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Determination of toxic elements in plastics from waste electrical and electronic equipment by slurry sampling electrothermal atomic absorption spectrometry

Mirian C. Santos[a], Joaquim A. Nóbrega[b], Nivaldo Baccan[a,c], Solange Cadore[a,*]

[a] Institute of Chemistry–University of Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil
[b] Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil
[c] Faculdade de Paulínia, 13140-000 Paulínia, SP, Brazil

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ABSTRACT

Cadmium, chromium, lead and antimony were determined in slurries prepared using pulverized samples of personal computers and mobile phones dispersed in dimethylformamide medium. Determinations were carried out by electrothermal atomic absorption spectrometry (ETAAS) using a graphite furnace atomic absorption spectrometer. The optimization of the experimental conditions (chemical modifier, pyrolysis time, pyrolysis temperature and atomization temperatures) was accomplished by evaluating pyrolysis and atomization curves. Optimization was also used to determine the temperatures corresponding to the best sensitivities and the lowest background signals. The pyrolysis temperatures were fixed at 600 °C (for Cd), 700 °C (for Pb), 1100 °C (for Sb), and 1200 °C (for Cr); atomization temperatures were established as 1400 °C (for Cd), 1300 °C (for Pb), 1900 °C (for Sb), and 2300 °C (for Cr), and the chemical modifier (50 μg $NH_4H_2PO_4$ + 3 μg $Mg(NO_3)_2$ was used for Cd and Pb while 5 μg Pd + 3 μg $Mg(NO_3)_2$ was used for Sb). The use of a chemical modifier for Cr determination was not necessary. The characteristic masses were 1.9 pg for Cd, 32.3 pg for Pb, 54.1 pg for Sb, and 9.1 pg for Cr. Calibration was performed using standard additions in a range of 5–20 $\mu g\,L^{-1}$ for Cd, 5–30 $\mu g\,L^{-1}$ for Cr, 12.5–50 $\mu g\,L^{-1}$ for Pb, and 25–100 $\mu g\,L^{-1}$ for Sb with linear correlation coefficients higher than 0.99. Limits of detection were 0.9, 1.4, 6.8, and 2.9 $\mu g\,L^{-1}$ for Cd, Pb, Sb, and Cr, respectively. The results indicate that recoveries for all metals agreed at a 95% confidence level when a paired *t*-test was applied and presented good precision. The accuracy of the proposed method was evaluated by addition–recovery experiments, showing results in the 96–112% range, and also by comparison of the results using Student's *t*-test with another method developed using ETAAS for digested samples. Analyte concentrations in the samples investigated varied from 5 to 525, 51 to 611, and 30 to 458 $mg\,kg^{-1}$ for Cd, Cr, and Pb, respectively, while the content of Sb was in the 0.2–1.65% range.

1. Introduction

Technological developments in the field of electric and electronic products are characterized by the rapid pace of innovations and diversity of products, wide consumption and the trend to miniaturization. These aspects generate products that are prematurely obsolete and discarded, leading to an increase of solid wastes. The politics of technological development generates severe environmental impacts. Many of these products contain toxic substances that require special treatment with respect to recycling and also to final disposal, beyond the natural resources, like precious metals, that are lost when they are not re-exploited [1,2].

Due to rapid improvements in electronic manufacturing, mobile phones and personal computers can be regarded as short-life-cycle electronic products [3]. The average lifetime for computers is 3 years and for mobile phone is between 2 and 3 years. On the other hand, the time of decomposition of these materials in the environment is, on average, 450 years for plastics and metals, and indeterminate for glasses [4].

The term waste electrical and electronic equipment (WEEE) has been used to categorize electric and electronic equipment residues at the end of their life-cycle [1,2,5,6]. Polymers represent approximately 20% of the total mass of WEEE and are based on more than 15 different types of engineering plastics, including ABS (acrylonitrile–butadiene–styrene) and some blends of ABS, HIPS (high impact polystyrene polymer), PP (polypropylene), PS (polystyrene), SAN (styrene acrylonitrile), polyesters, PU (polyurethane), PA (polyamide), blends of ABS/PC (polycarbonate) and blends of HIPS/PPO (polyphenylene oxide).

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* Corresponding author. Tel.: +55 19 3521 3125; fax: +55 19 3521 3023.
E-mail address: cadore@iqm.unicamp.br (S. Cadore).

