



Analysis of waste electrical and electronic equipment (WEEE) using laser induced breakdown spectroscopy (LIBS) and multivariate analysis

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ABSTRACT

This study shows the application of laser induced breakdown spectroscopy (LIBS) for waste electrical and electronic equipment (WEEE) investigation. Several emission spectra were obtained for 7 different mobiles from 4 different manufacturers. Using the emission spectra of the black components it was possible to see some differences among the manufacturers and some emission lines from organic elements and molecules (N, O, CN and C₂) led to the highest contribution for this differentiation. Some polymeric internal parts in contact with the inner pieces of the mobiles and covered with a special paint presented a strong emission signal for Cr. The white pieces presented mainly Al, Ba and Ti in their composition. Finally, this study developed a procedure for LIBS emission spectra using chemometric strategies and suitable information can be obtained for identification of manufacturer and counterfeit products. In addition, the results obtained can improve the classification for establishing recycling strategies of e-waste.

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1. Introduction

The increasing and continuous use of electronic and electrical devices is one of the factors for the generation of a great amount of residues in several countries. These materials are commonly named Waste Electrical and Electronic Equipment (WEEE) or simply e-waste. A general perspective can be observed for mobiles, where nowadays it is estimated that around 100 millions of these equipments are discarded every year worldwide. This panorama generates several problems: (i) with the technological development, new materials are introduced every year in the market and to predict e-waste elemental composition and identification of hazardous elements is not a simple task [1–4]; (ii) e-waste is subject to illegal commerce since these materials are indiscriminately sent to developing countries in Africa or Latin America; and (iii) in several countries there are not regulations for environmental recycling procedures to the recovery of precious and/or valuable metals and workers are in contact with toxic elements (Cd, Cr, Hg, Pb, among others) from the printed circuit board (PCB) [2,5–8].

Xinhui et al. [9] studied a low-tech recycling workshop in China and they found bisphenol A concentrations to be around 5 orders

of magnitude higher when compared with indoor and outdoor environments in the world. In addition, the authors identified high Cd, Ni and Pb concentrations in the particulate matter (PM). The chemical identification of the composition of these materials is an important step to lead to the establishment of safe recycling procedures and final disposal of e-waste. In 2009 Nnorom and Osibanjo [10] determined Ag, Cd, Pb and Ni in plastic housing of mobile phones and these authors observed concentrations varying from 4.6 mg/kg (for Cd) to 12,500 mg/kg (for Ag). Yamane et al. [11] characterized and compared the PCB's from mobile phones and computers and they showed that there are differences of metals composition (63% w/w in mobile phones and 45% w/w in computers). This topic is of concern in several countries and some articles about the situation in Germany [12,13], Norway [14], Austria [7,15] and Brazil [16], reporting the importance of recycling instead incineration and the need of a new Brazilian law for solid waste management, were identified in the literature.

Several analytical techniques have been applied to the identification of hazardous compounds in electronic devices. Santos et al. [17] determined Cd, Cr, Hg and Pb in plastics from e-waste using inductively coupled plasma mass spectrometry (ICP MS) and the authors observed the highest concentrations for Cr (from 16 to 43 mg/kg). In another study from this same group [18] these authors used electrothermal atomic absorption spectrometry (ETAAS) for direct slurries analysis of plastic samples and it was reported Sb levels from 0.2% to 1.65% (w/w).

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Additionally, using analytical techniques and chemometric tools, classification models can be proposed to identify the origin or the manufacturer of e-waste from the illegal commerce. Laser IBS can help in the accomplishment of these tasks because the analytical throughput is high and does not require extensive sample preparation [19]. In addition, the nature of the chemical data obtained requires the use of mathematical and statistical approaches for better interpretation, initial exploratory analysis and also for data mining [20–25]. The successful combination of LIBS and chemometric strategies was demonstrated by Shunchun et al. [26] where the authors presented a regression model using Partial Least Squares (PLS) for ash determination in coal. The versatility of LIBS was also demonstrated for sugar cane leaves [27], soil [28], toys [29] and warfare agent simulants classification [30], unburned carbon determination in fly ash for furnace efficiency evaluation [31], wastewater analyses [32], Cr determination in dyed wool fabric [33] and remotely identify Martian rock [34].

