

## Indium Recovery from End-of-Life E-Waste: Important Details Related to Spectroanalytical Determination and Recycling Viability

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Recycling has experienced great interest over the past five years, primarily driven by its strategic economic significance and the growing scarcity of natural resources. One element that has garnered attention is indium (In), especially due to its presence in flat panel displays (FPDs), particularly in devices utilizing liquid crystal display (LCD). The goal of this research was to establish a method for extracting In from LCD. The study faced challenges related to In determination using inductively coupled plasma optical emission spectroscopy (ICP OES), and furthermore, it proposed an optimized extraction method through design of experiments (DoE), focusing on extraction time and percentage of solid variables. Diverse sample types encompassing smartphones, monitors, and television screens were processed. Leaching was conducted utilizing a magnetic plate at 80 °C, employing a 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution along with 25% m v<sup>-1</sup> of the sample. This proposed method achieved a near-complete extraction rate (100%) for In. Moreover, in-depth interviews were conducted with several stakeholders in urban mining and various sectors within Brazil. The insights gleaned from these interviews showed the absence of a consolidated market for recycling LCDs with a specific emphasis on In recovery.

**Keywords:** In recovery, design of experiment, optimization, LCD, extraction rate

### Introduction

The industrial field of electrical and electronic equipment (EEE) employed for a long time an economic system based on the linear model: extraction-production-use-disposal of material. This concept transforms natural resources into products that end up being discarded into the environment. This massive use of natural resources has led to increasing impacts on the environment.<sup>1</sup> Due to these problems, the circular economy (CE) concept emerges as a new model based on rethinking and redesigning products and services. It is possible to implement the recirculation of natural resources within production value chains to regenerate natural systems, minimizing the generation of pollution and waste. Even with the growing interest in CE, the concept has gained relatively little attention in supply chain management, as indicated in the scientific literature.<sup>2</sup>

In this way, CE can be a practical solution for the reuse of geologically scarce elements applied in new technological products (smartphones, wind turbines, and solar panels).<sup>3,4</sup> These chemical elements, such as gallium (Ga), germanium (Ge), indium (In), tellurium (Te), tantalum (Ta), and platinum group metals (PGMs) are of particular concern in terms of geological scarcity and their difficult recovery in finished products.<sup>5</sup> The element In, for instance, presents special economic interest for several reasons, being classified as a “critical metal” due to scarcity and importance for the manufacturing industries of solar panels, liquid crystal display (LCD), and other applications of emerging technologies.<sup>6,7</sup>

LCDs are one of the main constituents of cell phones, as well as other electronic products such as high-definition television (HDTV), monitors, laptops, and digital watches. Considering a cell phone, 4.4% by weight corresponds to the LCD, 1.2% by weight is polymeric material (films adhered to the screens) and the rest of the mass corresponds to the other components: plastics for the case and frames

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and base elements such as Al, Cu and Fe (mass fraction superior to 1% m<sup>-1</sup>). A typical LCD contains conductive electrodes made of indium tin oxide (ITO, or tin-doped indium oxide), which are located between two glass plates. ITO is a mixture of two oxides: indium(III) (In<sub>2</sub>O<sub>3</sub>) and tin(IV) (SnO<sub>2</sub>), with mass fraction around 80-90% by weight of In<sub>2</sub>O<sub>3</sub> and 10-20% by weight of SnO<sub>2</sub>. In addition to the film that contains ITO, LCDs include glass and polymers in their composition, which can also be recovered.<sup>6-8</sup>

As mentioned by Ueberschaar *et al.*,<sup>9</sup> recycling of In from LCD is not yet carried out on an industrial scale; however, the authors comment that many scientific papers have been considered the topic of In recovery from LCD. One of the most used approaches to In recovery is the transfer of obtained ITO substrate to a liquid state via acidic dissolution.<sup>10</sup> The most used acids are sulfuric (H<sub>2</sub>SO<sub>4</sub>),<sup>7</sup> nitric (HNO<sub>3</sub>) and hydrochloric (HCl). Most of the approaches tested employ high temperatures for a better and more efficient reaction, but there is not a consensus about the type of acid. Other steps through hydrometallurgical procedures, such as solvent extraction, purify the In output and separate substances that are not of interest to the process.<sup>9</sup> Table 1 shows some selected recent papers about In recovery and its main remarks. Most of the studies employ H<sub>2</sub>SO<sub>4</sub> in several concentrations and conditions (with and without heating) as extractor, but there are alternatives.

The studies reported in Table 1 employed spectroanalytical (emission or absorption) techniques for In quantitative determination, but little information presenting experimental details were deeply discussed, jeopardizing the reproduction of the experiments by other groups. Indeed, one of the gaps that the present study is intended to solve is the experimental details for In determination using inductively coupled plasma optical emission spectroscopy (ICP OES).

Akcil *et al.*<sup>6</sup> reported that in the period 2013-2035, the demand for In could be much higher than the recovery rate of end-of-life (EoL) LCD technologies. The authors also highlight the need to improve existing In recovery technologies.<sup>6</sup> Considering the disparity of supply and demand, global competitiveness, In supply security, stable price and to maintain the technologically advanced lifestyle, new recycling technologies should be a reliable solution. An economically viable, eco-efficient, and sustainable recycling/recovery process for In can be viable from the concepts of CE, low carbon, clean energy and ecological perspective.<sup>6,8</sup>

In 2019, around 2 Mt of e-waste were generated in Brazil, and it is estimated that only ca. 4% were formally recycled.<sup>18,19</sup> A fraction of e-waste, including televisions (TVs) and LCD, is destined for selective collection in cities, that are most focused on separating common recyclables (plastics, metals, papers, glasses, packaging in general). However, selective collection only attends 35% of the Brazilian population and, approximately 50% reported having discarded e-waste mixed with Municipal Solid Waste (MSW).<sup>20,21</sup> When there is not a specific process or information for e-waste separation, or when the population do not deliver them at specific collection points, this residue is disposed as mixed MSW to landfills and dumps; or is retrieved informally by waste pickers, thus following the informality chain. In some cities, there are initiatives to e-waste processing integrated to the selective recyclables collection. In this case, the e-waste is separated and usually commercialized as mixed electronic scrap. Pre-sorting is carried out by device types, and, in some cases, there is also the disassembly and commercialization of separate components.<sup>22</sup>