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Moreover, plastics from WEEE may contain hazardous substances, such as heavy metals (Cd, Cr, Hg, Pb, and Sb) and brominated flame retardants (BFR) [7–9].

A large amount of used-up electronic equipment is sent to landfill sites for disposal [10] or incinerated with other industrial waste. Hazardous materials contained in computers and cellular phones [11] (i.e., various metals, fillers, brominated flame retardants in plastics, printed circuit boards with integrated circuits including epoxy resin reinforced by glass or carbon fiber, etc.) may cause serious pollution in the environment if they are not properly disposed of. Considering incineration processes they lead not only to toxic ash but also to toxic dust and the presence of hazardous substances, in the atmosphere. WEEE has been subject of studies and action in many countries that are establishing legislations to improve the reuse, recycling and other forms of recovery of such wastes so as to reduce disposal [1,2].

As a result of this rising concern, the European Union has introduced two Directives (2002/96/EC and 2002/95/EC) that regulate the management of plastic WEEE containing BFRs and to ban the use of certain BFR and new products and, consequently, in recycled plastics [12,13]. The Directives are grounded in waste prevention, recycling and reuse, in order to decrease the amount of WEEE.

The WEEE Directive has been specifically developed to reduce the levels of WEEE being consigned to landfill and to encourage resource efficiency through recycling and reuse. This Directive sets out measures for the collection, treatment, recovery and recycling of all electrical and electronic products [12]. The Restriction of Hazardous Substances (RoHS) Directive introduces an alternative requirement for those substances posing the main environmental problems during the disposal and recycling of WEEE [13]. According to this Directive, the most effective way of ensuring a significant reduction of risks to health and environment relating to hazardous substances is their substitution in electrical and electronic equipment by safe or safer materials. Restricting the use of these hazardous substances is likely to enhance the possibilities and economic profitability of recycling of WEEE.

The concentrations of polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), Pb, Cr(VI), Hg (maximum concentration 1000 mg kg^{-1} each) and Cd (100 mg kg^{-1}) in electronic and electrical equipment are restricted by the EC Directives from June 1st, 2006. Furthermore, all used electronic and electrical products have to be taken back and disposed of by their manufacturers [14].

For implementation of EC Directives the development of methods for characterization and quantification of elements and substances in WEEE is necessary. Characterization of the polymers from WEEE may therefore combine different analytical strategies, including polymer identification studies, elemental analysis of metals and halogens, and analysis of brominated flame retardants and their possible degradation products [7]. Analytical data of element concentration in plastics is an important prerequisite for recycling of WEEE. The elemental determination of additives in plastics, including metals and halogens, can be performed using a wide range of analytical procedures.

On the other hand these new European laws and restrictions cause technical problems and challenges for the producer [15]. The industry needs a fast and low cost analytical tool in order to control the quality of product and its compliance with RoHS and WEEE.

The challenge for the development of such an analytical tool is related to the varieties of materials used in this field of electronic applications [16]. The chemical analysis of the restricted compounds could therefore be accompanied by enormous problems.

Recently two reviews [9,17] discuss the techniques commonly used for elemental determination in polymeric materials, which include atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) that generally require samples in an aqueous medium. Nowadays the mostly used analytical protocols involve microwave-assisted digestion [18–22] of polymers. The digestion procedure has to ensure the complete digestion of the sample. However, this process is time-consuming and expensive, while the unavoidable sample dilution leads to a drastic increase in detection limits.

Another aspect related to elemental analysis is that analytical methods and the protocols used for polymers are widely different. None of the ISO 344 methods currently developed is appropriate for the elemental analysis of polymers [23]. Consequently, the application of a method for elemental analysis depends, among others factors, on the analyst's ability and on procedures established in his laboratory. This situation hinders the comparison of analytical results between governments, industries, institutions and other partners [24].

To improve the accuracy and precision of methods, certified reference materials (CRMs) are an ideal tool. However, there are only few commercially polymers CRMs available. From an analytical point of view the lack of CRMs is a continuous problem for the effective development of analytical methods, because it hinders elemental analysis during the development, production and control levels [24]. This lack prevents the full adoption of quality-assurance systems for elemental analysis. Concerning environmental aspects, the lack of polymer CRMs for elemental analysis impedes the effective implementation of the EC Directives.

Considering all these aspects, the aim of this work was to develop analytical methods that allow the determination of several potentially toxic elements (Cd, Cr, Pb, and Sb) in polymeric materials from WEEE using graphite furnace atomic absorption spectrometry without sample digestion, in order to meet the EU RoHS/WEEE directives.

