

## Determination of Inorganic Contaminants in Electrical and Electronic Equipment after Digestion Using Microwave-Assisted Single Reaction Chamber

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A method for digestion of plastics from waste of electrical and electronic equipment (WEEE) was developed using the microwave-assisted wet digestion in single reaction chamber (MAWD-SRC). The determination of As, Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP OES) was carried out after sample digestion. Mercury was determined by flow-injection cold vapor generation coupled to inductively coupled plasma mass spectrometry (FI-CVG-ICP-MS). Results obtained using MAWD-SRC for sample preparation were compared with those obtained using microwave-assisted wet digestion (MAWD) at high pressure. Acid mixtures (HNO<sub>3</sub> or HNO<sub>3</sub> + HCl) were evaluated and feasibility for further inorganic contaminants determination by ICP-MS and ICP OES was demonstrated. Sample preparation by MAWD-SRC using HNO<sub>3</sub> + HCl mixture resulted in better digestion efficiency in comparison to MAWD. In addition, lower limits of quantification were obtained using MAWD-SRC due to the higher sample mass that can be digested (500 mg). The combination of HNO<sub>3</sub> and HCl for digestion showed to be crucial for quantitative recovery of some elements, as Cr and Sb. Agreement with certified values was better than 96%.

**Keywords:** WEEE, sample preparation, contaminants, spectrometric techniques, RoHS Directive

### Introduction

The rapid replacement of electrical and electronic equipment (EEE) by other with better technology has contributed to the increasing amount of waste electrical and electronic equipment (WEEE).<sup>1,2</sup> In addition to the environmental impact, has been of concern the presence of hazardous substances in these WEEE, such as heavy metals and brominated flame retardants (BFRs).<sup>3</sup> These are substances added to improve the properties of polymeric materials and to avoid fires. Stabilizers or plasticizers (e.g., compounds of Cd, Pb, and Zn), pigments (e.g. TiO<sub>2</sub>, ZnO, and Cr<sub>2</sub>O<sub>3</sub>), and flame retardants (Sb compounds combined with brominated compounds) are used as additives.<sup>4,5</sup> Due to the toxicity of those substances and elements, the European Union has established the Restriction of the Use of Certain Hazardous Substances (RoHS) in EEE.<sup>3</sup> With the implementation of RoHS Directive, it is defined that the maximum concentration allowed by weight are: 0.01% for

Cd and 0.1% for Cr<sup>VI</sup>, Hg, Pb, polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PBDE).<sup>3</sup> In addition, compounds containing Co, Cu, Ni, Sb, Zn are also used as additives in polymeric materials and thus, can be also common contaminants.<sup>6</sup> Following RoHS Directive, the knowledge of contaminants content in waste of EEE is required.

In this context, the development of analytical methods for inorganic contaminants determination, such as As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb and Zn contained in polymeric materials is necessary for the quality control in industry, waste management and environmental monitoring.<sup>4</sup> The determination of inorganic contaminants can be normally, performed by spectrometric techniques.<sup>7</sup> In this purpose, the sample must be converted into a suitable solution for conventional nebulization. However, taking into account that EEE are mostly polymeric-based matrices, sample preparation can be considered an analytical challenge due to the stability and chemical resistance for digestion.<sup>8-10</sup> In order to overcome this difficulty, the determination of inorganic contaminants in WEEE has

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been alternatively performed by direct analysis using X-ray fluorescence, graphite furnace atomic absorption spectrometry, laser ablation and electrothermal vaporization coupled to inductively coupled plasma-mass spectrometry (ICP-MS).<sup>10-14</sup> However, several interferences due to changes in matrix composition are reported and calibration with certified reference materials (CRMs), which are not easily available, is usually required.<sup>15</sup>

Sample preparation with further analyte determination by spectrometric techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and ICP-MS, allow high sample throughput and suitable limits of quantification (LOQ). Wet digestion using concentrated acids is the most common approach for digestion of several organic samples.<sup>16</sup> In this way, closed systems that allows the use of high temperature and pressure are required for digestion of EEE in order to obtain relatively high efficiency of digestion, resulting in low values of residual carbon content (RCC) and low residual acidity.<sup>8,9</sup> These are important characteristics of digests to avoid interferences in the determination step by ICP OES<sup>17</sup> and ICP-MS<sup>18</sup> and can be considered dependent of the digestion method and system used as well as of the sample.

