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METAL IDENTIFICATION BY MEANS OF ICP-OES IN RECYCLING COMMINUTED PRINTED CIRCUIT BOARDS[1]

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Abstract

At present, the growth in population along with the great industrial development is exceeding the capacity of environment adaptation, not managing to comport all the different types of equipment and waste disposed in the natural cycle. Among the discarded equipment stands a large volume of printed circuit boards, in which recycling processes are still incomplete, thus the main source of motivation for this research. Using assembled and nude printed circuit boards, subjected to the same process of comminution and leaching, we analyzed the particle size obtained in the amount of metal identified by ICP-OES. The results showed that the assembled plates contained larger particles than the bare boards, containing 25.8% and 6.8% metal, respectively, and the particle sizes interfered in the leaching process used for extraction and identification of the metals by ICP -OES,with higher concentrations of metal in the particles around 600 µm.

Key words: printed circuit board, comminution, recycling.

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1. INTRODUCTION

At present, the growth in population along with the great industrial development is exceeding the capacity of environment adaptation, not managing to comport all the different types of equipment and waste disposed in the natural cycle Thus, we are confronted with a stream of artificial elements or at high concentrations, mostly toxic or harmful to life in the biosphere, frequently deposited in the various regions and sub-systems of the planet, returning to the life cycle of the human race in the forms of pollution, radiation, food contamination, acid rain, greenhouse effect, destruction of the ozone layer, depending on the dynamics of nature [(1)].

In Brazil, the evaluation of hazardous waste must be in accordance with the Rules ABNT NBR 10004 [(2)], 10005 [(3)], 10006 [(4)] and 10007 [(5)], which classify waste as potential risks to the environment and the public health, so these kinds of waste may have proper handling and disposal. Specific environmental standards for the electric-electronic sector have been defined by ABNT and IPC [(6)] to control the maximum content of harmful substances like lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers.

Currently, the sheer volume of disposed electronics and electrical products has motivated several researches in recycling so that some waste materials can be reused in a new cycle of production and not deposited in landfills, polluting the environment. For printed circuit boards (PCI) from electronic devices, recycling processes are still incomplete due to the complexity of the existing materials. The composition of the plates depends on the origin of the circuit, the type and age of equipment [(7)]. A recent work from Kui, Jie and Zhenming [(8)] shows that the PCBs are comprised of approximately 30% of metals, usually containing 20% copper, 8% iron, 4% tin, 2% nickel, 2% lead, 1% zinc, 0.2% silver, 0.1% gold and 0.005% of palladium. Together with the metal plates, we have 70% of polymers and ceramics. The plastic found on the printed circuit boards, due to being basically thermosets, present difficulty in recovery/recycling. Methods of separation, incineration, thermal degradation [(9)], pyrolysis [(10)], combustion power [(11,12)] have been analyzed in order to find the best destination for these materials.

Though plastic is very difficult to recycle, there is an increasing interest in the recovery of metals, not only for its value, due to its purity being ten times greater than the raw ore [(8),] but also in order to avoid the scarcity of natural resources. The recovery of metals has been investigated by mechanical milling [(13,14)], separation methods [(11,14)], hydrometallurgical processes [(15)], pyrometallurgical process [(16)] and processes electrometallurgical [(14)], among others.

Most technologies for the recycling of printed circuit boards employ the comminution process as an initial stage. There is a wide variety of grinding and cutting equipment which generates particles with different characteristics, influencing the subsequent processes of recycling and the identification of metals that are present in the plates. The possibility to contribute with new information about the influence of comminuted and leached particles in chemical analysis by optical emission spectrometry with induced coupled plasma (ICP-OES) motivated this work

2. MATERIALS AND METHODS

The printed circuit boards used in this work have the same origin of the laminate and part of the material consists of nude boards, without the electronics, and the rest of the plates, assembled, containing electronic components. The electronics were set

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by the manual process of welding, using soldering iron and alloy Sn-Pb. These plates were obtained from Exsto company and their nominal specifications are in Table 1. The photos of the assembled and nude boards are in Figure 1.

Table 1. Nominal specifications of printed circuit boards.