2. Experimental

2.1. Instrumentation

A Perkin Elmer (Norwalk, CT, USA) AAnalyst 600 atomic absorption spectrometer with Zeeman correction, equipped with THGA 800 pyrolytic graphite-coated L'vov platforms and an automatic sampler was used in all measurements of Cd, Cr, Pb, and Sb integrated absorbances. As radiation sources, hollow cathode lamps (HCL) were used for determination of Pb ($\lambda = 283.3$ nm) and Cr ($\lambda = 357.9$ nm), and electrodeless discharge lamps (EDL) for determination of Cd ($\lambda = 228.8$ nm) and Sb ($\lambda = 217.6$ nm), all with bandpass of 0.7 nm. Argon was employed as the inert gas at a flow rate of 250 mL min^{-1}. Measurements were performed in integrate absorbance units (integration of absorbance transient signal over time).

All the emission measurements were made with a Perkin-Elmer Inductively Coupled Optical Emission Spectrometer, Optima 3000DV, equipped with a peristaltic pump, a cross-flow nebulizer coupled to a Ryton double pass spray chamber (Scott type) and a central torch tube injector with an internal diameter of 2.0 mm. This instrument has a solid state segmented array charge coupled device (SCD) detector and operates sequentially in both radial and axial torch configurations. In the axial viewing mode, the cool plasma recombination area was stripped off with a shear gas interface. The entire system is controlled with PE Winlab software.

2.2. Reagents

All chemical reagents were of analytical grade. Deionized water (resistivity of 18.2 $\text{M}\Omega\,\text{cm}^{-1}$) was obtained with a Milli-Q System (Millipore, Bedford, MA, USA). Nitric acid, H_2O_2, and H_2SO_4 were obtained from Merck (Darmstadt, Germany). All sampler containers, autosampler cups and other materials were washed with neutral soap, soaked in 10% (v/v) nitric acid (Merck, Darmstadt, Germany) for 24 h and rinsed with deionized water prior to use.

The standard stock solutions of Cd, Pb, Sb, and Cr (1000 mg L^{-1}) were obtained from Merck (Darmstadt, Germany) and diluted as necessary to obtain the working solutions.

Chemical modifier solutions were prepared by appropriate dilution from individual 10.0 g L^{-1} stock solutions in water. The 1000 mg L^{-1} Pd solution was prepared from a stock solution of $Pd(NO_3)_2$ (40% (m/v) Pd, Merck) in 15% (v/v) HNO_3. Solutions of $Mg(NO_3)_2$ (Aldrich) and $NH_4H_2PO_4$ (Aldrich) were prepared by direct dissolution of the respective salts in 1% (v/v) HNO_3 solution or in dimethylformamide (DMF). The amounts of chemical modifiers used were: 50 μg $NH_4H_2PO_4$ + 3 μg $Mg(NO_3)_2$ for Cd and Pb and 5 μg Pd + 3 μg $Mg(NO_3)_2$ for Sb. The use of chemical modifiers for Cr determination was not necessary.

Quantifications of Cd, Cr, Pb, and Sb were carried out by the analyte addition method in the range of 5–20 μg L^{-1} for Cd, 12.5–50 μg L^{-1} for Pb, 25–100 μg L^{-1} for Sb, and 5–30 μg L^{-1} for Cr in DMF.

2.3. Polymeric samples from WEEEs

The plastic components from two different types of WEEE (mobile phone and personal computer) were chosen for analysis. Polymers from the dismantling of personnel computers and mobile phones were chosen based on polymer properties, namely density (for isolation of polymers) and solubility in DMF. The plastic samples analyzed were acrylonitrile–butadiene–styrene (ABS) and some blends of ABS totally or partially soluble in DMF. The highest relative occurrence among the samples was observed for ABS. Polymeric housing materials from eight mobile phones, three keyboards, five mice and one monitor were used. The plastic parts of personal computers and mobile phones underwent particle size reduction with the aid of a stainless steel grinder or by using a cutting mill under cooling with liquid nitrogen to increase the homogeneity of the samples. Ground samples were screened through a 45 Nylon sieve. Slurries were prepared using the sample fraction with particle sizes lower than 45 μm. Samples were washed with 1% (v/v) HNO_3 solution and dried at 60 °C for 2 h.