In this sense, a digestion system that allows the use of drastic operating conditions, such as high temperature and pressure (270 °C and 160 bar, respectively), called microwave-assisted single reaction chamber (SRC, UltraWAVE™ system) was recently developed.<sup>19</sup> The microwave-assisted wet digestion in single reaction chamber (MAWD-SRC) can be an alternative for hard sample digestion in order to achieve efficient digests and quantitative recoveries of inorganic contaminants.<sup>19,20</sup> This method can be applied for simultaneous digestion of various types of samples as polymer, biodiesel, and lubricant oil with good digestion efficiency.<sup>19</sup> In addition, high sample masses of nuts,<sup>20</sup> active pharmaceutical ingredients,<sup>21</sup> and crude oil<sup>22</sup> can be digested using MAWD-SRC allowing suitable digests for the determination of inorganic contaminants by ICP OES and ICP-MS providing low LOQs.

Taking into account the requirement to determine contaminants in waste of EEE and in an effort to attain this using plasma-based analytical techniques the MAWD-SRC method was evaluated in this work. Microwave-assisted wet digestion (MAWD) using a high-pressure system was used for comparison. Digestion efficiency was evaluated for each method by measuring the carbon content in final digests and the suitability of using MAWD-SRC method for analyte determination was evaluated. A keyboard was the EEE material used to evaluate both methods for further determination of

As, Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn by ICP OES and ICP-MS, as well as Hg by flow-injection cold vapor generation coupled to inductively coupled plasma mass spectrometry (FI-CVG-ICP-MS). Accuracy was evaluated by comparison of results obtained using both digestion methods for sample preparation as well as by using CRMs.

## Experimental

### Instrumentation

A microwave oven based on the Single Reaction Chamber (SRC) design (UltraWAVE™, software version EasyControl, Milestone, Sorisole, Italy) was used for MAWD-SRC. Experiments were carried out using a rack with fifteen quartz vessels (15 mL of internal volume). Microwave power was 1500 W, and maximum pressure and temperature were set at 160 bar and 270 °C, respectively. For comparison, MAWD at high-pressure was carried out using a microwave sample preparation system (Multiwave 3000, software version v2.02, Anton Paar, Graz, Austria), equipped with eight high-pressure quartz vessels (80 mL of internal volume). Microwave power was 1400 W and maximum pressure and temperature were set at 80 bar and 280 °C, respectively, which are the maxima conditions allowed for this system.

Determination was performed by ICP OES and/or ICP-MS depending on the concentration and suitability of these techniques. For this purpose, an inductively coupled plasma mass spectrometer (PerkinElmer-SCIEX, Model Elan DRC II, Thornhill, Canada) and an inductively coupled plasma optical emission spectrometer (PerkinElmer optima 4300 DV, Shelton, USA) were used. Mercury determination was performed by coupling a home-made flow-injection cold vapor generation (FI-CVG) system to the ICP-MS equipment (the same used for determination of other analytes). Conditions for Hg determination by FI-CVG-ICP-MS were used as described previously.<sup>9</sup> Carbon content in digests was analyzed by ICP OES to evaluate digestion efficiency.<sup>23,24</sup> Argon 99.998% (White Martins - Praxair, São Paulo, Brazil) was used for plasma generation, nebulization and auxiliary gas, as well as for pressurizing the chamber of microwave oven. In addition, argon was also used for removing carbonaceous gases dissolved into digests prior the determination of carbon. Plasma operating conditions used for inorganic contaminants determination are described in Table 1. The statistical calculations were performed using GraphPad InStat (GraphPad InStat Software Inc, Version 3.00, 1997) software.

