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Recycling-oriented methodology to sample and characterize the metal composition of waste Printed Circuit Boards

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1. Introduction

Many countries, including in the European Union (EU), are highly dependent on imports of raw materials that are crucial to a strong industrial base. Increasing global demand for minerals and metals and price volatility for certain raw materials, as well as the market distortions imposed by some countries on some raw materials, have heightened their importance for the global economy (UNEP, 2013). Supplies of raw materials are also being jeopardized by the depletion of many primary deposits that are easily accessible and easy to process. Consequently, recycling secondary resources such as waste electronic and electrical equipment (WEEE) offers good opportunities for diversifying the sources of raw material supplies. Because metals contained in spent printed circuit boards (PCBs) are of economic and strategic importance, they are among the most valuable WEEE components (Goosy and Kellner, 2003).

At present, pyrometallurgy is the technology most commonly implemented to recover metals from e-waste. In pyrometallurgical processes, spent PCBs are treated with ores in smelters to recover mainly copper and precious metals. This technology has several drawbacks, such as the loss of metals in slag (rare earth elements, tantalum), high energy consumption, toxic emissions, etc. (Cayumil et al., 2018; Cui and Zhang, 2008). Furthermore, only high-grade PCBs containing high gold concentrations (>400 mg kg⁻¹; Hagelüken, 2006) are processed using pyrometallurgy, as the addition of PCBs in smelters represents at most 15% of the materials input, the rest being ores (Ghosh et al., 2015; Goosey and Kellner, 2003). Goosey and Kellner (2003) estimated that, in the United Kingdom in 2003, only 15% of scrap PCBs were recycled in any way, the rest being consigned to landfill.

The composition of printed circuit boards depends on the location, year and type of appliance in which they were used. The average composition of PCBs is 40% metals, 30% ceramics and glass and 30% plastics (Kumar et al., 2018).

Many R&D studies have focused on the different operations involved in WEEE recycling (Akcil et al., 2015; Ghosh et al., 2015) which include dismantling, mechanical treatments (crushing, grinding), physical separation (magnetic separation, electrostatic separation, gravimetric separation), leaching and bioleaching, chemical separation and extraction (liquid-liquid and liquid-solid extraction). In addition to these conventional processes, original dedicated technologies are currently under development to address the specificities of e-wastes. As an example, non-conventional reagents can be used such as supercritical CO₂ for the extraction of polymers (Calgaro et al., 2015) and molten salts to dissolve glass and oxides and to destroy plastics without oxidizing the most valuable metals (Flandinet et al., 2012). The use of ionic liquids has also been investigated to dissolve epoxy resins (Zhu et al., 2012). These unit operations are usually combined in a common treatment flowsheet, thus producing a wide range of alternative processes that could be used for WEEE recycling. For instance, Mäkinen recently developed a process involving a combination of flotation and bioleaching (Mäkinen et al., 2015).
Developing these complex operations depends on establishing material balances so that the recovery of valuable elements in PCBs can be assessed and optimized. Consequently, the exact raw material compositions must be known and reproducible sampling must be feasible. The Gy sampling theory was developed to ensure a high reproducibility and representativeness of samples from primary resources at various scales (Gy, 1992). This theory allows estimations of the error generated by dividing samples into smaller samples. Other studies have applied adjustments from Gy theory to deal with sampling of municipal waste, plastics, metallurgical powders or soils. The International Standards Organization and other bodies have published methods for sampling various materials, such as soils (ISO 23909:2008 from AFNOR, 2008), waste plastics (XP CEN/TS 16010 from AFNOR, 2013), metallurgical powders (ISO 3954:2008 from AFNOR, 2008), particulate materials (ISO 11648-2:2001 from AFNOR, 2001), etc. These methods often also describe analytical methodologies to obtain reliable characterization. However, there is no similar theory applied to e-waste sampling and more especially to PCB sampling. Today, implementing reproducible and representative sampling of e-waste is still a major challenge because of their great heterogeneity.

PCB sampling also relies on implementing an efficient method to reduce the particle size of PCBs in order to release metals from the PCB matrix. Yamane et al. (2011) reported that metals in polymers and ceramics were not fully accessible in particles larger than 1 mm. In order to release metals efficiently, Wang et al. recommend impact or knife milling (Wang et al., 2005). However, several issues have been reported with shredding due to the presence of ductile metals (Ernst et al., 2003; Wienold et al., 2011; Yamane et al., 2011). Unfortunately, very few data are available from the recycling industry on sampling procedures, including size reductions, materials division and the methods implemented to assess the PCB composition of large samples.

Spent PCBs can be characterized by dry or wet techniques. Some of the techniques used to prepare and analyze samples are reported in Table 1 as an illustration. As these techniques are usually comple-

Table 1
Usual methods for the characterization of spent PCBs.