2.4. Sample preparation procedures

2.4.1. Slurry preparation

For slurry preparation masses of *ca.* 100 mg of plastic samples were directly weighed in PTFE vessels and DMF was added. The final volumes were adjusted to either 5, 10, 20 or 40 mL. Analytes contained in various polymeric samples from WEEE were determined by ETAAS using standard addition. Prior to measurements, samples were vigorously shaken and homogenized by sonication for 10 min in an ultrasound bath. The resulting slurries were analyzed by ETAAS by transferring 20 μL of slurries and 5 μL of chemical modifier (when necessary) to the graphite tube. Accuracy was evaluated by standard addition experiments and analyte recoveries at two concentration levels and also by comparison with ETAAS after acid digestion.

2.4.2. Microwave-assisted digestion and analysis of samples for comparison purposes

The accuracy of the method developed was evaluated by comparison of the values obtained using two other methods:

(A) Digestions were performed in a DGT 100 Plus microwave-oven (Provecto Analitica, São Paulo, Brazil) equipped with 12 closed PTFE vessels. About 100 mg of sample was weighed into a PTFE vessel and 1.5 mL of conc. H_2SO_4 was added. The vessels were closed and the samples were submitted to the heating program described in Table 1. The digested material was diluted to 50 mL with Milli-Q water. This procedure was adapted based on that recommended by the manufacturer for polymer samples. After microwave-assisted digestion, analytes were determined by GF AAS under previously optimized conditions, using the sample Cell2A for this purpose (Table 2). The residual carbon contents in the digests were determined using a total organic carbon (TOC) analyzer.

Results obtained for digested polymeric material analysis by ETAAS under the optimized heating programs were compared with those obtained by slurry analysis in DMF medium by ETAAS.

(B) A second microwave-assisted digestion procedure was carried out in an Ethos 1600 system (Milestone, Sorisole, BG, Italy). This system operates at high pressures and temperatures and is equipped with a 10 closed-vessel modified Teflon PFA flask rotor with pressure safety and auto-closing mechanism that acts when the pressure reaches 110 atm. The temperatures of the process were monitored using an internal sensor (T_{internal}) with external monitoring based on an infrared sensor located in the side wall of the cavity oven (T_{external}). Microwave-assisted digestions were carried out using a mass of 180 mg of sample (Cell2A), 5 mL of concentrated HNO_3 and 3 mL of H_2O_2. The heating program described in Table 3 was applied. The digests were transferred to polypropylene flasks and the final volume was adjusted to 25 mL with Milli-Q water.

Table 1
Heating program for microwave-assisted digestion.

Step[a]	Time (min)	Power (W)
1	2.0	400
2	5.0	700
Cooling and addition of 1.5 mL HNO_3 and 1.5 mL H_2O_2		
3	2.0	400
4	25.0	600
Ventilation	4.0	0

[a] This program was suitable for simultaneous digestion of four samples.

The digestion blanks were obtained using the same procedure for samples but the acid mixture was submitted to the microwave heating program without sample.

This same strategy was also applied for two certified reference materials (CRM) BCR 680 and BCR 681 (high density polyethylene and low density polyethylene). Microwave-assisted digestions

Table 2
Temperature programs used for the determination of Cd, Pb, Sb, and Cr in digested plastics samples.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Flow rate (mL min^{-1})
Drying	120	10	20	250
Pyrolysis				
Cd	500	10	20	250
Cr	800		20	
Pb	1000		20	
Sb	1100		20	
Atomization				
Cd	1500	0	5	0
Cr	2300			
Pb	1550			
Sb	1900			
Cleaning	2500	1	5	250
Cooling	20	1	5	250

Table 3
Heating program for microwave-assisted digestion.

Step	Time (min)	Power (W)	Temperature (°C)
1	7.0	400	120
2	5.0	400	140
3	5.0	800	180
4	10.0	800	200
5	30.0	800	240
Ventilation	10.0	–	–

were carried out using a mass of 180 mg of sample (CRM) and 5 mL of concentrated HNO_3 and 3 mL of H_2O_2. The heating program described in Table 4 was applied and the digests were transferred to polypropylene flasks and the final volume was adjusted to 25 mL with Milli-Q water.

2.5. Heating program optimization in ETAAS for determination of toxic elements in plastic slurries in DMF medium

The heating programs for the determination of Cd, Cr, Pb, and Sb in polymeric samples from WEEE in DMF medium were optimized using a polymeric sample (Cell2A) dissolved in DMF. This sample was not spiked since all analytes were naturally present. The dilution factors used to investigate the Cell2A sample were 1:50 (m/v) for Cd, Cr, and Pb and 1:400 (m/v) for Sb. The integrated absorbance measurements were accomplished using 20 μL of the sample solution.