**Table 1.** Operational conditions for the determination of inorganic contaminants and carbon by ICP OES and ICP-MS

Parameter	ICP OES	ICP-MS
RF power / W	1400	1300
Plasma gas flow-rate / (L min <sup>-1</sup> )	15	15
Auxiliary gas flow-rate / (L min <sup>-1</sup> )	0.20	1.20
Nebulizer gas flow-rate / (L min <sup>-1</sup> )	0.80	1.15
Spray chamber	cyclonic	baffled cyclonic
Nebulizer	concentric	concentric
View	axial	–
Sample and skimmer cones	–	Pt
Ion lens / V	–	auto lens
Dwell time / ms	–	25
Isotopes / <i>m/z</i> ratio	–	<sup>75</sup> As, <sup>114</sup> Cd, <sup>59</sup> Co, <sup>53</sup> Cr, <sup>65</sup> Cu, <sup>202</sup> Hg, <sup>60</sup> Ni, <sup>208</sup> Pb, <sup>121</sup> Sb, and <sup>66</sup> Zn
Wavelength / nm	193.696 (As), 228.802 (Cd), 228.626 (Co), 205.560 (Cr), 324.752 (Cu), 231.604 (Ni), 220.353 (Pb), 206.836 (Sb), 206.200 (Zn), and 193.030 (C) <sup>a</sup>	–

<sup>a</sup>Used for the determination of C content in digests. ICP OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry.

### Reagents, samples and solutions

All chemicals were of analytical grade. Water was purified using a Milli-Q system (Millipore, Billerica, USA, 18.2 MΩ cm) and it was used for dilution and preparation of all standards and solutions. Nitric (65%, Merck, Darmstadt, Germany) and hydrochloric acids (37%, Merck, Darmstadt, Germany) were distilled using a sub-boiling system (model DuoPur, Milestone, Sorisole, Italy), and they were used for both wet digestion methods (MAWD-SRC and MAWD). A multi element standard solution (PlasmaCal calibration solution, 10 mg L<sup>-1</sup>, SCP33MS, SCP Science, Quebec, Canada) was used for preparation of analytical standards (0.01 to 1 µg L<sup>-1</sup> for ICP-MS and 2.5 to 100 µg L<sup>-1</sup> for ICP OES) in 0.7 mol L<sup>-1</sup> HNO<sub>3</sub>. Analytical standards for Hg determination (0.05 to 1 µg L<sup>-1</sup>) were prepared by sequential dilution of a 10 mg L<sup>-1</sup> stock reference solution, in 0.7 mol L<sup>-1</sup> HNO<sub>3</sub>. For carbon determination, standards were prepared using a C reference solution (1000 mg L<sup>-1</sup>, Spex CertiPrep, Metuchen, USA) and yttrium (1000 mg L<sup>-1</sup>, Spex CertiPrep) was used as internal standard (1 mg L<sup>-1</sup>) for standards and samples.

A keyboard sample collected from waste was chosen as an example of EEE for optimization of MAWD-SRC

method. Plastic parts of this WEEE (polycarbonate with ABS (acrylonitrile butadiene styrene) copolymer) were separated and ground using a cryogenic mill (Spex Certiprep, model 6750, Metuchen, USA), with a pre-cooling time of 90 s followed by 3 min for grinding (this procedure was repeated three times). Powdered samples were dried in an oven (model 400/2ND, Nova Ética, São Paulo, Brazil) for 1 h at 60 °C. The accuracy was evaluated using a CRM of low-density polyethylene (ERM<sup>®</sup>, EC680k, European Reference Materials, Belgium).

