on the calibration curve presented in Figure 1, the detection limit can be calculated as follows:

$$LLD = 3 \times k \times \sqrt{\frac{I_{back}}{T}}$$

k: calibration constant
I_{back}: background intensity
T: measuring time

Detection limit (LLD)

A measuring time of 300 seconds resulted in a detection limit (LLD) of 24.8 ppm for the six standards. In this way, the legal threshold value of 1000 ppm for lead could be adhered to easily (Table 2).

Reproducibility

In addition to the detection limit, reproducibility is especially important as an indicator of the quality of a measurement. The certified reference standard 74X-E containing 262 ppm lead was measured sequentially ten times.

DX-720

Element	Pb (L_{b1})
Measuring time	300 s
LLD	24.8 ppm

Table 2: Results of the calibration for Pb (L_{b1})

Element	Pb (L_{b1})
Certified concentration (ppm)	262.0
Average value n = 10 (ppm)	259.3
Standard deviation (ppm)	7.4
CV (%) experimental	2.9
CV (%) theoretical	2.5

Table 3: Results of the repeated measurements

The average value of 259.3 ± 7.4 ppm obtained via the EDX-720 reflects an excellent reproducibility (Table 3).

Results

The results show that even without any sample preparation, high accuracy and precision are attained already after a measuring time of 300 seconds. The EDX-720 is therefore, the ideal tool for fast analysis of elements ranging from sodium to uranium in solid and liquid samples. Without adjusting the method, one measurement can cover the entire concentration range from ppm up to 100 %. The possibility of carrying out analyses without using standards (fundamental parameter method) enables the investigation of unknown samples with very high precision. In addition, the large sample compartment (300 mm internal diameter x 150 mm height) offers enough room for non-destructive analysis of most samples without the need for prior sample fractionation.

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Routine determination of hazardous compounds

Atomic absorption spectrometry and WEEE, RoHS, ElektroG

Figure 1: The AA-6300 fully automatic atomic absorption spectrometer

Atomic absorption spectrometry is primarily suitable for quantitative determination of hazardous compounds such as lead, cadmium, mercury and chromium in sample materials according to ElektroG (WEEE/RoHS). AAS is a relative method for quantification and is based on the elemental composition of the sample and absorption according to Lambert-Beer's law. In principle, calibration curves are calculated in the appropriate concentration ranges for each element to be determined. The calibration curves are then used to evaluate all unknown samples. A prerequisite for accurate results is, however, that calibration standards and samples represent the same composition with respect to other elements and matrix. This prerequisite is not always met and can, therefore, lead to problems – for example when, in addition to the elemental absorption, background absorption of the matrix contributes to the signal.

Interferences such as molecular absorption, particulate caused scattering and spectral interferences caused by absorption line overlap can be eliminated via high-performance background compensation techniques. For complete compensation of all known AAS interferences in the flame- as well as in the electrothermal atomization modes, the high-speed self-reversal method is well established. Another widely used method, deuterium background compensation is, however, only usable in the wavelength range up to 420 nm, while self-reversal background compensation can be applied over the entire 185 – 900 nm range.

Cadmium in polymers

Quantitative determination of elemental cadmium in polymers was carried out using an AA-6300 Shimadzu atomic absorption spectrometer (Figure 1), which is equipped as standard with deuterium- and self-reversal background compensation modes. For electrothermal atomization, the highly sensitive GFA-EX7i graphite furnace with digital control was used.

The experimental results were obtained from standard solutions, diluted measuring solutions and dissolved reference materials. For sample preparation of polymers, several dissolution procedures are possible, for example dry ashing or microwave-assisted acidic digestion using nitric acid and, if necessary, hydrogen peroxide under addition of hydrofluoric acid.

Cadmium determination (Fig. 2) was carried out in a concentration range of 0.1 up to 0.4 mg/L using flame atomization and in the concentration range of 0.1 up to 0.4 µg/L using electrothermal atomization. Due to spectral interference of the cadmium line at 228.8 nm by arsenic and iron, the deuterium method can lead to overcompensation. In this case, the self-reversal method was applied for background compensation. In this way, AAS can be applied as a suitable routine analysis method for the reliable determination of cadmium and other hazardous compounds according to the ElektroG directive.

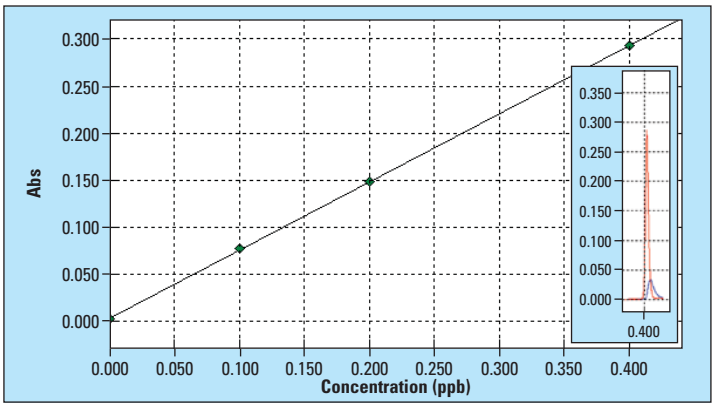

Figure 2: Calibration curve for cadmium