The optimization of the experimental conditions (chemical modifier, pyrolysis time, pyrolysis temperature and atomization temperatures) was accomplished evaluating pyrolysis and atomization curves. The heating programs were based on the manufacturer's recommended conditions and the effect of chemical modifiers on matrix behavior was independently examined. Sensitivity, magnitude of background signal and minimum temperature of atomization (to increase the lifetime of the graphite tube) were selected as criteria for finding the best conditions.

2.6. Quantification of Cd, Cr, Pb, and Sb in plastic slurries from WEEE by ETAAS

The applicability of the DMF slurry sample for plastics from WEEE was demonstrated by the determination of Cd, Cr, Pb, and Sb using ETAAS. The temperature heating programs used for each element are presented in Table 4.

Analyses were performed in triplicate and quantification was based on the standard addition method.

Table 4
Temperature programs used for the determination of Cd, Cr, Pb and Sb in WEEE samples in DMF medium.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Flow rate (mL min^{-1})
Drying	120	10	20	250
Pyrolysis				
Cd	600	10	20	250
Cr	1200		20	
Pb	700		20	
Sb	1100		30	
Atomization				
Cd	1400	0	5	0
Cr	2300			
Pb	1300			
Sb	1900			
Cleaning	2500	1	5	250
Cooling	20	1	5	250

Table 5
Analytical characteristics for the determination of Cd, Cr, Pb and Sb in acid digested samples.

Parameter	Cd	Cr	Pb	Sb
Linear dynamic range (μg L^{-1})	5–20	5–30	12.5–50	25–100
R	0.9999	0.9962	0.9931	0.9910
LOD[a] (μg L^{-1})	0.9	0.9	1.4	6.8
Characteristic mass	1.9	8.5	32.3	53.3
Recovery (%)	96–104	93–104	95–106	98–107
Precision (%)	4.6	5.0	5.1	3.9

[a] Calculated from ten measurements of blank solution ($n = 10$).

3. Results and discussion

Direct analysis of slurries requires control of their stability and homogeneity. A highly stable and homogeneous slurry is required in order to achieve a reliable sample mass that will be introduced to the graphite tube to provide precise and accurate analytical results. The behavior of slurries for determination of Cd, Cr, Pb, and Sb in plastics from WEEE was evaluated. Known volumes of DMF were directly added to the previously weighed polymeric samples. After DMF addition, the formation of stable slurries was observed where the suspended particles took more than 24 h to sediment or did not sediment at all. Some samples were completely dissolved in DMF.

To optimize the heating programs in ETAAS, pyrolysis and atomization temperature curves were built for each element to determine the best conditions. In this step, the temperatures leading to the best signal sensitivities and the lowest background signals were used as criteria for selection of the temperature interval that offered the best conditions. This means that temperatures resulting in high values of background signals and peaks with irregular shapes were excluded. The pyrolysis and atomization temperature curves are shown in Fig. 1 and the final experimental parameters were set as presented in Table 5.

3.1. Analytical characteristics

The analytical characteristics were determined using the optimized conditions for each of the elements. The limits of detection (LOD, μg L^{-1}) were calculated by using the equation ($LOD = 3 \times S_{BL}/b$), where S_{BL} is the standard deviation of ten blank measurements and b is the analytical curve slope. Sensitivity is expressed as the amount of analyte that results in an analytical signal of absorbance 0.0044. For comparison purposes, the analytical figures of merit for slurry and for a digested sample analyzed by ETAAS are presented in Tables 5 and 6.

Method accuracy for the determination of the analytes by ETAAS using slurries prepared in DMF was verified by analyte additions and recovery experiments and by comparing the results obtained with another method using ETAAS with digested samples, using Student's *t*-test. The addition and recovery studies were performed with sample Cell2A spiked at two concentration levels. The recov-

Table 6
Analytical characteristics for the determination of Cd, Cr, Pb and Sb using slurry analysis.

Parameter	Cd	Cr	Pb	Sb
Linear dynamic range (μg L^{-1})	5–20	5–30	10–50	25–100
R	0.99397	0.99028	0.99421	0.98124
LOD[a] (μg L^{-1})	1.2	2.9	1.0	3.3
Characteristic mass	1.9	9.1	28.1	54.1
Recovery (%)	96–106	106–112	98–104	98–111
Precision (%)	1.9	2.5	2.1	1.9

[a] Calculated from ten measurements of blank solution ($n = 10$).