### Sample preparation by MAWD-SRC and MAWD at high pressure

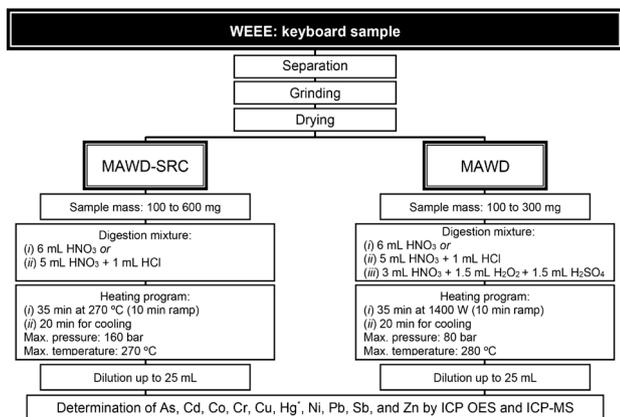
Samples were weighed into digestion vessels and were digested using the following mixtures for both methods: (i) 6 mL of 14.5 mol L<sup>-1</sup> HNO<sub>3</sub> and, (ii) 5 mL of 14.5 mol L<sup>-1</sup> HNO<sub>3</sub> + 1 mL of 12 mol L<sup>-1</sup> HCl. Sample mass was from 100 to 600 mg for MAWD-SRC and from 100 to 300 mg for MAWD. The volume of acid mixture (6 mL) was set following the recommendations of manufacturer. Particularly in the case of MAWD-SRC, the chamber was previously charged with 130 mL of H<sub>2</sub>O and 5 mL of HNO<sub>3</sub> and it was pressurized up to 40 bar of Ar, according to the recommendations of the manufacturer.<sup>25</sup> The irradiation program for MAWD-SRC and MAWD was applied as shown in Figure 1 and limit pressure and temperature was used according to the condition allowed for each system. After the irradiation program, the solutions were diluted with water up to 25 mL for posterior analysis. A digestion method published in the literature was also used as reference for comparison, using 18.2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (1.5 mL), 14.5 mol L<sup>-1</sup> HNO<sub>3</sub> (3 mL), and 30% H<sub>2</sub>O<sub>2</sub> (1.5 mL).<sup>26</sup>

All procedures evaluated in this work for digestion of WEEE samples are illustrated in Figure 1, showing experimental conditions for all methods.

## Results and Discussion

### Feasibility of digestion using MAWD-SRC

In general, UltraWAVE<sup>™</sup> system is based on a microwave cavity with a stainless steel reaction chamber and a polytetrafluoroethylene (PTFE) cover, which accommodates up to 15 vessels and allowed efficient distribution of microwave radiation. This system is pressurized with inert gas to prevent sample boiling and cross contamination prior to application of microwave irradiation. Using this system, a high efficiency of digestion has been demonstrated for several hard-to-digest samples, for relatively high sample mass.<sup>19-22</sup> Particularly, for



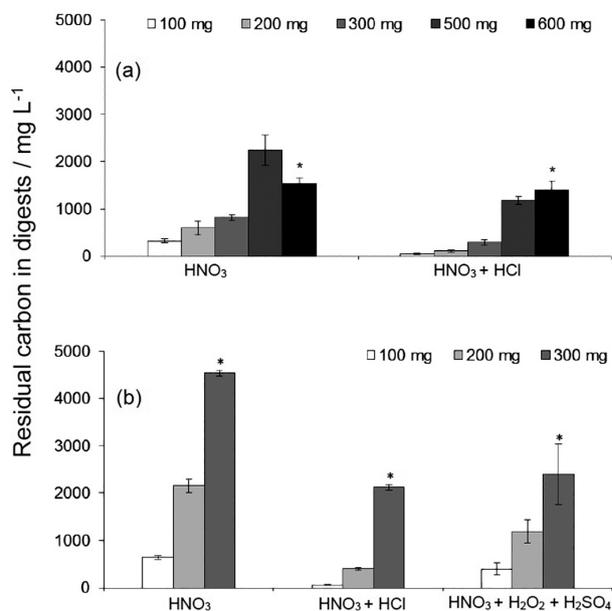
**Figure 1.** Methods evaluated for digestion of WEEE and further analysis by plasma-based techniques (\*FI-CVG-ICP-MS for Hg).

digestion of polymers and related materials as WEEE, suitable digestion conditions must be selected once polymers can be considered difficult to digest even using high pressure and high temperature.<sup>8</sup>

In this work, MAWD-SRC was evaluated for WEEE, initially for a keyboard sample. Comparatively, MAWD was carried out for comparison using the same conditions. Each system allows a particular maximum temperature and pressure, as described in the Experimental section. For MAWD-SRC and MAWD, the same heating program was applied as well as the amount and composition of the acid mixture used for digestion. In addition, a mixture of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> was used for MAWD, according to a procedure previously described in the literature.<sup>26</sup> Digestion efficiency was evaluated by the amount of residual carbon in digests determined by ICP OES. The residual carbon (C in solution after digestion and dilution up to 25 mL) is shown for HNO<sub>3</sub> and HNO<sub>3</sub> + HCl mixtures and using 100 to 600 mg of sample, for MAWD-SRC (Figure 2a) and 100 to 300 mg for MAWD (Figure 2b).