The formal e-waste reverse logistics chains are enforced by the Brazilian National Solid Waste Policy

**Table 1.** Selected papers from 2018 up to 2023 about In recovery from electronic waste

Recycling strategy	Remark	Reference
Phytoextraction using <i>Eleocharis acicularis</i>	the accumulated In concentration in the biomass varied from 59 up to 122 mg g <sup>-1</sup>	Upadhyay <i>et al.</i> <sup>11</sup>
Acid extraction	the H <sub>2</sub> SO <sub>4</sub> concentration was 5.3 mol L <sup>-1</sup> , and the extraction temperature was 87 °C	Qin <i>et al.</i> <sup>12</sup>
Acid extraction	the In extraction rate was 98.2% using H <sub>2</sub> SO <sub>4</sub> 0.5 mol L <sup>-1</sup> at room temperature and 99.3% using HCl 6 mol L <sup>-1</sup> at 60 °C	Gabriel <i>et al.</i> <sup>13</sup>
Acid extraction	the authors used H <sub>2</sub> SO <sub>4</sub> (120 g L <sup>-1</sup> ) and sulfur dioxide (200 kPa) to extract In with 95% of recovery	Yang <i>et al.</i> <sup>14</sup>
Acid extraction mixture	the authors used a mixture of H <sub>2</sub> O:HCl:HNO <sub>3</sub> (6:2:1) and ultrasound for In extraction	Vucinic <i>et al.</i> <sup>15</sup>
Acid extraction	the authors compared H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> for In extraction; the first acid presented a recovery of 20%; on the other hand, H <sub>2</sub> SO <sub>4</sub> was temperature dependent and presented a recovery of 80%	Drzazga <i>et al.</i> <sup>16</sup>
Acid extraction	H <sub>2</sub> SO <sub>4</sub> 0.25 mol L <sup>-1</sup> presented the best results for In extraction (> 99%)	Illés <i>et al.</i> <sup>17</sup>

(Law 12.305/2010).<sup>23</sup> This system was formalized through a sectorial agreement (SA) in 2019, where the mechanisms and their implementation goals were established. The SA is a contract between the Federal Government and producers, importers, distributors, and retailers of EEE in Brazil. Currently, formal e-waste reverse logistics is managed by two entities responsible for the process operation and resources—Green Eletron and ABREE (Brazilian Association of EEE recyclers). In these systems, the e-waste is collected and sent to licensed operators, who carry out the stages of sorting, disassembly, mechanical processing, sale of recyclables and disposal of hazardous waste and tailings. Still, it is reported that only 30% of the Brazilian population destinate LCD to proper collection points, whilst 70% do not wait more than one year to discard waste LCDs.<sup>21</sup>

The aim of this study was to obtain more information about the procedure for sample preparation and determination of In via ICP OES in order to better understand some analytical problems and propose a simple analytical method to extract this element from LCD. As mentioned previously, the specialized literature devoted to spectroanalytical techniques do not bring enough and detailed information about In determination when an ICP OES is used. In addition, this research is intended to shed some light the potential In recycling market in Brazil.

## Experimental

### Samples description

LCDs from smartphones, monitors and TVs (42 inch) were acquired from a local market in the São Paulo state, Brazil. The availability of screens of different sizes, manufacturers and models in electronic repair workshops is remarkable, whereas in just one, more than 500 smartphone screens were collected. It is important to mention that as smartphones are abundant, many of the experiments were performed using this type of sample.

### Samples preparation

The disassembly of the collected material was performed manually. Table S1 (Supplementary Information (SI) section) presents some details of the dismantling and milling process, which was performed using a knife mill (TE-650 mill type Willye, Tecnal, Piracicaba, Brazil). Some experiments were performed using samples in small fragments (1 × 1 cm) that were obtained with the help of a scissor.

The TV screen collected was a single sample (42 inch) containing only the frontal part (without the ferrous from

the rear), so the percentage of the film that contained the ITO was high (76%). Only this film was milled, and Table S1 presents the particle size distribution, evaluated using different sieves with several apertures.

For TV and monitor samples, 50 and 45% of the film that contained ITO substrate mass, respectively, presented particle size higher than 600 μm and, for smartphone, 50% of this type of film presented particle size between 212 and 600 μm. There was a polymer adhered to the film that contain the ITO substrate, which was not removed during the milling process (more details will be presented in Results and Discussion section).

### Samples particle size investigation

To investigate each particle size of the sample, experiments were performed using the smartphone LCD sample (i) cut in small fragments (around 1 × 1 cm); (ii) with particle size higher than 600 μm; (iii) between 212 and 600 μm and, (iv) less than 212 μm. The experimental procedure was performed with 500 mg of the sample, 10 mL of 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and a digester block, that also permits a high analytical frequency. The temperature and time of leaching were 90 °C and 2 h, respectively. The samples were filtered and diluted for further ICP OES (Thermo Fisher Scientific, Waltham, MA, USA, iCAP7000 series model) elements determination, where the analytical curve solutions were prepared in the same medium as the samples, using standards with high degree of purity (Specsol, São Paulo, SP, Brazil). A standard addition procedure was also performed using In and Sn standards (Specsol) to calculate the recovery.

### Overview of preliminary experiments

#### First test for In extraction and determination

Our first attempt was to remove the polymer that is adhered to the substrate, where the ITO is located. The main hypothesis is that the polymeric film can compromise the contact between the substrate and the acids used for recycling/extraction. Two strategies to remove the polymer adhered to the substrate were performed: (i) thermal shock using an oven or hot air blower and, (ii) pyrolysis at a temperature of 580–600 °C for 30 min. The first test for the In extraction was accomplished using a full factorial design <sup>23</sup>. In this type of design, 3 variables are tested in two levels and the effects (individual and interaction) can be calculated and compared for further decisions.<sup>24</sup> The variables tested in two levels were: (i) sample type (monitor and smartphone), (ii) sample mass (300 and 500 mg) and (iii) extractor type (aqua regia, 3 parts of HCl and 1 part

of  $\text{HNO}_3$  and inverted aqua regia). All acids and reagents are from Neon (Suzano, SP, Brazil). The first (sample type) and the last variables (extractor type) are qualitative. On the other hand, the second variable (sample mass) is quantitative (300 and 500 mg).