<table>
<thead>
<tr>
<th>Sample preparation methods</th>
<th>Analytical methods</th>
<th>Advantages</th>
<th>Drawbacks</th>
<th>Study</th>
<th>Element studied</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry techniques</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcination</td>
<td>X-ray fluorescence (XRF)</td>
<td>Destruction of plastics, which can interfere with analysis</td>
<td>Not compatible with volatile elements (Hg, As, Pb, Sn, Zn…)</td>
<td>Birloaga et al. (2013)</td>
<td>Cu, Al, Fe, Sn, Ni, Zn, Pb, Au, Ag</td>
</tr>
<tr>
<td>No preparation</td>
<td>XRF</td>
<td>– 10–20% more Cu compared to wet characterization</td>
<td>– Not precise&lt;br&gt;– Need for calibration with particle of similar size and composition, but no existing reference materials</td>
<td>Ernst et al. (2003)</td>
<td>Ag, Br, Cr, Cu, Fe, Ni, Pb, Pd, Sb</td>
</tr>
<tr>
<td><strong>Wet techniques</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqua regia</td>
<td>Inductively Coupled Plasma Mass Spectroscopy (ICP AES)</td>
<td>Large quantities&lt;br&gt;Less milling&lt;br&gt;Easily performed&lt;br&gt;Repeatability&lt;br&gt;Reproducible</td>
<td>– Incomplete digestion (40–50% residues&lt;br&gt;– Not compatible with Ta, Sn&lt;br&gt;– Doubt for Cu</td>
<td>Ernst et al. (2003)</td>
<td>Ag, Au, Be, Cd, Cr, Cu, Ni, Pb, Pd, Sb</td>
</tr>
<tr>
<td>Micro-wave (MW) and aqua regia</td>
<td>ICP-AES</td>
<td>Higher dissolution of Cr and Sb than without MW</td>
<td>– Incomplete digestion (10% residues&lt;br&gt;– Time consuming&lt;br&gt;– Difficult to implement</td>
<td>Wienold et al. (2011)</td>
<td>Pb, Cd, Hg</td>
</tr>
<tr>
<td>Aqua regia followed by calcination and fusion LiBO₂</td>
<td>Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)</td>
<td>Digestion almost total (&gt;10% residues)</td>
<td>– Time consuming&lt;br&gt;– Difficult to implement</td>
<td>Holgersson et al. (2017)</td>
<td>Cu, Al, Fe, Sn, Ni, Zn, Pb, Au, Ag</td>
</tr>
<tr>
<td>Calcination followed by acid leaching (aqua regia + HF) under micro-wave</td>
<td>Atomic Absorption Spectroscopy (AAS)</td>
<td>Destruction of plastics, which can interfere during analysis</td>
<td>Not compatible with volatile elements (Hg, As, Pb, Sn, Zn…)</td>
<td>Birloaga et al. (2013)</td>
<td>Pb, Cd, Hg</td>
</tr>
<tr>
<td>Fusion with sodium peroxide followed by HCl leaching</td>
<td>ICP-AES and ICP-MS</td>
<td>Digestion total</td>
<td>Difficult to implement</td>
<td>Oganniyi et al. (2009)</td>
<td>44 elements</td>
</tr>
<tr>
<td>Micro-wave (MW) and HNO₃/HBF₄/H₂O₂</td>
<td>ICP-AES</td>
<td>Digestion almost total (2.5% residues)</td>
<td>– Sample mass &lt; 1 g&lt;br&gt;– Difficult to implement</td>
<td>Ernst et al. (2003)</td>
<td>Ag, Au, Be, Cd, Cr, Cu, Ni, Pb, Pd, Sb</td>
</tr>
<tr>
<td>Micro-wave (MW) and HNO₃/HCl/HF/H₂O₂</td>
<td>ICP-AES</td>
<td>Digestion almost total</td>
<td>– Sample mass &lt; 1 g&lt;br&gt;– Difficult to implement</td>
<td>Xiang et al. (2010)</td>
<td>Cu, Pb, Al, Sn, Zn, Fe, Ni, Mg, Sb, Ag, Au, Mn, Co, Pd</td>
</tr>
</tbody>
</table>
mentary, it could be of great interest to combine several methods to obtain a full characterization of the waste materials (metal contents, elemental speciation, etc.). Various analytical methods could be combined such as elemental analyses after digestion with an appropriate reagent, X-Ray Fluorescence spectroscopy (XRF), Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy (SEM-EDX) and Transmission Electron Microscopy (TEM). However, some of these techniques (particularly XRF analysis or microwave-assisted digestion) can only characterize materials in very small amounts (below 1 g), which can raise representativeness and reproducibility issues, and therefore cause large characterization errors. Because of the high temperatures involved, techniques such as calcination and fusion are not compatible with the characterization of volatile elements. Thanks to its ease of implementation and the possibility of treating large quantities of PCBs, aqua regia digestion is the most frequently used technique in the literature. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), as well as atomic absorption spectroscopy (AAS), are widely used to analyze leachates from spent PCB digestion.