In general, digestion using MAWD-SRC presented better efficiency in comparison to MAWD once lower residual carbon was present in the digests (Figure 2a). In addition, digests obtained using only nitric acid resulted in lower digestion efficiency when compared to the results obtained using the mixture with hydrochloric acid. Moreover, digestion was not complete with visible not digested sample residues for MAWD-SRC method using 600 mg, for both acid mixtures and for MAWD using 300 mg, for all acid mixtures. Then, it is important to emphasize that results presented for those conditions (the limit mass for each method, identified as \* in Figures 2a and 2b) can be underestimated once sample not completely digested remained after the irradiation program.

According to the literature, a carbon content in digests of about 5000 mg L<sup>-1</sup> can interfere on the measurement of hard-



**Figure 2.** Residual carbon (mg L<sup>-1</sup>) in digests using 100 to 600 mg, obtained by (a) MAWD-SRC and (b) MAWD, using HNO<sub>3</sub> and HNO<sub>3</sub> + HCl mixtures (n = 3; \*digestion was not complete and results were obtained after centrifugation of digests).

to-ionize elements in plasma-based techniques.<sup>17,18,23,27,28</sup> On the other hand, polyatomic interferences due to the presence of C must also be considered, in particular for Cr determination.<sup>28</sup> This makes important to develop digestion methods able to generate digests containing low carbon content as well as low residual acidity, which are suitable for analyses using plasma-based techniques. Another important aspect that can be considered with regard to the quality of digests and solutions with high carbon content is the deposition of carbon at the interface and the influence in the nebulizing system. Both problems can require unexpected maintenance for cleaning the system and this can be troublesome for routine analysis. Then, based on the results, it must be considered that a suitable digest can be obtained by MAWD-SRC using HNO<sub>3</sub> + HCl up to 500 mg. In contrast, 250 mg was defined as the limit sample mass for MAWD, once this mass could be digested for both mixtures. Then, the sample mass for digestion using MAWD-SRC was set at 500 mg, the highest mass that can be digested among the methods investigated in this work.

The higher efficiency of digestion using this method can be mainly attributed to the high temperature that can be achieved in this system (270 °C) in comparison to that obtained using MAWD. In spite of MAWD at high pressure allowing a maximum temperature of 280 °C, this value was not reached during digestion because the pressure inside vessels reached the maximum value (80 bar) in about 20 min. Then, heating was controlled by the microwave power applied, which was limited by pressure, and in

practice a maximum temperature of about 205 °C was reached. To support this idea, a program using MAWD-SRC was applied for 300 mg of sample, with a temperature limit of 205 °C. In this experiment, residual carbon in digests was about 4000 mg L<sup>-1</sup> using HNO<sub>3</sub> and 2900 mg L<sup>-1</sup> using HNO<sub>3</sub> + HCl. These values are higher than those obtained in this method using maxima temperature and pressure, showing that a higher temperature is required to improve digestion efficiency, and this can be reached using MAWD-SRC. A power, temperature, and pressure profile is shown in Figure 3.

As a general rule, both MAWD-SRC and MAWD methods showed to be suitable to digest up to a certain sample mass. In order to obtain suitable digests and avoid interferences, which must be specifically evaluated depending on the analyte and the detection technique, as well as taking to account the available instrumentation, the method can be chosen. Based on the results, it is important to point out that by using MAWD-SRC a higher sample mass can be digested, improving LOQs and a lower residual carbon in digest is obtained.