The process was performed in a digester block (Marconi, Piracicaba, SP, Brazil) with PFA (perfluoroalkoxy alkane) closed vessels (Saville, Eden Prairie, MN, USA) with a temperature of 90 °C for 4 h. The elements were determined by ICP OES.

#### Second test for In extraction and determination

For the second test, experiments using a microwave (CEM, model MarsXpress, Matthews, NC, USA) system with more oxidizing concentrated ( $\text{HNO}_3$ ) and complexing (HF) acids were used. The remaining HF was neutralized using boric acid ( $\text{H}_3\text{BO}_3$ ). These experiments were performed using the samples where the polymer was previously removed by pyrolysis. The elements were also determined by ICP OES.

#### Third test for In extraction and determination

Another studied strategy was the extraction using diluted acids ( $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ ) using samples that were previously submitted to thermal shock and pyrolysis, and subsequent milling. The extraction method was performed using an ultrasonic bath (Delta Ultrasons, São Paulo, SP, Brazil).

#### Fourth test for In extraction and determination

The next step was conducted with new samples from other forms of LCD pre-processing: (i) with polymer film and milling; (ii) with polymer film and without milling, where the samples were previously fragmented in small pieces (around 1 × 1 cm); (iii) without polymer (after thermal shock) and with milling; (iv) without polymer and samples in small fragments. In this case,  $\text{H}_2\text{SO}_4$  efficiency was tested in three concentrations: 1, 4 and 7 mol L<sup>-1</sup>. The extractions were made in a digester block and magnetic plate (Fisatom, model 752A, São Paulo, SP, Brazil) using temperature of 90 °C and 2 h of leaching.

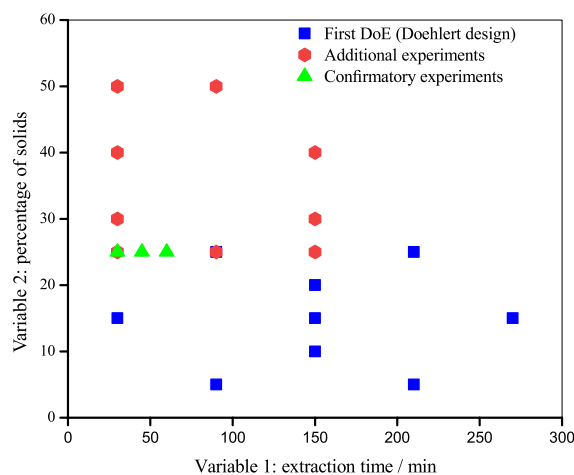
#### Optimization of leaching process

Some variables were studied through design of experiments-DoE (Doehlert approach) to optimize the solid liquid ratio and the extraction time and to observe their interaction.<sup>25</sup> Both variables are important in an industrial process: the higher the percentage of solids and the shorter the extraction time, the faster the process. Table S2 (SI section) shows the Doehlert experimental design performed.

With the help of Doehlert design it was possible to evaluate both variables (extraction time and percentage of solids) in different number of levels. The extraction time (variable 1) for instance was studied in 5 levels that varied from -1 (30 min) up to 1 (270 min) due to its clear relevance in the recycling process, playing an important role in the final cost of the process. The percentage of solids was verified in 3 levels ranging from -0.866 (5%) up to +0.866 (25%).

The experiments were performed using 1 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$  and magnetic plate with and without stirring, and temperature of 80 °C; these conditions were optimized beforehand. The sample was the milled film that contains the ITO substrate from smartphones. After extraction, the leachate solutions were filtrated and diluted for subsequent determination by ICP OES. In this case, just In was determined. The In concentration obtained from ICP OES was used as response for the Doehlert design and evaluated using a regression model: analysis of variance (ANOVA) and contour plot were prepared to visualize the most appropriate experimental condition.

After these preliminary experiments, others were performed to verify the previous design. Figure 1 shows the performed experimental domain of the design. The percentage of solids was tested in more levels: 25, 30, 40 and 50% and, the extraction time was tested in 30, 90 and 150 min.



**Figure 1.** Experimental domain of the first DoE (Doehlert, blue squares, see Table S2, SI section) and subsequent experiments (red and green lozenges and triangles, respectively).

The experimental conditions were the same (1 mol L<sup>-1</sup>  $\text{H}_2\text{SO}_4$  and magnetic plate with stirring and temperature). Then, all the expected chemical elements were determined (Al, Ba, Ca, Cu, Cr, Fe, In, Mg, Ni, Sn, Sr, Si, Zn). The results were also evaluated using regression models (ANOVA) and contour plots were prepared to visualize the most favorable condition.

After visualizing the optimal conditions according to DoE, it was necessary to perform three confirmatory new experiments (see green triangles in Figure 1) to identify the most appropriate extraction time and to apply it for the other samples. The extraction time levels tested were 30, 45 and 60 min. After leaching, the samples were filtrated and diluted for further determination by ICP OES. The combination of extraction time of 30 min and 25% of solids was tested twice.

## Results and Discussion

### Difficulties in the In determination when ICP OES is used

During several preliminary experiments, the In concentrations determined by ICP OES were very low when compared to those results observed in the scientific literature. In these experiments, the polymer adhered to this part was not removed and, our main hypothesis was this could compromise the In determination. Therefore, some alternatives to remove the polymer adhered to the substrate were tested and more experiments were proposed (from first to fourth sets of experiments).

With thermal shock, while heated, the polymer can be easily removed. On the other hand, it cools down quickly, adhering again on the substrate. Furthermore, the substrate is a very brittle glass, with fragments in small parts, being an inviable process. Besides, during the process of pyrolysis, the polymer was totally removed, and the resulting substrate was grinded for further mineralization.

For the first test, the In concentration ranged from 9 to 12 mg kg<sup>-1</sup>, and no difference in the concentration values among the experiments was observed. Even using a more energetic extraction method (second test), the results were not favorable with In concentration of 9 mg kg<sup>-1</sup> for monitor LCD samples and 13 mg kg<sup>-1</sup> for smartphones.

In the third test, it was possible to verify the influence of different acids, their concentration and extraction method, but there was no significant improvement in the In concentration, ranging from 6 to 14 mg kg<sup>-1</sup>.