The aims of this study are (i) to establish and assess a sampling procedure for a large sample of spent PCBs in order to obtain reproducible sub-samples and (ii) to develop a methodology to determine the metal composition of PCBs. The experimental protocol proposed, tested and assessed in this study was designed specifically to be applied to large quantities of PCBs that are further used for the development of dedicated metallurgical treatments, from laboratory to pilot scale. The aim was to produce sub-samples of the same composition from a few grams to several kilogramgs, which would then allow calculation of the mass balances at every step of the process, as well as assessments and comparisons of the efficiency of metal recovery. The protocol developed in this study includes several milling stages, division of the materials into sub-samples and determination of the metal contents, as well as their partitioning into the different size fractions. This protocol was applied to 526 kg of spent PCBs and the accuracy of the analytical methods and the reproducibility of the subsamples was assessed. The methodology developed was assessed against the following criterions:

- Reproducibility: <10% of variation in metal concentrations between two samples was expected.
- In order to obtain the metal concentration closest to the true value, digestion had to be as complete as possible, with 98% (in mass) of metal digested considered satisfactory.

2. Materials and methods

2.1. The electronic scrap sample

A sample of 526 kg of medium-grade spent PCBs from the small waste electrical and electronic equipment category (wSWEEE) was collected and provided by the Envie 2E Midi-Pyrénées WEEE sorting center (France). The grade of the sample, which was medium (100 to 400 mg/kg of gold; Hagelüken, 2006), was estimated by the sorting centre from the origin of the PCBs (type of appliances), and not by elemental analyses. These PCBs were collected from small appliances such as computer, audio and video equipment, toys, personal care products, small kitchen appliances, etc.

2.2. Sample preparation

Fig. 1a shows the successive steps in the milling and sampling procedure implemented for this study: (i) the PCBs were shredded to reduce the particle size to less than 30 mm with a shear shredder from Bohmier Maschinen GmbH; (ii) the particles were then shredded to less than 10 mm with the same equipment; (iii) the particle size was then further reduced using a laboratory knife mill (Retsch SM-2000) with a bottom sieve mesh size of 750 μm. Intermediary bottom sieves with mesh sizes of 10 mm, 4 mm, 2 mm and 1 mm were used for this step. To reduce the particle size to a smaller diameter, the following were tested with two 500 g-samples: laboratory knife mill (Retsch SM-2000) with a bottom sieve mesh size of 500 μm, and disk mill (Bico Inc). At each reduction stage, the particles retained on the bottom sieve of the mill were added to the milled sample to ensure representativeness.

After the successive reductions to 30 mm, 10 mm and 750 μm, the milled samples were divided into smaller samples so that the final mass of each final sample was equal to approximately 4 kg (initial mass of the batch = 526 kg). The details of these sample divisions are given in Fig. 1b. These operations were carried out with a rotary divider for large samples (30 mm fraction) and a riffle-divider for smaller samples (10 mm and 750 μm fractions) with openings more than three times the particle size (see supporting information).

For purposes of comparison between sampling procedures, the Umicore procedure is also presented in Fig. 1a. As far as we know, this procedure is the only industrial methodology published in the literature to date (Hagelüken, 2006). At each step in the procedure, the size reduction and mass ratios obtained in this study were of the same order of magnitude as those achieved with the Umicore procedure.

2.3. Particle size distribution

Particle size distributions were determined for three samples: (i) sample reduced with a bottom sieve mesh size of 750 μm (step 3), (ii) sample reduced with a bottom sieve mesh size of 500 μm (step 4) and (iii) sample ground with a disk mill (alternative step 4). These distributions were obtained by wet sieving of 290 g samples to 1.25 mm, 1 mm, 800 μm, 400 μm, 200 μm, 100 μm and 63 μm. Each size fraction was dried at 40 °C before weighing and before performing any analyses.

2.4. Analyses

Given the particle sizes, analyses should be performed with 40 g-samples (see Section 3.2). However, for safety reasons, aqua regia digestion was performed with 5 g-samples. Consequently, the initial 40 g-samples were divided into 8 sub-samples by a quartering method. The 5 g-PCB samples were leached with 56 mL of aqua regia (HNO₃:HCl 1:3) prepared by mixing 42 mL of 32% HCl with 14 mL of 67–69% HNO₃, or with reverse aqua regia (HNO₃:HCl 3:1) (14 mL of 32% HCl + 42 mL of 67–69% HNO₃). The nitric acid (67–69%, trace metal grade) and hydrochloric acid (32%, certified for analysis) were provided by Fisher Chemical. The leaching reactors were heated to 200 °C for 2 h by means of a Kjeldahl-therm-Gerhardt digestion system. After cooling, solid/liquid filtration was performed with cellulose nitrate membrane filters (Sartorius Stedim Biotech, pore diameter = 0.45 μm) in order to separate the residues from the leachates. The residues were rinsed with water and dried at 40 °C. Metal concentrations in the filtrate were determined after dilution in 0.5 mol L⁻¹ HNO₃ prepared by diluting concentrated nitric acid in milliQ water (resistivity = 18.2 MΩ cm). A Varian SpectraAA-300 flame atomic absorption spectrometer (FAAS) was used to determine Fe, Cu, Zn, Pb, Co and Ni concentrations. An ICP-AES Horiba Jobin Yvon Ultima 2 or an ICP-MS Thermo Scientific X Series were also used to determine the concentrations of other metals: Ag, Al, Au, Cr, Ga, Ge, In, Mg, Mn, Mo, Pd, Sn, Ta, V and W.