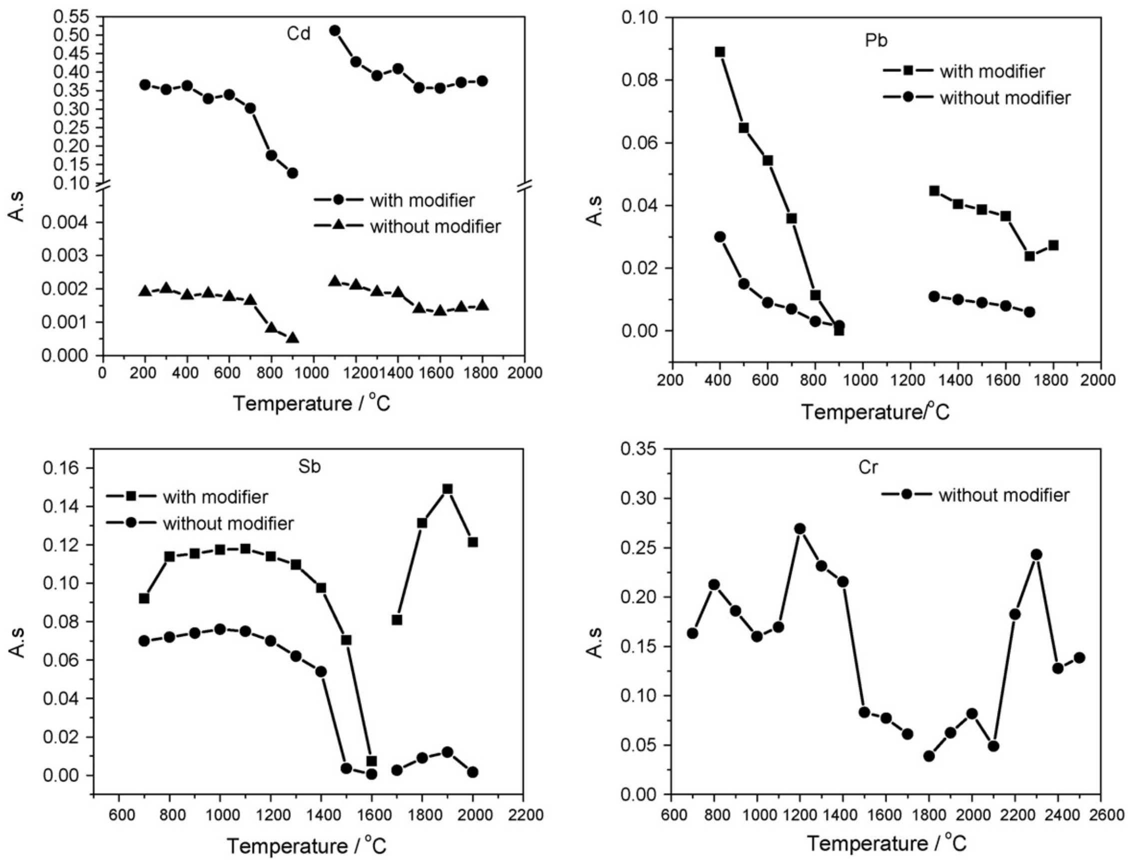

Fig. 1. Pyrolysis and atomization temperature curves for Cd, Pb, and Sb in plastic slurries using chemical modifiers (Cd and Pb: 50 μg $NH_4H_2PO_4$ + 3 μg $Mg(NO_3)_2$ and Sb: 5 μg Pd + 3 μg $Mg(NO_3)_2$). Cr was without chemical modifier.

ery values obtained were between 94 and 107% in DMF medium and 96 and 112% in acid medium. The results indicated that both methods were in agreement at a 95% confidence level when a paired *t*-test was applied and presented good values of precision for analyses using ETAAS.

Based on recovery values it may be seen that in general the digested sample method led to higher values than the slurry method. Also standard deviations for the slurry method were higher than those for digestion sample method.