Plate dimensions	78,3 X 59,0 X 1,6 mm
Bare boards average weight	12,8 g
Assembled boards average weight	32,7 g
Composite Laminate	fiber ceramics, epoxy resin, phenolic resin and copper foil without coating
Estimated thickness of copper foil	17µm
Layers (copper sheets)	1
Electric copper contact surface	Cooper

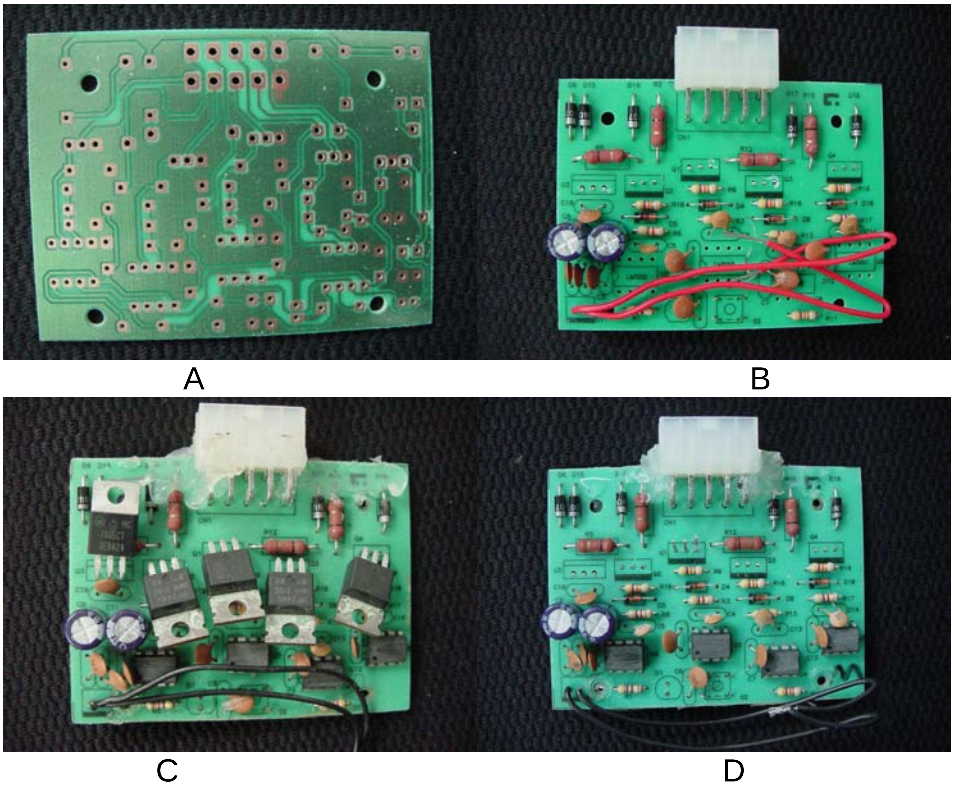

Figure 1. Printed circuit boards. A: Nude; B, C and D: Assembled.

Initially, a sample material consisting of 3.0 kg of assembled plates and 4.0 kg of nude plates were comminuted using a knife mill - manufactured by Tria of Brazil, model XT Series 30-BM, with a capacity of 150-220 kg / h, 3/2 number blade/counter-blades and 3.0 mm grid - resulting in particles with dimensions equal to or smaller than 3.0 mm.

Subsequently, the particles were separated into different grain sizes using a sieve with apertures of 1.19 mm; 600 µm and 250 µm.

In order to analyze the metals contained in the assembled and bare printed circuit boards, the samples with different grain sizes were subjected to chemical analysis using optical emission spectrometry with induced coupled plasma (ICP-OES), made by Varian, Vista MPX model. The samples, separated by sieves, were leached with

an acid mixture as the procedure described below and tested in duplicates for each sample size.
1) 2.0 g of each sample were placed in a borosilicate glass beaker of 250 mL.
2) 20 mL of the acid solution (3.0 N HCl + 1.0 N HNO3) was added.
3) The beakers were placed on a hot plate at a temperature of ± 200 ℃ for 60 minutes.
4) The samples were taken off the plate and cooled down at room temperature.
5) The samples were filtered and placed in a 100mL volumetric flask.
From the solution obtained in section 5 was determined the concentrations of metals via optical emission spectrometry with induced coupled plasma (ICP-OES). The results are in Table 2.