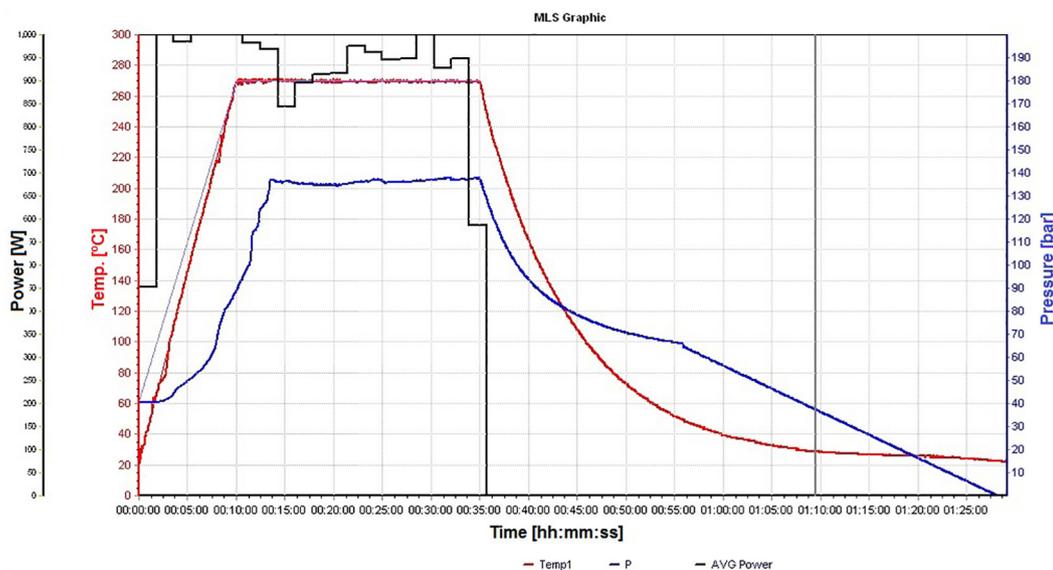
Suitability of MAWD-SRC for sample preparation of WEEE and further determination of inorganic contaminants by ICP OES and ICP-MS

Interferences during the analysis of metals and metalloids by plasma-based techniques can be expected, as a consequence of the residual carbon in digests and also depending on the acid composition used for digestion (mainly HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>).<sup>26,28-30</sup> As a consequence, the suitability of digests for analysis

must be evaluated. In order to evaluate the suitability of digests obtained using MAWD-SRC and MAWD, for 500 and 250 mg, respectively, As, Cd, Cr, Hg, Pb, and other elements were determined by ICP OES and ICP-MS. With the exception of Cr by ICP-MS, which was dependent on the carbon content in digest, as well as for As depending on the residual carbon, digests were suitable for both determination techniques. In addition, As determinations in digests containing HCl were preferentially performed by ICP OES due to isobaric interferences in ICP-MS. Despite the fact that the use of HNO<sub>3</sub> + HCl has resulted in a low residual carbon in digests, no interferences were observed for Cd, Co, Cu, Ni, Pb, Sb, and Zn, when using only HNO<sub>3</sub>. Then, digests were considered suitable for the determination of these elements.

Results obtained for all analytes in a keyboard sample using MAWD-SRC and MAWD, are shown in Table 2. The determination of As, Cd, Co, Cu, Hg, Ni, Pb, and Zn was performed in digests using HNO<sub>3</sub>. No statistical difference was observed between the results obtained using only HNO<sub>3</sub> and HNO<sub>3</sub> + HCl (*t*-test, 95% confidence level) for these analytes. On the other hand, for Cr and Sb results were up to 30% lower using only HNO<sub>3</sub> and thus the mixture HNO<sub>3</sub> + HCl was required to assure accurate results.

No statistical difference (*t*-test, 95% confidence level) was observed for all analytes for results obtained by MAWD-SRC and MAWD. These results show that both methods can be considered suitable options for sample preparation of WEEE for further determination of inorganic contaminants, including those required in RoHS Directive. Considering that results for Hg were lower than the LOQ for both methods (Table 2), an aliquot of a reference solution



**Figure 3.** Temperature (—), pressure (—) and power (—) profile for MAWD-SRC for a typical run, obtained using Software EasyControl (UltraWAVE, Milestone Srl., Sorisole, Italy).