Based on the experimental results it was verified that the polymeric matrix is complex and the use of external calibration employing reference standard solutions was not indicated for analyte quantification. Recovery values for digested samples obtained by external calibration were 8–13% greater than those obtained by the standard addition method. Probably, the presence of H_2SO_4 in the digests affected blank repeatability and consequently the analytical measurements, as described by Ernst et al. [25], to whom digestion using microwave radiation did not lead to a linear relation between concentration and absorbance. To avoid this problem these authors used addition and recovery experiments for digested samples. Recovery values obtained for slurry analysis by ETAAS using external calibration were in general lower than those established using the reference standard solution method. In both cases it was possible to verify that the standard addition method was an important tool for correction of matrix effects. Considering the need for the standard addition method for analyte quantification with both the slurry preparation and the digestion procedure, the sample preparation time becomes an important aspect to be considered. The slurry preparation procedure was simpler than the sample digestion procedure.

Another aspect that must be considered is the sample dilution factor in different media (DMF or acid). Some digested samples showed concentration values for Pb and Cd below the LOQs. The dilution factor (100 mg of sample: 50 mL of solution) makes the determination of Cd and Pb present in low concentrations in some samples difficult. This problem was not observed with the slurry analysis method due to the fact that analytes present in slurries were at greater concentrations due to the low dilution factor. To avoid the high dilution factors for digested samples, they were diluted to 15 mL instead of 50 mL in order to increase concentrations of Pb and Cd in the digested samples. However, the acidity of the digested samples was too high (~6%) and the graphite tube did not support very many heating cycles, *e.g.* only 25–40 measurements for determination of Pb. Moreover, this limited lifetime was not long enough to obtain pyrolysis and atomization temperature curves when performing triplicate measurements.

The shape of transient absorbance and background peaks is also important to select a method. The peak profiles for Cd in sample Cell2A obtained in DMF and in an acid medium were studied. Both methods generate suitable analytical signals but the background signal in DMF medium was around two times lower than in acid medium, probably because of the low DMF boiling point (153 °C), that means that almost all solvent was eliminated in the pyrolysis step. The same behavior was observed for the other analytes.

Considering sample digestion, microwave radiation was not enough to destroy all of the organic matrices in several samples. In general, there were no solid residues in the digested samples and the resulting solutions were yellow, red or in some cases, colorless. Different heating programs for sample digestion using different masses were investigated, but did not contribute to improvements

Table 7
Values determined for Cd, Cr, Pb and Sb using slurry analysis by ETAAS for the different samples analyzed.

Sample	Component	Sample color	Determined value			
			Cd ($\mu g\,g^{-1}$)[a]	Cr ($\mu g\,g^{-1}$)[a]	Pb ($\mu g\,g^{-1}$)[a]	Sb ($g\,g^{-1}$)[a]
M1A	Shield	Beige	6.0[b]	191.2	115.3	8.0
M1B	Shield	Grey	10.7[b]	154.2	150.4	1.3
M1C	Shield	Dark Grey	90.1	77.9	30.2	3.4
M1D	Internal	Black	91.9	212.7	101.2	9.4
M2A	Shield	Grey	56.9	115.2	239.9	11.
M2B	Shield	Beige	201.1	185.0	30.1	2.0
M2C	Shield	Dark Blue	136.2	388.4	123.5	9.5
M3A	Shield	Black	97.5	169.7	256.3	15.4
M3B	Shield	Black	31.3[b]	281.0	90.8	14.9
M3C	Shield	Black	59.7	238.3	60.3	9.3
M4A	Shield	Light Grey	90.9	256.7	231.1	13.5
M4B	Shield	Grey	42.3[b]	64.2	187.3	6.5
M4C	Shield	Dark Grey	130.2	361.6	303.1	11.6
M5A	Shield	Beige	245.3	278.1	154.2	12.6
M5B	Shield	Beige	33.1[b]	299.7	111.4	8.6
M5C	Shield	Beige	451.4	445.0	57.5	14.7
M5D	Internal	Beige	64.9	278.9	457.9	9.5
Cell1A	Shield	Black	117.2	51.0	133.5	10.3
Cell1B	Internal	White	42.7[b]	194.7	122.3	9.6
Cell2A	Shield	White	470.7	237.5	256.1	7.5
Cell2B	Shield	Grey	97.5	347.1	156.7	8.0
Cell2C	Internal	White	33.9[b]	141.4	45.9	9.6
Cell3A	Shield	Black	97.3	584.0	259.4	8.3
Cell3B	Interior	White	99.9	240.1	50.5	6.5
Cell4A	Shield	Blue	79.7	102.2	49.3	7.4
Cell4B	Shield	Beige	158.9	174.5	184.7	7.9
Cell4C	Internal	White	123.3	313.2	67.9	9.1
Cell5A	Shield	Black	456.1	375.4	233.5	16.5
Cell5B	Internal	White	243.3	212.6	455.9	7.9
Cell6A	Shield	Black	435.5	169.0	198.1	13.7
CellB	Internal	White	42.6[b]	368.5	238.9	8.9
Cell7A	Shield	Grey	300.4	183.9	53.2	7.9
Cell7B	Shield	Beige	425.5	345.0	145.9	8.2
Cell7C	Internal	White	458.7	183.4	258.9	4.3
Cell8A	Shield	Grey	90.0	367.5	168.7	9.6
Cell8B	Shield	Beige	525.8	611.2	56.7	18.9
Cell8C	Internal	White	48.9[b]	345.6	90.8	9.1
K1	Shield	Beige	90.4	313.0	156.7	9.8
K2	Shield	Beige	46.6[b]	118.3	145.8	7.2
K3	Shield	Black	156.2	219.0	178.9	6.9
Mon1A	Shield	Beige	368.5	194.8	246.9	8.4
Mon1B	Internal	White	202.2	169.7	200.4	7.9