What could be happening to In determination? Could it be lost during the sample pre-processing or some important detail (spectral and/or physical interference) is missing during the determination via ICP OES? After these experiments, it was noticed that the removal of the polymer from substrate was not interfering in the In determination. Therefore, the next steps were focused in preparing new samples using other pre-processing forms.

Even varying the pre-processing of the samples (fourth test), the In concentration remained low (from 3 to 8 mg kg<sup>-1</sup>). However, it was possible to visualize that the

samples with polymer and milling showed the best results, and there is no difference between leaching by digester block and magnetic plate. In addition, using 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> as extractor, the best results for In determination were obtained.

To verify if the analytical problem was due to the samples or to the determination using ICP OES, it was performed an extraction with a commercial ITO sample with known In and Sn concentration (Aldrich, No. CAS 50926-11-9, Saint Louis, MO, USA). But even so, the results were below expectations (recovery around 4%). The recovery was calculated according to equation 1:

$$\text{Recovery (\%)} = \frac{\text{Obtained In concentration after ICP OES determination}}{\text{In expected concentration}} \times 100 \quad (1)$$

where “In expected concentration” is the known added In concentration using commercial ITO sample. The “Obtained In concentration after ICP OES determination” was subtracted from the In concentration determined in the sample without addition of commercial ITO. It is clearly noted that this type of experiment requires always at least two replicates for each sample: one with and another without the addition of commercial ITO.

Other test performed was a standard addition using an aqueous commercial standard of In (Specsol) on a smartphone LCD sample using 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for leaching. This test also did not show good results. Therefore, it was concluded that the problem was during the determination by ICP OES.

### How to solve the In determination problem?

A detailed study using standard addition with known In and Sn concentrations was performed to investigate each experimental procedure step. The experimental procedure employed a digester block with 90 °C and 2 h using 10 mL of 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. In this way, standard additions of 1 mg L<sup>-1</sup> of In and Sn were added in different steps from the procedure: (i) before and (ii) after leaching (for the samples) and (iii) in solutions containing only standard (without sample).

Another point was the calibration curve, which was previously prepared with the same acid used in the leaching, but its concentration was 1% v v<sup>-1</sup> (around 0.2 mol L<sup>-1</sup>). In this case, the calibration curve was prepared with the same concentration and acid. For example, after the leaching and further dilutions, the final solution is 0.55% v v<sup>-1</sup> or 0.1 mol L<sup>-1</sup>. Therefore, solutions for the ICP OES standards were also prepared at this concentration.

After all experiments, the recovery values calculated using equation 1 ranged from 101 to 122% for In and,

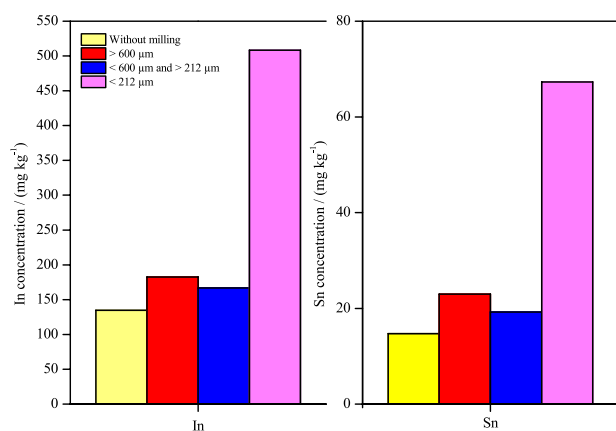
from 112 to 121% for Sn. The In concentrations observed for the samples were 188 mg kg<sup>-1</sup> (samples with polymer and milling), 257 mg kg<sup>-1</sup> (samples with polymer and small fragments), 142 mg kg<sup>-1</sup> (samples without polymer and with milling) and 117 mg kg<sup>-1</sup> (samples without polymer and small fragments).

With this study, it was possible to conclude that In determination is very sensitive (more than our expectations) to fluctuations in acid concentration in the analytical curve, suffering a high transport effect in ICP OES determinations. This important aspect is mentioned and discussed in the scientific literature, but it is not reported its crucial impact for In determination. From that point on, all calibration curve solutions were prepared using the same H<sub>2</sub>SO<sub>4</sub> concentration employed in the sample solutions.

### Optimization of leaching process

#### Particle size of the samples

A study about the particle size was performed to identify the In concentration in each fraction of the sample. Figure 2 shows the In and Sn concentrations obtained. With these results, it was concluded that In and Sn in the samples with particle sizes less than 212 μm are more easily extracted when compared with larger particle sizes. When performed the grinding, it was noticed that the polymer fragments were more present in the fraction that has particle sizes higher than 600 μm, but there is also In.



**Figure 2.** In and Sn concentrations (mg kg<sup>-1</sup>) in the smartphone LCD sample with different particle size range.

To grind the entire mass of the sample to particle sizes smaller than 212 μm, more than one grinding step may be required compromising the analytical frequency and the economic viability of the recycling process. Therefore, it is better to operate with the sample containing all particle sizes as long as it is homogenized, avoiding loss of In in the

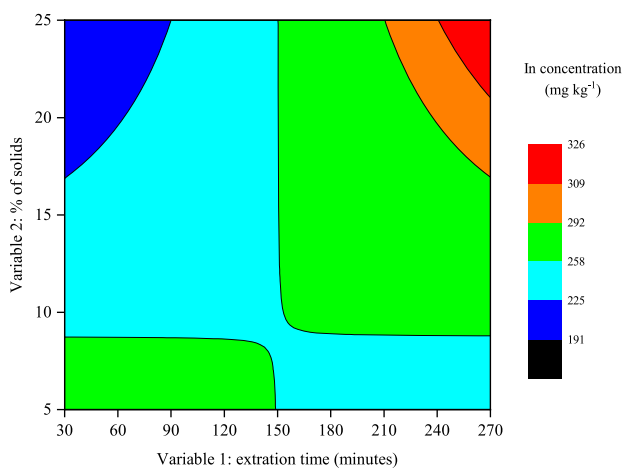
other fragments. The sieve of the knife mill was 20 mesh (800 μm), being the particle sizes less than 800 μm.

### Design of experiments

The extractor type and its concentration were well defined with the experiments mentioned in the previous section: 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Therefore, the first design of experiment studied the extraction time (v1) and percentage of solids (v2) (Experimental section and Table S2, SI section). The In concentration obtained from ICP OES determination was used to calculate a regression model as described in equation 2:

$$[\text{In}] = 258.11 + 25.75v1 + 47.63v1v2 \quad (2)$$

Figure 3 shows the contour plot obtained with the help of equation 2.