After characterizing these 8 sub-samples by applying the above-mentioned methodology, the metal concentrations in the 40 g-samples
were calculated by means of the following equation:

\[ m_{40g}x_{40g} = \sum_{i=1}^{8} m_{5g}x_{5g} \]  

(1)

where \( m_{40g} \), \( x_{40g} \), \( m_{5g} \) and \( x_{5g} \) denote the effective mass of the 40g-sample, the metal concentration in the 40g-sample, the effective mass of the 5g-sub-sample \( i \) and the metal concentration in the 5g-sub-sample \( i \), respectively.

The same methodology was used for reverse aqua regia digestion of one 40g-sample and for reverse aqua regia digestion of each size fraction.

The solid residues resulting from partial leaching by aqua regia were milled for 20 min at 710 rpm in a planetary mill containing ferro-chromium grinding bowls (Siebtechnik). After milling, the solid residues were leached a second time using two different methods: (i) 5 g of residues were leached by aqua regia in triplicate in the same conditions as the first digestion and (ii) 200 mg of residues were leached using a mixture of 1 mL of hydrofluoric acid (Merck, 40%w for analysis), 1 mL of hydrochloric acid (Fisher, 32%w certified for analysis) and 3 mL of nitric acid (Fisher, 67–69%w, trace metal grade) in duplicate at 150°C at 125 bars for 20 min, then at 260°C at 125 bars for 2 h. The leachates were analyzed by ICP-MS. Some samples of these residues were also examined by scanning electron microscopy (SEM HIROX-SH 3000 with integrated EDS Bruker Nano).
3. Results

3.1. Sampling

The entire initial 526 kg sample was reduced to 30 mm except 41 kg of large pieces (called “Withdrawal”, see Fig. 1b), mostly corresponding to heat sinks and coils that were removed because it was not possible to shred them. The milled material was then divided by quartering into 4 samples of 110 kg, 142 kg, 108 kg and 122 kg respectively (see Fig. 1b). The differences found between the sample masses might be explained by the formation of clusters of copper wires that changed the flow rate of materials into the rotary divider. During this step, 3 kg of materials were lost (0.6% of the total mass). Only one of the four samples (122 kg) was used for this study. During step 2, this sample was entirely shredded to 10 mm and divided to obtain sub-samples of 4 kg. Unlike in step 1, the mass of the sub-samples obtained during the different quartering operations in step 2 were similar and close to the target value. Clusters were no longer observed as the copper wires were cut during this step, so that the material was more evenly distributed. During step 3, four of these 4 kg-samples were milled using a laboratory knife mill with a bottom sieve mesh size of 750 µm. Some particles did not pass through the bottom sieve (7.9% in mass) and were collected with the milled sample. Less than 0.6% of the mass of the initial sample was lost when ground down from 10 mm to 750 µm. This result is promising. For comparison, Wienold et al. (2011) reported 0.05% (mass) of material losses during grinding of 4 kg of PCBs from 1.5 mm to 500 µm with an ultra-centrifugal mill cooled by a continuous flow of liquid nitrogen. Finally, during step 4, some samples were then milled with a disk mill or a laboratory knife mill with a smaller bottom sieve mesh size (500 µm) in order to further reduce the particle size. 20% of the mass of the sample milled with the Retsch SM-2000 with a 500-µm bottom sieve did not pass through the sieve, while 2.0% of the material was lost. Material loss from the sample treated with the disk mill was below the weighing scale precision (1 g).

The particle size distribution of the samples obtained after step 3 and step 4 is given in Fig. 2. The 80th percentile, $d_{80}$, of the particle size distribution was equal to 750 µm when using the Retsch SM-2000 with a bottom sieve mesh size of 750 µm, equal to 700 µm when using the same device with a bottom sieve mesh size of 500 µm and equal to 850 µm after the 4th milling with the disk mill. The use of a 500 µm bottom sieve mesh size did not reduce the size of the larger particles to less than 700 µm. Even after 2 h of milling, a large number of particles did not pass through the 500 µm-sieve. As indicated above, particles that did not pass through the bottom sieve were added to the milled sample to preserve the representativeness of the subsample. Conversely, the disk mill had a negative impact, since it was responsible for an increase in the $d_{80}$ of the milled sample. The samples mentioned in the next sections of this paper were those obtained at the end of step 3, using the Retsch SM-2000 with a bottom sieve mesh size of 750 µm.

