



# Multi-element analysis in plastics by laser ablation inductively coupled plasma mass spectrometry



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## ABSTRACT

A method for the determination of Cr, Cd, Hg, and Pb in plastics by laser ablation inductively coupled plasma mass spectrometry is proposed. The laser ablation parameters were optimized to achieve maximum intensities and the lowest relative standard deviations. The obtained detection limits in the matrix-matched standard calibration were 1 mg kg<sup>-1</sup>, 2 mg kg<sup>-1</sup>, 1 mg kg<sup>-1</sup> and 3 mg kg<sup>-1</sup>. The proposed method was confirmed with energy dispersive X-ray fluorescence spectrometry and interlaboratory proficiency test results. The analytical results obtained by the proposed method for Cr, Cd, Hg and Pb showed relative deviations between 0% and 40% from the assigned value of the proficiency test results and were within the 95% confidence interval. The proposed method can also be used for the simultaneous determination of other substances restricted by the RoHS directive.

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## 1. Introduction

Many electrical and electronic equipment (EEE) products, which contain large quantities of plastic parts, are produced and transported around the world. The producers are compelled to demonstrate compliance with the EU RoHS (Restriction on Hazardous Substances) directive, which has restricted the use of hazardous materials in almost all electric and electronic materials. This quality assurance policy implies that plastic manufacturers should strictly control the entire analytical process and guarantee the reliability of the analytical results [1].

The protection of living beings and the environment against hazardous substances is the objective of the RoHS Directive (2002/95/EC of the European Parliament and of the Council, 2003). The RoHS bans the placing of new electrical and electronic equipment containing more than the agreed levels of lead (Pb), cadmium (Cd), mercury (Hg), hexavalent chromium (Cr<sup>6+</sup>), polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants on the EU market. The maximum allowed mass fractions are 0.1% of lead (Pb), mercury (Hg), chromium (Cr), PBB and PBDE, and 0.01% of cadmium in homogeneous materials (Directive

2005/618/EC of the European Parliament and of the Council, 2005). If it is not properly pretreated, WEEE (Waste electrical and electronic equipment) may cause environmental problems due to its content of hazardous substances. Recycled materials, because of their further use, must also fulfil the related regulations [2]. Different analytical techniques have been used for the determination of heavy metals in polymers, such as X-ray fluorescence spectrometry (XRFS), atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). XRFS offers the possibility of analysing solid materials without previous sample treatment; however, this advantage is limited by the need of suitable certified reference materials (CRMs) for calibration. ICP-MS and AAS generally require liquid or dissolved samples; hence, the samples have to be digested. This procedure can be laborious and may introduce systematic errors due to incomplete analyte extraction or solubility [3]. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be a good alternative for the determination of trace elements, such as Cr, Cd, Hg and Pb, in plastics and has limits of detection that are comparable to XRFS. Laser ablation (LA) as well as subsequent detection by ICP-AES or ICP-MS is one of the most widely employed techniques for analysing solid samples. In general terms, LA sample introduction does not require complex sample preparation procedures and it can be applied to spatially resolved analysis [4].

Solid sampling spectrometry, such as XRFS or LA-ICP-MS, needs suitable and reliable reference materials (RMs) to allow accurate

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quantification. Both methods are known to be matrix dependent, and an important condition for a suitable RM is that the matrix of the RM should match that of the sample. In LA-ICP-MS and  $\mu$ -XRF, small spots of the sample are measured. The homogeneity of the analytes in the calibration materials must be assured for these techniques. In a similar manner, the determination of heavy metals in plastics strongly depends on the polymer matrix. Each polymer type has to be evaluated separately because chemical interactions between contaminants and the polymer matrix can create interferences. Reports of RM and/or CRM preparation studies currently in progress for different matrices can be found in the literature [1,5,6,7].

External calibration and internal calibration are calibration techniques used extensively. External calibration is one of the easiest and preferred techniques; it involves the preparation of standards containing varying amounts of the analyte in a matrix and the generation of a calibration curve using ICP-MS. The response of the analyte is generally assumed to be linearly dependent on its concentration. Inaccuracies in the results can occur if the standards do not accurately represent the sample matrix [8]. Studies using the LA-ICP-MS technique have recognized the problem of elemental fractionation, which refers to non-representative sampling during the ablation process prior to introduction into an ICP-MS. To correctly calibrate an LA-ICP-MS, a matrix-matched solid material of known and certified elemental composition is normally required; however, this can be a problem if no such material is available [9]. Few studies of the laser ablation of a polymer sample for ICP-AES and ICP-MS have been carried out. Todoli et al. reported in their study that Marshall et al. performed an analysis of plastic materials by LA-ICP-MS with the use of a Nd:YAG laser at 1064 nm. Carbon-13 was chosen as the internal standard. Their results on polyvinylchloride (PVC) and poly-olefin ablation suggested that carbon could be used as an efficient internal standard for semiquantitative analysis by ICP-MS, although the authors found that the accuracy of the result was within a factor of two of the known value. Nevertheless, more recent studies carried out using ICP-AES demonstrated that carbon could not be considered an efficient internal standard for some inorganic elements because its behaviour was different from that observed for the additives. Moreover, the type of polymer and the chemical nature of the additives were crucial parameters affecting the ablation processes [4].