**Figure 3.** Contour plot for the model calculated using the In concentration (mg kg<sup>-1</sup>).

To obtain the highest In concentration, a high percentage of solids, v1 (positive aspect) and a long time of extraction, v2 (aspect that reflects a high cost) are required (red part from the graph in Figure 3). The red part presented in Figure 3 shows that the predicted In concentration can reach values around 300 mg kg<sup>-1</sup>. On the other hand, there was not a huge variation among the different experiments. The In concentration obtained experimentally ranged from 228 to 297 mg kg<sup>-1</sup>.

These results are from the experiments using stirring, which were very similar to those without this step. Even introducing an additional cost for the process, the stirring can be important to avoid saturation in the region of the solution close to the solid, requiring a movement of the solute in the medium, which is known as diffusion. Therefore, the next experiments were performed using the magnetic plate with stirring.

The variables extraction time (v1) and percentage of solids (v2) were investigated in more details (see Figure 1), and Figure 4 shows the contour plots using the regression model calculated. In this case, several chemical elements (In, Sn, Fe, Cu, Al, Ca, Mg, Ba, Si, Sr, Cr, Mn, Ni and Zn) concentrations were determined, and two regression models were calculated: one for In concentration (see equation 3) and other for all chemical elements using the desirability calculate (see equation 4).<sup>26</sup>

$$[\text{In}] = 300.98 + 33.76v1 \quad (3)$$

$$D = 0.26 - 0.22v1 \quad (4)$$

The desirability is calculated to normalize the responses obtained between 0 and 1. These parameters (0 and 1) describe the worst and the best obtained responses, respectively. The goal was to maximize In extraction and minimize the concentration of the other elements, i.e., the best condition is to leach more In and less the other elements, aiming selective recycling steps. The equations used to desirability are:

$$d = \left( \frac{y-L}{T-L} \right)^s \quad (\text{maximize}) \quad (5)$$

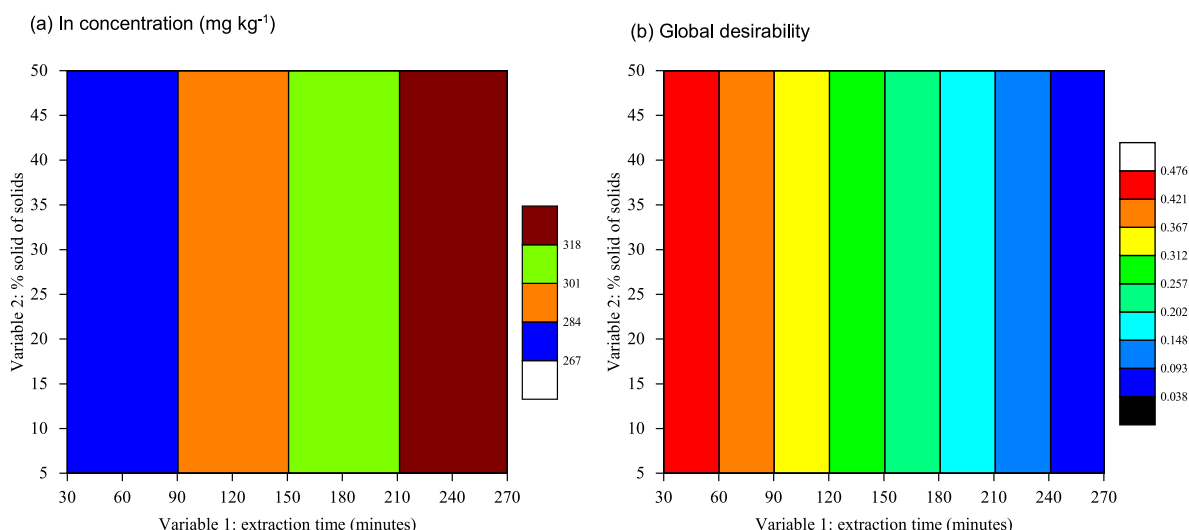
where  $y$  is the monitored response (In concentration),  $L$  is the lower acceptable working condition (lower In concentration),  $T$  is the target value (highest In concentration) and,  $s$  is the weight (1 in this particular case). To minimize:

$$d = \left( \frac{U-y}{U-T} \right)^s \quad (6)$$

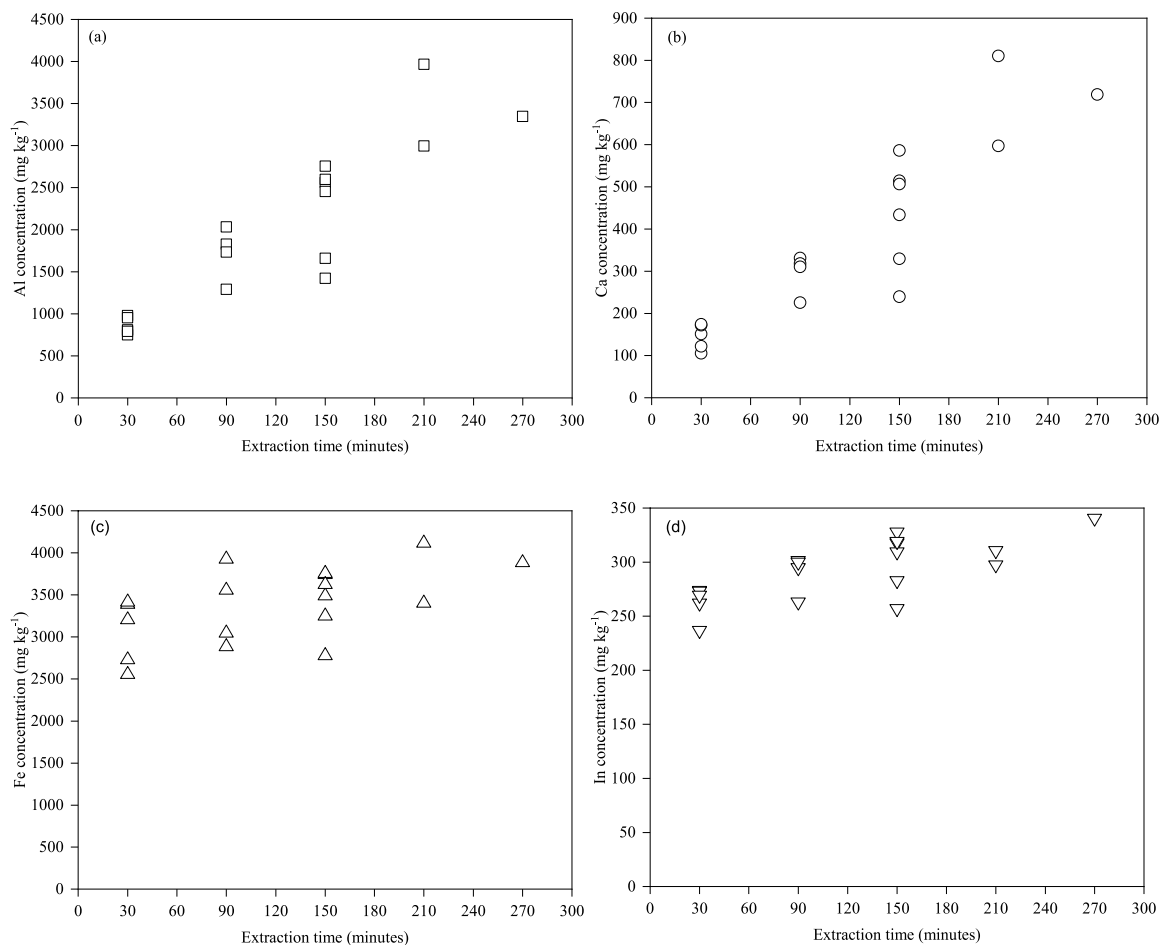
where  $U$  is the acceptable response (highest concentration of the elements),  $T$  is the target value (lowest concentration of the elements) and,  $s$  is the weight (also 1). For the model with all chemical elements (14 responses), it is necessary to calculate the individual desirability ( $d_i$ ) for each one, and calculate the geometric mean, generating the global desirability ( $D_{\text{global}}$ ), which is used in the regression model calculation:

$$D_{\text{global}} = \sqrt[m]{d_1 \times d_2 \times \dots \times d_m} \quad (7)$$

As can be noted from Figure 4a and equation 3, the percentage of solids, v2 does not statistically interfere in the result. On the other hand, when the percentage of solids is greater than 25%, it makes the leaching process difficult due to the lack of liquid extractor in contact with the solid residue, therefore, it was chosen to work with 25% of solids. Regarding the variable time (v1), it is noted that the longer the extraction time, the greater the number of chemical elements obtained in the substrate (including In). On the other hand, when looking at the contour plot using the global desirability (Figure 4b and equation 4), the best option is to work in shorter times, where it is possible to obtain an average desirability. Figure 5 shows a comparison of four elements in relation to extraction time. For the case of Al (Figure 5a), Ca (Figure 5b) and Fe (Figure 5c), the concentrations presented a strong linear correlation with the time (mainly for Al and Ca). When In was evaluated (Figure 5d), there was not such a significant increase from shortest to longest extraction times. Therefore, the main observation derived from the results described up to this point is that it is more appropriate to carry out extractions with shorter leaching times, a more profitable process.



**Figure 4.** Contour plots for (a) In concentration ( $\text{mg kg}^{-1}$ , see equation 3), and (b) all chemical elements using the global desirability (see equation 4).

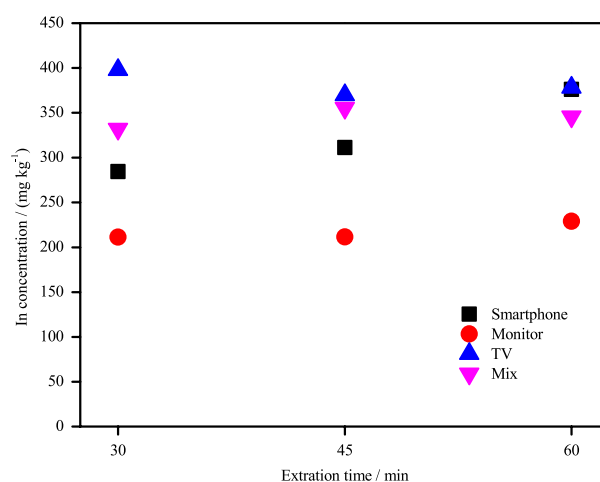


**Figure 5.** Concentrations (mg kg<sup>-1</sup>) for (a) Al, (b) Ca, (c) Fe and (d) In in relation to extraction time.

Additionally, smaller amounts of the other chemical elements are extracted, that are not of commercial interest, and further separation must be performed.

The optimized conditions were obtained using: (i) 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; (ii) ratio of solid/liquid: 1 g per 3 mL (25% of solids); (iii) magnetic plate with stirring and (iv) temperature (ca. 80 °C). The samples tested were smartphone, monitor, TV, and mix (smartphone, monitor and TV mixed). All the films that contain the ITO substrate were ground and, to mix the three types, a manual homogenization was performed.

Figure 6 shows the In concentration results (mg kg<sup>-1</sup>) for smartphone, monitor, TV and the mix (prepared from the three sample types) for 30, 45 and 60 min of extraction. There is no remarkable difference among the studied samples. The monitor and TV samples have the lower and the highest In concentration, respectively. With the mix sample (inverted triangle in Figure 6), the In concentration is in an intermediary range, so, it is better to carry out the experiments with a mix, mainly thinking in an industrial process, where the samples should be prepared together. In relation to time, there was not a huge



**Figure 6.** In concentration (mg kg<sup>-1</sup>) in relation to extraction time for the different samples analyzed (smartphone, monitor, TV and mixture).

difference among the tested intervals, therefore, 45 min of extraction was chosen.