3.2. Analyses

As explained above, the grinding methodology proposed in this study did not reduce the size of the spent PCB particles below 50 µm. Such fine grinding is probably not required for metals to be completely accessible, but it reduced the heterogeneity of composition, which allowed to decrease the mass of the sample used to perform the chemical analysis of the metal content. In our study, based on the empirical formula (2) used by the BRGM (French geological survey) to characterize complex materials (unpublished data), 40 g-samples were analyzed.

$$\text{Sample mass for analysis} = 0.06 \times d_{80}(\mu m)$$

Table 2 shows the metal concentrations determined by the ICP-AES, ICP-MS and FAAS analyses of three 40 g-samples after aqua regia digestion. For Fe, Cu, Ni, Zn, Co and Pb, leachate concentrations were measured with both FAAS and ICP-MS which produced similar results. These three samples were taken from two different 4 kg-samples to determine the variability of their metal contents, as given in Fig. 1b. Sample n°3 was only analyzed by FAAS.

The relative standard deviation (RSD), defined as the ratio of the standard deviation to the mean value, was lower than 2% for Cu and Fe and ranged from 5% to 10% for Zn, Pb, Ni and Co. When only a

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Metal contents in three samples (mass = 40g). Samples were leached by aqua regia at 200 °C at a liquid/solid ratio of 11 mL·g⁻¹ (N.A. = not analyzed).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentrations in %w</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>Sample N°1</td>
<td>14.60%</td>
</tr>
<tr>
<td>Sample N°2</td>
<td>14.32%</td>
</tr>
<tr>
<td>Sample N°3</td>
<td>14.82%</td>
</tr>
<tr>
<td>Average</td>
<td>14.58%</td>
</tr>
<tr>
<td>RSD</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

Fig. 2. Particle size distributions of three 290 g-samples of milled material with a disk mill and a Retsch SM-2000 laboratory knife mill with a bottom sieve mesh size of 500 µm and 750 µm.
duplicate was analyzed, RSD were not calculated but the relative
difference between the two values obtained was estimated. For Al, Ga
and Ta, this relative difference was limited (0.9% for Ga, 6.8% for Al,
11.8% for Ta), while large discrepancies in metal concentrations be
tween samples were found for Sn and Au (31.3% for Sn and 46.9% for
Au).
The metal concentrations obtained after aqua regia digestion were
compared with those obtained after digestion with reverse aqua re-
gia, which is supposed to be more oxidative than aqua regia (Fig. 3a).
The same metal concentrations were obtained except for Ag, whose
concentration was 60 times lower than that obtained with aqua regia.
Likewise, a factor of 15 between aqua regia and reverse aqua regia
was observed for Pd. Given these results, aqua regia digestion was
chosen for further studies.

3.3. Analysis of solid residues

After digestion with aqua regia, 40% of the solid residues attrib-
uted to non-metal elements of PCBs remained in the reactor. In order
to assess the metal concentrations in the residues, they were milled to
achieve a high accessibility of potentially remaining metals for leach-
ing. Milling was efficient (particle size <100 μm) and the residue size
was more easily reduced than the PCB size. No metal was detected
through SEM-EDX analysis (see supporting information), which, on
the other hand, revealed the presence of Sr, Cl, Ca in the residues;
these elements are derived from plastics, ceramics and glass.

The residue remaining after the digestion of sample n°2 was di-
gested with aqua regia after milling. The residue remaining after the
digestion of sample n°1 was digested with a mixture of HF, HCl and
HNO3. During the second digestion with aqua regia, only 10% of the
mass of the residue was dissolved, whereas digestion with hydrofluor-
ic acid dissolved 100% (in mass) of the residue. The metal concen-
trations were also much lower in the leachate obtained after the sec-
ond digestion than after the first digestion. Table 3 shows (i) the metal
concentrations in the spent PCBs calculated from the data obtained af-
after the first digestion and after both digestions and (ii) the proportion
of metal that was leached during the first digestion vs. the total mass,
derived from the following equation:

\[
\frac{\text{weight of metal leached during the } 1^{\text{st}} \text{ digestion}}{\text{total mass}} = \frac{m_1}{m_1 + m_2} \times 100
\]  

where \(m_1\) denotes the mass of metal dissolved by the first digestion
and \(m_2\) the mass of metal dissolved by the 2nd digestion.
The digestion of the residues showed that more than 90% (in mass)
of all metals contained in spent PCBs were satisfactorily dis-
solved by using aqua regia for the first digestion. Digestion was par-
icularly efficient for Cu, Zn, Sn, Pb, Co and Pd, with less than 2% in
mass of undissolved metals. In that case, digestion with HF/HCl/
HNO3 was able to dissolve small quantities of Cu (0.1% in mass), Zn
(2.1% in mass), Sn (0.3% in mass), Pb (0.7% in mass), Co (1.1% in
mass) and Pd (1.2% in mass). Samples were milled finely enough for

![Fig. 3.](image-url) Fig. 3. (a) Metal concentrations after leaching 40 g samples of PCBs by aqua regia or reverse aqua regia (temperature = 200 °C, liquid/solid ratio = 11 mL g−1, analyzed with FAAS for Cu, Fe, Zn, Pb, Ni and Co and with ICP-AES and ICP-MS for others); (b) Distribution of metal elements in the different size fractions.
these metals to be efficiently accessible at 750 µm and easily digested with aqua regia. Digestion with aqua regia was efficient for Ni, Ag, Au and Ga, since more than 93% (in mass) of the metal was digested. For Ta, aqua regia was not appropriate at all, as it only digested 0.5% of the mass (see Section 3.2).