3. RESULTS AND DISCUSSION

The assembled and nude printed circuit boards subjected to the same process of comminution, showed particles ≤ 3.0 mm. Particles from the nude boards can be seen in Figure 2. It was observed, after milling, for both types of boards, that the particles had heterogeneous dimensions. To acknowledge the variations in particle size, samples were separated by sieves into different particle sizes.

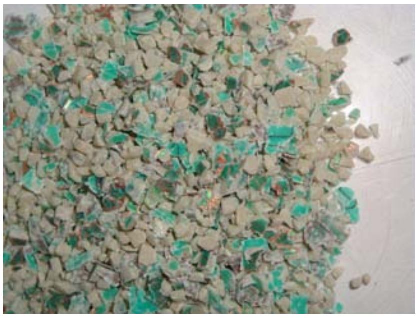

Figure 2. Particles ≤ 3.0 mm nude printed circuit board after knife mill.

The resulting particles, for both types of plates, even after the process of comminution (knives mill) and sieves separation were:
For mounted boards:
Particles ≤ 1.19 mm, particles > 600 µm and particles ≤ 600 µm.
For nude boards:
Particles ≤ 1.19 mm, particles ≤ 600 µm, particles > 250 µm and particles ≤ 250 µm.
The mounted plates resulted in larger particles due to the presence of weld metals and electronic components, which made the cards more resistant to cuts. The shear strength came from the plasticity of the metals that were deformed during shear stress, hindering the reduction of the particles. On the other hand, the nude boards showed smaller particles because the polymeric and ceramic materials are more fragile and have little metal plates that add the particles, which facilitated the cut.
The results of the chemical analysis to identify the metals contained in the assembled and nude printed circuit boards, obtained by ICP-OES, are presented in Table 2. In this table, for each metal analyzed there were 2 readings. For the assembled plate, each reading has 3 values concerning the size of the board, and for the nude board, each reading has 4 values, also concerning its size. The values of the percentages of the metals represent the amount of metal presented in 2 g of each sample. The average values, with their standard deviations, are in yellow for the mounted boards

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and in green for the nude boards. At the end of the table there is the sum of the average values of metals for each type of plates.

Table 2. Metals contained in the assembled and bare printed circuit boards identified by optical emission spectrometry with induced coupled plasma (ICP-OES).

METALS	Assembled PCI % of metals			Average	Nude PCI % of metals				Average
	≤1,19mm	≤600µm	>600µm		≤1,19mm	≤600µm	>250µm	≤250µm	
Al reading 1	3.08285	3.03015	3.74375	3.28558	1.95686	2.87045	2.2543	2.58581	2.41685
Al reading 2	4.1756	4.40147	3.755	4.11069	1.96294	2.57932	2.19155	2.48409	2.30448
Average Al				3.69814					2.36067
Stand/deviat				0.55727					0.323987
Cu reading 1	5.16035	22.4577	12.7989	13.4723	4.16467	4.56124	3.50637	1.31527	3.38689
Cu reading 2	6.80197	14.2563	13.0186	11.359	3.46735	4.35095	3.71496	1.3719	3.22629
Average Cu				12.4156					3.30659
Stand/deviat				6.146446					1.272907
Fe reading 1	1.75306	1.9005	1.59233	1.74863	0.00648	0.01444	0.01522	0.13392	0.04251
Fe reading 2	2.11228	0.96521	1.26946	1.44898	0.0073	0.015	0.01752	0.0073	0.01178
Average Fe				1.59881					0.02715
Stand/deviat				0.421527					0.043358
Ni reading 1	0.00818	0.31267	0.00766	0.1095	0.0005	0.0005	0.0005	0.0005	0.0005
Ni reading 2	0.00721	0.01656	0.00831	0.01069	0.0005	0.0005	0.0005	0.0005	0.0005
Average Ni				0.0601					0.0005
Stand/deviat				0.123784					0
Pb reading 1	4.04219	7.57341	3.75029	5.12196	0	0.00288	0.002	0	0.00122
Pb reading 2	3.15921	5.63894	3.65257	4.15024	0	0.0097	0.00642	0	0.00403
Average Pb				4.6361					0.00262
Stand/deviat				1.668496					0.003635
Pd reading 1	0.00221	0.1251	0.00285	0.04339	0.0005	0.0005	0.0005	0.0005	0.0005
Pd reading 2	0.00192	0.0061	0.00294	0.00365	0.0005	0.0005	0.0005	0.0005	0.0005
Average Pd				0.02352					0.0005
Stand/deviat				0.049786					0
Sn reading 1	6.6965	12.5318	3.85337	7.69388	0.00167	0.00912	0.00401	0.00275	0.00439
Sn reading 2	5.15659	8.90129	3.55724	5.87171	0.00146	0.01857	0.01439	0.00362	0.00951
Average Sn				6.78279					0.00695
Stand/deviat				3.440256					0.006442
Zn reading 1	0.06795	0.68632	0.17947	0.31125	0.0621	0.06662	0.0552	0.0244	0.05208
Zn reading 2	0.33987	0.2045	0.18595	0.19522	0.0524	0.0687	0.0583	0.0255	0.05123
Average Zn				0.25323					0.05165
Stand/deviat				0.218291					0.017353
Sum % average metals – assembled PCI				**25.7702**	**Sum % average metals – nude PCI**				**5.75663**