Table 2 shows the concentrations for all chemical elements present in the mix sample with 45 min of leaching and temperature of ca. 80 °C. The In concentration was around 355 mg kg<sup>-1</sup>, and the highest concentration obtained



**Table 2.** Chemical elements concentration present in mix sample (n = 3)

Chemical element	Remark	Emission line monitored using ICP OES / nm	Concentration $\pm$ standard deviation / (mg kg <sup>-1</sup> )
In	target element	325.609	355 $\pm$ 18
Sn	possible byproduct	189.989	28 $\pm$ 3
Fe		259.940	2192 $\pm$ 15
Cu	base elements <sup>27</sup>	327.396	46 $\pm$ 2
Al		393.152	927 $\pm$ 23
Ca	elements used as flame retardants or in the composition of the components (insulation) <sup>4</sup>	393.366	388 $\pm$ 20
Mg		279.553	60 $\pm$ 3
Ba		455.403	5.0 $\pm$ 0.4
Si		251.611	162 $\pm$ 3
Sr		407.771	76 $\pm$ 3
Cr	additional elements present in the composition of the printed circuit boards (PCB) <sup>28</sup>	283.563	51 $\pm$ 7
Mn		257.610	13 $\pm$ 1
Ni		231.604	6 $\pm$ 1
Zn		213.856	5.0 $\pm$ 0.3

ICP OES: inductively coupled plasma optical emission spectroscopy.

was for Fe (2192 mg kg<sup>-1</sup>). Figure 7 shows an overview of the optimized method.

#### Proposition for method validation

Besides the standard addition of In during all the experiments performed, it was also made an ITO addition in the optimized method in order to observe its recovery (see equation 1) as In. Besides the mix sample, an analysis

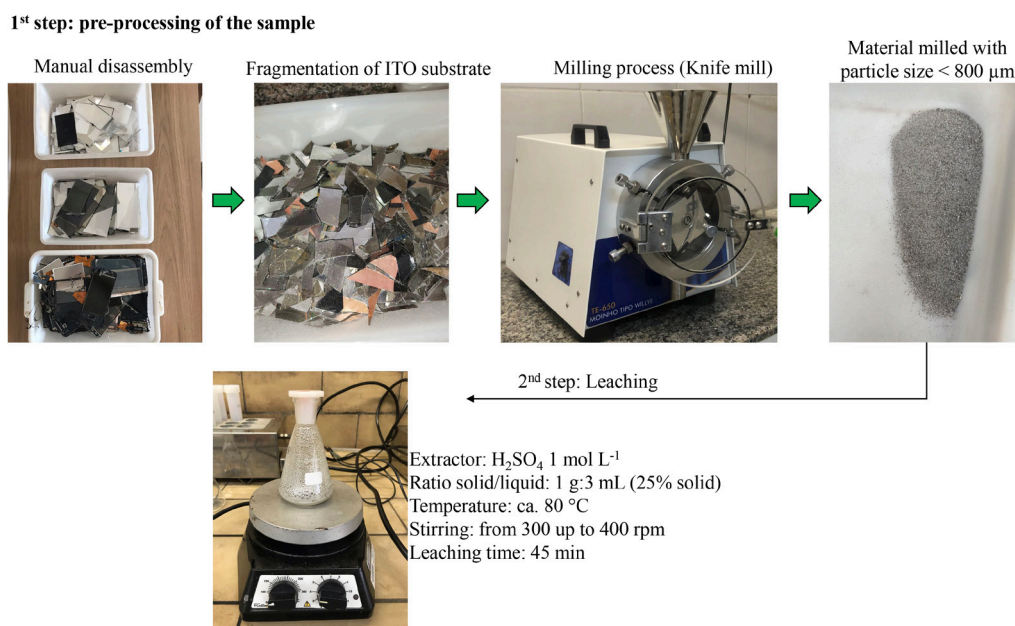
of leaching residues (solid residue obtained) was performed to visualize if there is remaining In. Additions of 15 mg from the oxide were made before the leaching for the mix sample and residue.

The In concentration was 321  $\pm$  58 mg kg<sup>-1</sup> (n = 3) for the original mix and for the residue it was 8.0  $\pm$  0.4 mg kg<sup>-1</sup> (n = 3), this shows that practically all the In (98%) were extracted from LCDs in the first leaching process. The recovery of the In added was 105% (n = 3) for the mix sample and 86% (n = 3) for the residue, being within the acceptable range and validating the proposed method. The validation was performed in this way due to the lack of certified reference material for this type of sample.

#### In recycling in Brazil

The present study carried out a total of 20 interviews with key actors in the Brazilian e-waste chain, including representatives of: (i) the e-waste reverse logistics management entities, key operators, recyclers (urban mining), (ii) EEE producers, distributors and (iii) In processing. Figure S1 (SI section) shows the interviewees characteristics: the majority (47%) are from the field of EEE producers and distributors. The study also monitored the e-waste recycling market through groups in social networks, where scrap dealers negotiate e-waste components.

In this analysis, it was observed that there is no consolidated market for recycling LCD with a focus on In recovery in the country. The processing of this type of e-waste is concentrated in reverse logistic operators and in international companies with branches in Brazil. The

**Figure 7.** Overview description of the optimized method.

main destinations after device disassembly are: (i) foundry in metallurgical and steel furnaces, targeting base metals, where probably In is considered an impurity (there is no much information about In); (ii) pyrometallurgical processes to extract other elements in oxide form (with no information about In) or, (iii) the In is processed together with other precious metals and sent to companies abroad for further refining. Usually, LCDs are not commercialized for recycling, but are associated with metal scrap to base metals (Al, Cu, Fe, for example) recyclers. The only identified value for EoL LCDs was in the repairing business for second-hand equipment, in which the identified price ranged between R\$ 5-10 kg<sup>-1</sup> (Brazilian Reais, ca. US\$ 1-2).

The only recyclers who recover In from LCD are in other countries, especially Belgium. However, as LCD waste has not been commercialized separately from scrap metals, it is possible to assume that the share of LCD destined for In recycling abroad is inexpressive. At formal e-waste reverse logistics operators, LCD have been usually destined as hazardous waste, with expenses rather than revenue from this waste.

The key potential clients for high purity recycled In are ITO manufacturers who are suppliers of the international EEE industry. In Brazil, there are no such manufacturers, as the LCD TVs and monitors are only assembled in the country, after importing LCD displays from international producers. Therefore, an In recycling business in Brazil would need to compete with the international In supply chain and reach for large ITO and EEE producers, mainly in China.