### 3.4. Chemical analysis of size fractions

The initial sizes of the different elements making up PCBs can vary greatly from one PCB to another and the distribution of metals is heterogeneous. Furthermore, when subjected to mechanical constraints, the different types of PCB components behave in different ways. For example, the materials present in PCBs can exhibit different mechanical properties that will cause plastic deformations in some cases, while others will tend to break. This leads to heterogeneous grinding: some materials are easily shredded, producing homogeneous reductions in particle size, while other materials are only partially reduced. These phenomena may lead to an uneven metal distribution in the sample, which may affect both digestion by aqua regia and the representativeness of the sampling protocol. It was therefore important to evaluate this phenomenon, all the more so as it would be of interest to identify a particular size fraction in which valuable metals are present in order to concentrate these for further extraction.

To do so, chemical analyses of each size fraction with reverse aqua regia were performed. The results were then added together to reconstitute an overall sample, which was compared with the analysis results for the initial sample. It should be pointed out that the Ag and Pd concentrations were underestimated when using this method of characterization of spent PCBs, as previously demonstrated (see Section 3.2). The metal concentrations in the “reconstituted” sample were calculated with the following equation:

\[
X_{\text{sample}} = \sum_{i=1}^{7} W_{\text{fraction}_i} \times X_{\text{fraction}_i}
\]

where \(X_{\text{sample}}\), \(W_{\text{fraction}_i}\) and \(X_{\text{fraction}_i}\) denote the metal concentration in the reconstituted sample, the mass fraction of the size fraction \(i\) and the metal concentration in the size fraction \(i\), respectively. Metal concentrations in the reconstituted sample, as well as in each size fraction, are given as supporting information.

To estimate the heterogeneity resulting from the size reduction, the ratio of metal contents of a specific size fraction compared to others and the ratio of metal contents of a specific size fraction compared to the contents of the entire sample had to be calculated. For most metals (Al, Cu, Pb, Sn, Zn, Ni, Ga and Ta), these ratios were not high enough (<5) to be sufficiently significant.

However, for precious metals (Ag, Au and Pd) and for Fe and Co, particular size fractions were enriched. The highest concentration of metals was found in the coarser fraction for Ag and Fe (size>1000 µm), in fine particles (size<100 µm) for Au and in mid-sized fractions (100 µm<size<400 µm) for Pd and Co (see supporting information).

The differences in metal contents between a 40-g-sample digested by reverse aqua regia and a reconstituted sample were calculated and are given in the supporting information. For most metals, the relative difference in metal concentrations between the two methods was lower or of the same order of magnitude as the intrinsic variability between replicates (See RSD in Table 2).

Finally, Fig. 3b shows the distribution of metals according to size fractions. Some fractions were enriched in some metals as previously shown. In the fine fraction (size<63 µm), precious metals (Ag and Au) and Ga, which is a strategic metal, were particularly concentrated since it contained 24% Ag, 27% Au and 23% Ga (in mass). Pd and Co were mainly distributed in the ~400 µm+200 µm fraction (47% for Pd and 28% for Co in mass). Despite this specific enrichment, all metals were widely distributed in the intermediate size fraction (400 µm<particle size<800 µm) since this intermediate fraction represented 47% of the total mass of the sample. In particular, more than 40% of the total mass of Au and Ag were present in this size fraction. This high distribution in the “~800 µm+400 µm” fraction was also...
observed for Ga and Cu as it contained at least 38% and up to 59% in mass, respectively.

4. Discussion

4.1. Results interpretation

This study aimed to develop a sampling and characterization procedure for the production of reproducible and well-characterized samples. Regarding the sampling procedure, two types of technologies were tested to reduce particle sizes: shredding (knife mills) and crushing (disk mills). The use of the disk mill increased the particle size, probably because of the formation of clusters, as a result of heat dissipation. The knife mill enabled to reduce the particle size under 750 µm, but for the particles comprised between 500 and 750 µm, no further reduction can be obtained with this technology, probably because they contain ductile metals. Given these results, it can be concluded that technologies based on crushing (with a disk mill for example) were less suited to reducing PCBs particle sizes than technologies based on shredding. The particle sizes obtained with this technology (below 750 µm) should enable to reach a complete accessibility of metals in the samples according to Yamane et al. (2011): these authors determined that metals are not sufficiently accessible if particles’ size is above 1 mm. This accessibility is closely related to the type of insertion and soldered joints of the components in the board. It should be noted that the samples obtained after the 3rd shredding step contained 17% (in mass) of fine particles (size <63 µm). These can easily be lost and are potentially hazardous. Zhang and Forsberg (1999) showed that the fine fraction may be toxic because they contain high Br concentration.

Regarding characterization, digestion with aqua regia was first compared to digestion with reverse aqua regia. A high degree of consistency was observed between the results obtained by the two methods, except for Ag and Pd. More studies would be required to fully understand the associated mechanisms.