**Table 2.** Results for inorganic contaminants ( $\mu\text{g g}^{-1}$ ) in a WEEE sample obtained by ICP OES,<sup>a</sup> ICP-MS,<sup>b</sup> and FI-CVG-ICP-MS<sup>c</sup> after MAWD-SRC<sup>d,e</sup> or MAWD<sup>d,e</sup> (mean  $\pm$  standard deviation,  $n = 3$ )

Analyte	MAWD-SRC	MAWD
As <sup>b,d</sup>	0.056 $\pm$ 0.007	0.053 $\pm$ 0.005
Cd <sup>b,d</sup>	0.018 $\pm$ 0.002	0.020 $\pm$ 0.004
Co <sup>b,d</sup>	0.121 $\pm$ 0.010	0.124 $\pm$ 0.009
Cr <sup>a,e</sup>	1.19 $\pm$ 0.14	1.24 $\pm$ 0.06
Cu <sup>a,d</sup>	0.650 $\pm$ 0.032	0.646 $\pm$ 0.037
Hg <sup>c,d</sup>	< 0.029	< 0.054
Ni <sup>b,d</sup>	0.301 $\pm$ 0.010	0.292 $\pm$ 0.010
Pb <sup>b,d</sup>	0.139 $\pm$ 0.012	0.140 $\pm$ 0.014
Sb <sup>a,e</sup>	28.3 $\pm$ 2.3	27.0 $\pm$ 2.9
Zn <sup>a,d</sup>	75.7 $\pm$ 2.4	73.0 $\pm$ 2.3

<sup>a</sup>ICP OES; <sup>b</sup>ICP-MS; <sup>c</sup>FI-CVG-ICP-MS; <sup>d</sup>results for As, Cd, Co, Cu, Hg, Ni, Pb, and Zn were obtained using HNO<sub>3</sub>; <sup>e</sup>results for Cr and Sb were obtained using HNO<sub>3</sub> + HCl. ICP OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; FI-CVG-ICP-MS: flow-injection cold vapor generation coupled to ICP-MS; MAWD-SRC: microwave-assisted wet digestion in single reaction chamber; MAWD: microwave-assisted wet digestion.

was added into the vessel containing sample and acid mixture before heating program. Recoveries for Hg were better than 94%, showing that this analyte also can be determined using sample preparation by MAWD-SRC and MAWD methods.

#### Accuracy and figures of merit

In order to evaluate the accuracy of sample preparation by MAWD-SRC method and determination by ICP OES and ICP-MS, a polymeric CRM (ERM EC680k, low density polyethylene) was evaluated under optimized conditions. Results are presented in Table 3.

Results presented a good agreement between obtained and certified values. No statistical difference (*t*-test, 95% confidence level) was observed between the results obtained using sample preparation by MAWD-SRC followed by ICP OES or ICP-MS (FI-HG-CVG-ICP-MS for Hg) determination and the certified value. In order to obtain lower LOQs and better digestion efficiency with solutions suitable for analysis by plasma-based analytical techniques, MAWD-SRC showed to be an advantageous method once higher sample mass can be digested and a solution with low residual carbon was obtained. Table 4 summarizes some analytical figures of merit for MAWD-SRC and MAWD for comparison.

Using MAWD-SRC, fifteen samples can be digested simultaneously whereas using MAWD it is possible to digest up to eight samples per run, at the same time. The heating program was the same applied for both wet

**Table 3.** Results obtained for some inorganic contaminants in CRM EC680k using MAWD-SRC (determinations by ICP OES,<sup>a</sup> ICP-MS,<sup>b</sup> and FI-CVG-ICP-MS,<sup>c</sup>  $\mu\text{g g}^{-1}$ , mean  $\pm$  standard deviation,  $n = 3$ )

Analyte	MAWD-SRC <sup>d,e</sup>	Certified value
As <sup>b,d</sup>	4.30 $\pm$ 0.12	4.1 $\pm$ 0.5
Cd <sup>b,d</sup>	19.2 $\pm$ 0.5	19.6 $\pm$ 1.4
Cr <sup>a,e</sup>	20.0 $\pm$ 0.6	20.2 $\pm$ 1.1
Hg <sup>c,d</sup>	4.75 $\pm$ 0.18	4.64 $\pm$ 0.20
Pb <sup>b,d</sup>	13.3 $\pm$ 0.5	13.6 $\pm$ 0.5
Sb <sup>a,e</sup>	9.82 $\pm$ 0.4	10.1 $\pm$ 1.6