An analyst has to use validated methods to achieve the best reproducibility and to ensure accuracy. The accuracy of a laboratory can only be achieved by comparing its own performance with that of other laboratories. This can be done by using CRMs and by participating in proficiency tests (PTs). CRMs are materials guaranteed for their stability and homogeneity, and their parameters are accurately and precisely determined. However, CRMs are not available for all analytical problems. PTs are accepted by modern, accredited laboratories and may be considered as the most stimulating and therefore effective tool for external quality control [7,10,11].

In a PT, the participants analyse a material without knowledge of the correct result and return the result of the measurement to the PT provider. The provider converts the results into scores that reflect the performance of the participant laboratory. Such studies also help laboratories to link their performance to the scientific community [10,12]. The Institute for Interlaboratory Studies (iis, the Netherlands), for example, has been organizing PTs for plastics analyses since 1998 (in the beginning only for Cd). Many laboratories from different countries participate in these PT schemes. For example, in September 2009 and 2011, 106 laboratories from 29 countries and 143 laboratories from 33 countries participated, respectively. It can be seen from the iis09P02X and iis11P02 reports and other reports that most participants have been using mostly EN 1122 (for only Cd), IEC 62321 (wet techniques mostly) and EPA test methods (for sample digestion) [13–17].

The aim of this study is to develop an effective method that enables rapid and ready determination of the amount of Cr, Cd, Hg and Pb present in plastics by LA-ICP-MS. Furthermore, the parameters relating to the effects of the laser and ICP-MS conditions for metals of interest were also investigated for analytical accuracy.

## 2. Materials and methods

### 2.1. Reagents and materials

The calibration standard, ERM EC681k (low density polyethylene), was purchased from the Institute for Reference Materials and Measurements (IRMM). The plastic materials, sample #950 [13] which is a yellow coloured PP and sample #11051 [14] which is a yellow coloured PVC sample were obtained from The Institute for Interlaboratory Studies, iis, the Netherlands. SRM 612 trace elements in glass were obtained from the National Institutes of Standards and Technology (NIST).

### 2.2. Instrumentation

The experimental set-up consisted of a laser ablation (LA) (CETAC Technologies, LSX-213 G2+ LA) system where the evaporation of sample material by a focused laser beam in a helium atmosphere and the ablated sample material is transported with a helium gas stream into ICP-MS (Agilent 7700x-Octapole Reaction system, ORS<sup>3</sup>) where it is ionized. The tuning of the ICP-MS was performed using a commercial tuning solution according to the manufacturer's instructions, the same as would be applied for routine ICP-MS analysis. After tuning of the ICP-MS, the LA instrument was tuned by ablating SRM 612 and monitoring the ions 43, 88, 137, 232, and 238, as well as the thorium oxide ratio (248/232) and the laser induced mass bias as measured by the uranium (U) to thorium (Th) ratio (232/238). In the SRM 612, U and Th concentrations were approximately the same. For a 50  $\mu$ m spot, at a pulse rate of 10 Hz, with energy >1 mJ/pulse (approximately 25% of laser energy) the SRM 612 will give >500,000 cps for most elements, with a ThO/Th ratio of <1% and a Th:U bias of 1:1. Th:U will be affected by gas flow through the cell and the gas plasma, as are oxides species that can potentially cause measurement interference. Typically, the ThO/Th ratio is set using the nebulizer (argon) gas flow, and the Th:U bias is controlled by the carrier gas flow (helium) [18]. For tuning and controlling the laser induced mass bias, SRM 612 was line-scanned and the ThO/Th ratio and the Th:U were obtained by changing the gas flow rates mentioned above using ICP-MS. The most abundant isotopes with less interference, <sup>52</sup>Cr, <sup>111</sup>Cd, <sup>202</sup>Hg and <sup>208</sup>Pb were investigated. The ORS<sup>3</sup> was used to reduce possible interferences; <sup>40</sup>Ar<sup>12</sup>C (52), <sup>36</sup>Ar<sup>16</sup>O (52) and <sup>35</sup>Cl<sup>16</sup>O<sup>1</sup>H (52), <sup>35</sup>Cl<sup>15</sup>N<sup>+</sup> (52), <sup>39</sup>K<sub>2</sub><sup>16</sup>O<sub>2</sub><sup>1</sup>H<sup>+</sup> coming from argon and air, chlorine and potassium were present in the standard and samples, respectively. The analytical data were generated in and evaluated by the Agilent Mass Hunter and DigiLaz Software.

The energy dispersive X-ray fluorescence (EDXRF) spectrometer used in this study was a Spectro X-Lab 2000 (Spectro A.I., Kleve, Germany) equipped with a 300 W Pd end window X-ray tube and a liquid nitrogen cooled Si(Li) detector (<150 eV Mn K $\alpha$ ). In this polarized EDXRF spectrometer, the available targets were molybdenum (Mo) as the secondary target, with Al<sub>2</sub>O<sub>3</sub> and highly oriented pyrolytic graphite (HOPG) used as polarization targets. The EDXRF measurements in this work cover two different methods: The first method was developed by Tümay et al. for PP and polyethylene (PE) samples and was used for sample #950, which consisted of the PP sample chips. In this method, for one sample measurement, approximately 0.9 g of plastic was weighed onto a Kjeldahl flask, to which 10 g of xylene was added. The flask was

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