According to Table 2, it is observed that the assembled plates showed 25.7707% of metal and the nude plates showed 6.75663% of metal. The largest concentration of

metal in assembled boards is the result of solders and electronic components, which can be seen when one observes the average weight of the nude boards, 12.8 g, and the assembled plates, 32.7 g, with a difference of 19.9 g, which contributed to the increase of metal in assembled boards.
The data presented in the literature (7,8) reports that the assembled printed circuit boards contain 30% of metal, and this value was higher than the 25.8% found in the present study. This discrepancy can be attributed to the nature of the printed circuit boards analyzed. The research done by Menetti and Tenorio (7) reports that the origin, age and complexity of PCI interfere in the percentage of metals presented in the plates.
Based on chemical analysis by ICP-OES, the assembled plates were composed of 3.7% Al, 12.4% Cu, 1.6% Fe, 4.6% Pb, 6.8% Sn, 0.3% Zn and traces of Ni and Pd. For the nude board we found Al 2.4% and 3.3% Cu and traces of Fe, Pb, Sn, Ni, Pd. The aluminum identified is probably concentrated in the ceramic fibers. It is interesting to mention the work of Veit (14), where the results of the chemical analysis by scanning electron microscopy of particles of aluminum plates also identified and the content of this element was more concentrated in smaller particles, which had a higher proportion of polymers and ceramics
Looking at the standard deviations of the metals analyzed, the values were high, but when compared with the values of the readings 1 and 2, the changes were small. These observations indicate that the particle size interfere with the results of chemical analysis of samples comminuted and leached subjected to ICP-OES, which can best be seen in the scatter plots presented in Figures 3 and 4 for assembled and nude boards, respectively.
It is interesting to note that the leaching process consisted of extracting the comminuted metal plates using HCL and HNO3 acids for subsequent analysis with ICP-OES.