<sup>a</sup>ICP OES; <sup>b</sup>ICP-MS; <sup>c</sup>FI-CVG-ICP-MS; <sup>d</sup>results for As, Cd, Co, Cu, Hg, Ni, Pb, and Zn were obtained using HNO<sub>3</sub>; <sup>e</sup>results for Cr and Sb were obtained using HNO<sub>3</sub> + HCl. ICP OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; FI-CVG-ICP-MS: flow-injection cold vapor generation coupled to ICP-MS; MAWD-SRC: microwave-assisted wet digestion in single reaction chamber.

**Table 4.** Summary of analytical figures of merit obtained for inorganic contaminants using MAWD-SRC and MAWD for WEEE digestion

Parameter	MAWD-SRC	MAWD
Sample mass / mg	500	250
Reagents	6 mL HNO <sub>3</sub> or 5 mL HNO <sub>3</sub> + 1 mL HCl	6 mL HNO <sub>3</sub> or 5 mL HNO <sub>3</sub> + 1 mL HCl
Digestion time / min	55	55
Runs <i>per</i> replicate	15	8
Residual carbon in digests / (mg L <sup>-1</sup> )	1120 $\pm$ 84	2120 $\pm$ 336
LOQ / ( $\mu\text{g g}^{-1}$ )		
As <sup>b,d</sup>	0.020	0.035
Cd <sup>b,d</sup>	0.025	0.045
Co <sup>b,d</sup>	0.005	0.015
Cr <sup>a,e</sup>	0.260	0.500
Cu <sup>a,d</sup>	0.040	0.270
Hg <sup>c,d</sup>	0.029	0.054
Ni <sup>b,d</sup>	0.030	0.065
Pb <sup>b,d</sup>	0.040	0.060
Sb <sup>a,e</sup>	4.5	11.5
Zn <sup>a,d</sup>	0.260	0.920

<sup>a</sup>ICP OES; <sup>b</sup>ICP-MS; <sup>c</sup>FI-CVG-ICP-MS; <sup>d</sup>results were obtained using HNO<sub>3</sub>; <sup>e</sup>results were obtained using HNO<sub>3</sub> + HCl. MAWD-SRC: microwave-assisted wet digestion in single reaction chamber; MAWD: microwave-assisted wet digestion; LOQ: limit of quantification.

digestion methods (MAWD-SRC and MAWD) requiring 55 min for each run including the cooling time. If Cr and Sb are not included among the analytes, only HNO<sub>3</sub> can be used for digestion. As expected, better LOQs were obtained using MAWD-SRC once this method allowed an efficient digestion up to 500 mg. It is important to mention that both evaluated methods allowed to reach LOQs actually required

in the RoHS Directive<sup>3</sup> but the possibility to improve LOQs by digesting high sample mass while presenting high digestion efficiency can be considered an important advantage of MAWD-SRC.

## Conclusions

Determination of inorganic contaminants in WEEE has become necessary due to growing consumption combined with an increased generation of wastes of EEE and the established restriction with regard to the content of some elements. Plasma-based techniques have been extensively used for most samples, commonly after sample digestion. Microwave-assisted wet digestion using the single reaction chamber technology was evaluated and its efficiency and suitability for the determination of elements was studied and compared with conventional MAWD at high pressure. Both methods were suitable for digestion of polymeric components from a keyboard sample of up to a certain sample mass, which was dependent on the maximum pressure and temperature for each system. Regarding to this aspect, results showed that samples masses of up to 500 mg can be digested using the MAWD-SRC whereas 250 mg is the maximum mass that can be digested by MAWD, even at high pressure, using the same heating program and acid mixture. In general, HNO<sub>3</sub> + HCl mixture resulted in digests containing lower residual carbon in comparison to the use of only HNO<sub>3</sub> for digestion. Using MAWD-SRC, lower carbon content in digests was obtained in comparison to MAWD which is advantageous for avoiding possible interferences in the determination of elements by ICP OES and ICP-MS. In addition, higher sample mass could be digested using MAWD-SRC, thus resulting in lower LOQs.

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