There is a large amount of data about metal concentrations in spent PCBs in the literature. However, analytical and sampling procedures are often not described. Results depend greatly on the type and origin of the WEEE. Despite this wide variability, we compared our data with the literature to be sure that this study was consistent with others reported elsewhere. Fig. 4 compares the metal concentrations in spent PCBs reported by the United Nations Environment Program (UNEP), the United Nations University (UNU) and Bizzo et al. in 2013, 2008 and 2014 respectively (Bizzo et al., 2014; UNEP, 2013; UNU, 2008). The UNEP study does not provide any information about the type of PCBs and the methodology used for the characterization. The PCBs used in the report published by UNU are from the same category as in our study, i.e. small WEEE. The study by Bizzo et al. was performed on computer PCBs with aqua regia digestion.

The results of our own study generally concurred well with the PCB compositions analyzed in the above three studies. Large amounts of Fe, Cu (>10% in mass) and Al (6–8% in mass) came from various parts of PCBs such as heat sinks, copper layers for conduction, coils, etc. Sn, Zn and Pb, mainly used for soldered joints, accounted for approximately 1% of the mass of PCBs. A very large difference was observed for Ta, since its content was approximately 5000 times lower in our study than the value reported in the literature.

After assessing the validity of our methodology, each size fraction was analyzed to determine the metal distribution. Some enrichments were reported for Ag, Au, Pd, Fe and Co. Several hypotheses could account for this phenomenon: (i) the particle size reduction was heterogeneous for these metals; (ii) they were associated with other elements for which grinding was heterogeneous; (iii) they were included in PCB items of different sizes on PCBs and this had an impact on the final content of the size fractions of the milled samples. However, the enrichments observed were not substantial enough to be of use. Therefore, sieving to recover enriched fractions would result in the loss of a large part of the metal in other fractions that would not be kept. In addition, the distribution was not homogeneous enough to use only the fine fraction to characterize the whole sample for the development of metallurgical processes, as done in other studies (Ogunniyi et al., 2009), because the samples would no longer be representative of the initial sample.

4.2. Metals classification

From our results, the metals were classified into three different categories: those that met our criterions (less than 10% of variation between metal concentrations in replicates and more than 98% of the metal digested), those that partially met the goals or those for which our procedure did not meet the needs.

Fig. 4. Comparison of metal concentrations in spent PCBs from the present study, UNEP (UNEP, 2013), UNU (UNU, 2008) and Bizzo (Bizzo et al., 2014).
4.2.1. Metals for which the criterions were met

For Cu, Fe, Al, Zn, Pb, and Co, the sampling and characterization procedures were relevant and produced reproducible samples: for these metals, RSD and relative differences were lower than 10% for the 40 g-samples (see Table 2). Moreover, from the digestion of the residues, we were able to conclude that digestion of the PCBs samples was efficient with aqua regia, since no more than 0.1% to 2% (in mass) of the metals remained in the solid residues after digestion.

4.2.2. Metals for which the criterions were partially met

For some other metals, the sampling and characterization procedure did not produce high reproducibility and/or a high yield of digestion of metals in the PCB samples. Regarding reproducibility, despite the low number of replicates, three phenomena could explain the wide variation in RSD values: metals were not evenly distributed between the different replicates; metal species were not evenly distributed between the different replicates and the digestion with aqua regia may depend on metal speciation; accessibility of metals was not the same in all replicates and it affected the digestion. Regarding digestion, different hypotheses could explain why part of these metals was not digested during the first digestion: partial accessibility at 750 μm, too short digestion time or metal speciation. The lack of replicates and the variability of the samples did not allow us to confirm or reject these hypotheses. Other experiments, such as digestion with longer reaction time, with finer particles, etc. could help to understand these results.

Regarding Ni and Ga, there was limited variation in the contents of the different samples (7.2% RSD and 0.9% of relative difference respectively), which allowed us to conclude that reproducibility was high. With 94.5% (in mass) of Ni and 93.0% (in mass) of Ga digested by aqua regia, the concentrations in the samples were under-estimated but this could be considered acceptable depending on the process of metal recovery that will be developed.

Conversely, Pd was well digested with aqua regia but the reproducibility requirement was only partially met: the relative difference between the duplicates was 17%.

Finally, for Ag, neither the reproducibility, nor the digestion requirements were met. Part of the Ag content was still in the residues after aqua regia digestion (92.6% in mass of the Ag digested) and the relative difference between the duplicates was 19.3%. The precipitation of silver chloride may explain these results (Petter et al., 2014). Using nitric acid alone could improve the dissolution of silver, and thus its characterization.

As a conclusion, reproducibility and digestion criterions initially set for this study were only partially reached for Ni, Ag, Au and Ga whose concentrations were generally slightly under-estimated using this methodology. However this could be acceptable depending on the objectives and the precision pursued. The use of hydrofluoric acid is not useful. It slightly improved the accuracy of the metal analysis but was much more complicated to use due to its toxicity compared to aqua regia. Aqua regia offers a good compromise between the accuracy and the simplicity of implementation.