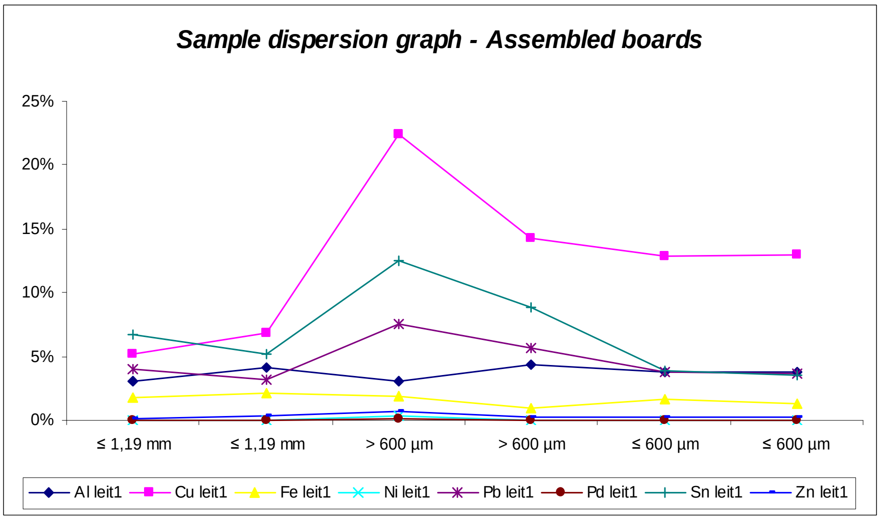

Figure 3. Scatter plot of values of the metals in samples of assembled boards.

Looking at Figure 3, it is possible to observe that the copper had a higher dispersion of values, followed by tin and lead, decreasingly. For the other metals, the dispersions were small. This figure also observed a trend of greater dispersion around the particles > 600 µm in readings 1 and 2, indicating a higher metal content.

Exception occurs for aluminum, which presented the lowest metal content in reading 1 and had a more homogeneous behavior.

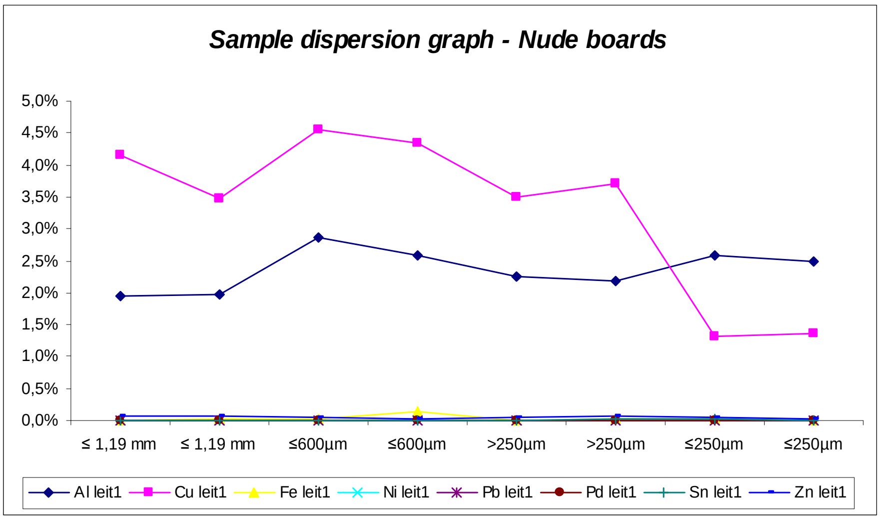

Figure 4. Scatter plot of values of the metals in the samples of nude boards

In Figure 4 shows that copper had a higher dispersion of values than Aluminum. For the other metals analyzed, the dispersions were negligible. In these plates the higher metal concentrations tended to occur around the ≤ 600 µm particles, both in reading 1 and reading 2 of each metal.

The dispersion of the data in Figures 3 and 4 indicates that the assembled plates had higher concentration of metals in particles > 600 µm plates and the nude plates in the ≤ 600 µm particles, in which presence hampered the reduction of metal particles. Associated with this fact, the smaller particles of the plates contained more polymers and ceramics, presenting lower concentrations of metals, which facilitated the reduction of particles. In both types of plates, copper was the metal that presented more dispersion and aluminum was the most stable. As copper is a metal of great plasticity, resulted in larger particles. On the other hand, aluminum, as it is combined with ceramic fibers, had homogeneously concentrated itself in particles of different sizes.

With the results given, it is evident that the particle sizes of comminuted plates greatly interfere in the extraction of metals by leaching, which should be considered in the recycling processes that uses this medium for the recovery of metals, as well as in chemical analysis by ICP-OES.

4. CONCLUSION

Whit the data obtained in this study it can be concluded that:

- After the process of comminution in a knife mill, particles assembled plates were larger than the nude boards due to the presence of weld metals and electronic components.
- The chemical analysis with ICP-OES revealed that the assembled bords display 25.8% of metal and the nude boards 6.8% of metal.
- The size interferes with the leaching process used for extraction and identification of metals by ICP-OES, with higher concentrations of metal in the particles around 600 µm.

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