Cell = mobile phone. Key = keyboard. Mon = monitor.

[a] Mean ± standard deviation, $n = 3$ (rsd–Cd rsd 2.2–4.6%, Pb 1.9–4.4%, Sb 2.9–5.4%, and Cr 3.1–5.0%).

[b] In agreement with the limit established by the European community (limit 0.1% in weight).

in digestion efficiency. Residual carbon content was <5% in five polymeric samples.

Acid digestion was optimized to evaluate the accuracy of the proposed method using slurry prepared in DMF for sample Cell2A. This results in a digest with the lowest carbon content.

The complete digestion of BCR 680 and BCR 681 was not possible using the sample preparation procedure developed for ABS samples because these polymeric materials (polyethylene) were different from those used in the proposed method. The BCR materials were used only to compare the elements concentration in the sample. To avoid problems caused by incomplete digestion, a more drastic heating condition and a longer decomposition time were applied for CRM (PE) and Cell2A (ABS). Results for standard reference materials were in agreement with certified values at a 95% confidence level when a paired *t*-test was applied.

3.2. *Determination of Cd, Pb, Sb, and Cr in plastics from WEEE*

Considering the advantages of direct analysis of plastic samples as slurries by ETAAS the method developed was applied for determination of Cd, Pb, Sb, and Cr in samples from WEEE. Analyte concentrations are shown in Table 7 that also presents the samples and their respective descriptions.

The results indicate that Cd, Cr, Pb and Sb were present in all the samples investigated and that they could be determined using slurries prepared in DMF. Analyte concentrations vary over a large range. The ranges for Cd, Cr and Pb were 5–525, 51–611 and 30–458 mg kg^{-1}, respectively, while the content of Sb was 0.2–1.65%, indicating the addition of additives and pigments containing these elements into the polymeric matrix. The elevated concentration of Sb indicates the use of antimony trioxide as flame retardant [7].

Another aspect that needs special attention is related to element concentrations and legislation. According to Directives 2002/96/CE and 2002/95/CE, that regulate the adequate management of residues and restrict the use of dangerous substances in electric and electronic equipment, the contents of Cd, Cr and Pb present in WEEE must be lower than 0.01%, 0.1% and 0.1%, respectively, related to homogeneous material's weight [12,13]. The percentages obtained for Cd in some samples were at the upper limit or higher than the value established by the EC Directive. Only ten of the analyzed samples were within the values specified by the Directives for

Cd. For Pb and Cr the values measured for all the samples analyzed are in agreement with the Directives.

4. Conclusion

The method developed for the determination of these four analytes in slurries prepared from polymeric materials was suitable and the use of chemical modifiers contributed to an efficient volatilization of the matrix. The use of DMF in sample preparation provided a fast and simple sample preparation step. The procedure presented adequate detectivity, precision and accuracy. Addition and recovery studies indicated that the method developed can be applied for the determination of Cd, Cr, Pb, and Sb in plastics from WEEE. Results show that some of the analyzed samples contain metallic species in concentration above the recommended value by the European Community. These aspects suggest that much more attention should be addressed to the challenges involved in controlling heavy metals in products used in the electrical and electronic industries, to avoid subsequent problems when recycling is required.

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