4.2.3. Metals for which the criterions were not met

For Au, the sampling could not be considered satisfactory, since the relative difference in Au concentration between duplicates was 46.9%. This variation could be attributed to the poor accessibility of fine Au layers in larger particles. 4.8% of the total mass of Au was still present in the residues after the first aqua regia digestion.

For Sn, the sampling and characterization procedure could not be considered satisfactory since the relative difference in concentrations between duplicates was 31.3%. The methodology recommended in the standard for the Sn content determination uses hydrobromic acid, as Sn is often contained in alloys with Pb and Cd (AFNOR, 2014). Differences in the efficiency of digestion by aqua regia digestion according to the speciation of Sn in the initial PCB could perhaps explain this high relative difference. Moreover, it has been demonstrated that tin slowly precipitates as metastannic acid H₂SnO₃, which could affect its characterization (Mecucci and Scott, 2002).

Finally, aqua regia digestion was absolutely not suitable to determine Ta concentrations: 99.5% (in mass) of the Ta was present in the residues after digestion. The use of fluoro hydroic acid was necessary for this metal. It is likely that the Ta came from the capacitors and was present as a metal or oxide (Ta₂O₅), which does not dissolve well in aqua regia. As an example, Theron et al. (2011) reported that only 3.9% of Ta₂O₅ and Ta were dissolved in aqua regia, even with microwave. The use of fluoro hydroic acid was necessary for this metal.

4.2.4. Overall interest of the methodology developed

Table 4 summarizes, for numerous metals, the overall interest of our procedures for determining the metal contents of PCB samples, taking into account the variation in concentrations between different samples and the efficiency of digestion with aqua regia. These methods seemed entirely suitable for Cu, Fe, Al, Zn, Pb and Co. They were slightly less suitable for Ni, Ag, Ga and Pd, but could nevertheless be used depending on the aim of the study. Concerning Au and Sn, the relevance of our procedures was not clearly demonstrated. For Ta, the characterization method was clearly unsuitable.

5. Conclusion

This study focused on the development of a procedure to produce small samples from large amounts of spent PCBs (more than 500 kg) and to determine their metal contents. The aim was to provide a rigorous sampling and characterization procedure to obtain reproducible and well-characterized sub-samples of spent printed circuit boards. These materials are complex and heterogeneous, and although numerous studies have been published about the development of metallurgical processes to recover the metals they contain, very few data about such procedures are currently available in the literature.

Our strategy to sample and characterize large samples of spent PCBs combined two main procedures: (i) first, a methodology to reduce the particle size, which released the elements making up the PCBs and enabled us to divide the initial samples into homogeneous and reproducible sub-samples; (ii) secondly, characterization of the sub-samples (40 g). The first procedure involved the use of a shredder to reduce the particle size to less than 30 mm and 10 mm, then milling...
with a laboratory knife mill to 750 μm. The characterization procedure first involved digestion of the sub-samples with aqua regia, then analysis of the leachates with ICP-AES, ICP-MS and FAAS. This approach was completed by additional steps to assess the suitability of the methodology: milling with other laboratory tools, characterization of the solid residues obtained after aqua regia digestion, and then sieving and characterization of the size fractions.

Regarding the sampling procedure, the use of large shredders followed by knife milling enabled us to reduce particle sizes to less than 1 mm, the threshold below which it is usually considered that metals can be released from polymers, ceramics and glass, or at least accessible. Material losses were negligible and the measured particle size distribution showed that the d50 reached 750 μm, which demonstrated that the shredding methodology was efficient. Additional milling steps did not enable us to reduce the particle size further, mainly because of the presence of ductile metals.

The digestion of the sub-samples with aqua regia dissolved more than 98% (in mass) of most metals except for Ta, which was only slightly dissolved by aqua regia (95% of the Ta initially present in the sample remained in the solid residue after digestion). This led to a substantial underestimation of its concentration and showed that the methodology developed in this study was not suited to the determination of Ta concentration in PCBs. Some issues were also encountered with Ni, Ag, Au and Ga: these were not completely dissolved during aqua regia digestion (4 to 7% remained in the solid residues), which led to slight underestimations of their contents.

The combination of the sampling and digestion methods was suitable for Cu, Fe, Al, Zn, Pb and Co. For Ni, Ag, Ga and Pd, the methodology was less accurate but remained an efficient tool when used to estimate the efficiency of metallurgical processes developed to recover these metals in waste PCBs (Hubau et al., 2018). Other analytical methodologies could be established to complete this characterization in the case of a need for accurate determination of metal contents (as XRD; Clearfield et al., 2008). For Au and Sn, wide variations of their concentrations were observed between replicates, while for Ta, the characterization methodology was not suitable.

Finally, the evaluation of the metal composition of each size fraction enabled us to conclude that the enrichments observed were not substantial enough to benefit from them with simple sieving and that the distribution was not homogeneous enough to use only the fine fraction for further studies.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2019.04.041.

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