Another possibility is to focus on producing an In concentrate. For this product, the target clients could be large e-waste recyclers in Brazil, who are used to negotiate with e-waste and special metals refiners in Europe and Asia. These refiners usually process a wide range of input material, not just e-waste, and they determine the purchase price of these, based on a laboratory analysis of special elements. In this case, an In concentrate could be an interesting product to export, and some of the interviewed from the reverse field operators in Brazil declared that they would be potentially interested in producing and exporting such concentrate. Another positive point with this product is that it does not require an advanced refining of In to the highest purity, so the recycling process can be more feasible.

## Conclusions

It was possible to investigate in deep the details of the In determination by ICP OES and to extract the In from

LCDs using a simpler experimental procedure. For the pre-treatment of the sample, it was not necessary to remove the polymer film adhered to the ITO substrate, reducing one step in the process. In addition, there was a mix of several types of displays: TV, smartphone and monitors, being a positive aspect to process the materials together. The use of diluted acid (H<sub>2</sub>SO<sub>4</sub>) and a magnetic plate with stirring and heating was effective to extract almost all the In with an extraction rate greater than 90%.

## Supplementary Information

Supplementary information is available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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## References

1. Korhonen, J.; Honkasalo, A.; Seppälä, J.; *Ecol. Econ.* **2018**, *143*, 37. [Crossref]
2. Marquina, M. V. H.; Dain, M. A. L.; Zwolinski, P.; Joly, I.; *Procedia CIRP* **2022**, *105*, 607. [Crossref]
3. Costa, V. C.; Castro, J. P.; Andrade, D. F.; Babos, D. V.; Garcia, J. A.; Sperança, M. A.; Catelani, T. A.; Pereira-Filho, E. R.; *TrAC, Trends Anal. Chem.* **2018**, *108*, 65. [Crossref]
4. Andrade, D. F.; Castro, J. P.; Garcia, J. A.; Machado, R. C.; Pereira-Filho, E. R.; Amarasiriwardena, D.; *Chemosphere* **2022**, *286*, 131739. [Crossref]
5. Worrel, E.; Reuter, M. A.; *Handbook of Recycling State-Of-The-Art for Practitioners, Analysts, and Scientists*; Elsevier: London, UK, 2023.
6. Akcil, A.; Agcasulu, I.; Swain, B.; *Resour., Conserv. Recycl.* **2019**, *149*, 622. [Crossref]
7. Silveira, A. V. M.; Fuchs, M. S.; Pinheiro, D. K.; Tanabe, E. H.; Bertuol, D. A.; *Waste Manage.* **2015**, *45*, 334. [Crossref]
8. Swain, B.; Lee, C. G.; *Waste Manage.* **2019**, *87*, 597. [Crossref]
9. Ueberschaar, M.; Schlummer, M.; Jalalpoor, D.; Kaup, N.; Rotter, V. S.; *Recycling* **2017**, *2*, 7. [Crossref]
10. Andrade, D. F.; Fortunato, F. M.; Pereira-Filho, E. R.; *Anal. Chim. Acta* **2019**, *1061*, 42. [Crossref]
11. Upadhyay, A.; Alimohammadi, F.; Aken, B. V.; Tehrani, R.; *ACS Sustainable Chem. Eng.* **2021**, *9*, 16082. [Crossref]

12. Qin, J.; Fujita, T.; Xu, J.; Wei, Y.; Dobida, G.; *J. Environ. Chem. Eng.* **2022**, *10*, 107930. [Crossref]
13. Gabriel, A. P.; Kasper, A. C.; Veit, H. M.; *J. Environ. Chem. Eng.* **2020**, *8*, 103758. [Crossref]
14. Yang, F.; Deng, Z.; Wei, C.; Zhu, B.; Li, X.; Li, M.; Li, C.; *Can. Metall. Q.* **2023**, *62*, 125. [Crossref]
15. Vucinic, A. A.; Simunic, S.; Radetic, L.; Presecki, I.; *Processes* **2023**, *11*, 1662. [Crossref]
16. Drzazga, M.; Prajsnar, R.; Chmielarz, A.; Benke, G.; Leszczynska-Sejda, K.; Ciszewski, M.; Bilewska, K.; Krawiec, G.; *Metals* **2018**, *8*, 1041. [Crossref]
17. Illés, I. B.; Nagy, S.; Kékesi, T.; *Hydrometallurgy* **2022**, *213*, 105945. [Crossref]
18. Baldé, C. P.; Forti, V.; Gray, V.; Kuehr, R.; Stegmann, P.; *The Global E-waste Monitor-2017*; United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA): Bonn/Geneva/Vienna, 2017. [Link] accessed in December 2023
19. Dias, P.; Palomero, J.; Cenci, M. P.; Scarazzato, T.; Bernardes, A. M.; *Cleaner Waste Syst.* **2022**, *3*, 100022. [Crossref]
20. CEMPRE; *Pesquisa Ciclossoft-Panorama da Coleta Seletiva no Brasil*, <https://ciclossoft.cempre.org.br>, accessed in December 2023.
21. Green Eletron, Resíduos Eletrônicos no Brasil, <http://greeneletron.org.br/>, accessed in December 2023.
22. Souza, R. G. In *Handbook of Electronic Waste Management*; Prasad, M. N. V.; Vithanage, M.; Borthakur, A., eds.; Butterworth-Heinemann: London, UK, 2019.
23. Lei No. 12.305/2010, *Institui a Política Nacional de Resíduos Sólidos, altera a Lei No. 9.605, de 12 de fevereiro de 1998 e dá outras Providências*; [https://www.planalto.gov.br/ccivil\\_03/\\_ato2007-2010/2010/lei/112305.htm](https://www.planalto.gov.br/ccivil_03/_ato2007-2010/2010/lei/112305.htm), accessed on December 14, 2023.
24. Leardi, R.; *Anal. Chim. Acta* **2009**, *652*, 161. [Crossref]
25. Ferreira, S. L. C.; dos Santos, W. N. L.; Quintella, C. M.; Neto, B. B.; Bosque-Sendra, J. M.; *Talanta* **2004**, *63*, 1061. [Crossref]
26. Derringer, G.; Suich, R.; *J. Qual. Technol.* **1980**, *12*, 214. [Crossref]
27. Castro, J. P.; Pereira-Filho, E. R.; *Detritus* **2020**, *13*, 131. [Crossref]
28. Andrade, D. F.; Machado, R. C.; Bacchi, M. A.; Pereira-Filho, E. R.; *J. Anal. At. Spectrom.* **2019**, *34*, 2394. [Crossref]

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