The aim of the present study is to show the potentialities of the combination of LIBS and chemometric strategies for e-waste characterization and classification. Some mobile samples from different manufacturers and countries were selected as a case study and important aspects are here highlighted.

2. Experimental section








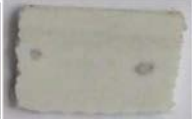

2.1. Samples

Seven mobiles from different manufacturers, models and colors were selected in order to show the applicability of LIBS for e-waste analysis and how to obtain useful information from the emission spectra. Table 1 shows the mobiles main characteristics. Four manufacturers were selected with 6 different models and the color of most analyzed parts was black. The mobiles were dismounted, external and internal polymers were cut (around 1 mm thickness) and analyzed as well as the PCBs.

2.2. LIBS system, data set collection and chemometric evaluation

The LIBS system was composed by a Nd:YAG laser (model HYL Handy-YAG, Q-switched, Quanta System S.P.A., Varese, Italy), emitting pulses of 180 mJ energy (pulse width 10 ns FWHM) at 1064 nm. The laser was operated in single shot mode and the laser beam was focused on the samples by a biconvex lens with a 100 mm focal length. The emission of the laser-induced plasmas was collected using a fiber optic and detected by a five channels

Table 1
Mobile samples description.

Sample identification	Coded manufacturer	Coded model	Origin	Polymers color	Parts example	Remarks
Mobile 1	A	1	Brazil	Black only		These two mobiles are from the same manufacturer and model
Mobile 2	A	1	Brazil	Black only		
Mobile 3	A	2	Brazil	Black and brown (internal)	 	–
Mobile 4	B	3	China	Black only		–
Mobile 5	C	4	South Korea	Black with internal plating	 	–
Mobile 6	D	5	Hungary	White only	 	This mobile has a digital camera and a transparent polymer in the screen.
Mobile 7	D	6	Hungary	Black and gray (internal)		

spectrometer (model AvaSpec-2048-SPU, Avantes, Apeldoorn, The Netherlands) covering wavelengths from 197.146–852.190 nm (8192 variables). A delay system consisting of two pulse generators (Digital delay/pulse generator, model DG 535, Stanford Research Systems, Inc. and 1 Hz–50 MHz pulse generator, model PM-5715, Philips) was used for synchronization of laser firing and data acquisition. Spectra were collected 1.3 μ s after the plasma generation, with 1 ms acquisition time (minimum time settings available on the spectrometer). A LG laptop (Intel Core 2 processor, 1.00 GB of RAM and Windows Vista) equipped with AvaSoft (Avantes,

version 7.5.3 Full software) was used for data acquisition and visualization. Fig. 1 shows a pictorial description of the used system.

Several spectra were acquired from a single laser shot at different points of the samples and two approaches for data treatment were applied. First, information from the surface was obtained in order to identify general trends in the mobile samples. In this case, the emission spectrum from the first pulse was collected. Later, after 10 successive pulses in the same sample position, spectrum from the bulk was obtained in order to identify the origin of the samples and to establish a fingerprint of the manufacturers. The bulk of the samples was identified after some initial experiments and it was concluded that this part was reached after emissions of elements mainly located on the surface disappear from the spectra and the emissions of elements located in the bulk become constant.

After data collection, a procedure to identify useful information was performed. Fig. 2 shows a description of the mathematical procedures performed. Two different strategies were applied. In the first one a Savitzky–Golay digital filter for first derivative calculation was performed, and later on the data was mean centered. In the second strategy, \log_{10} was calculated for each variable and then mean centered. This second approach was based in the procedure described by Pereira et al. [35] and was used for investigating manufacturers. Calculations were performed with Matlab 2009a (The Math Works, Natick, USA).

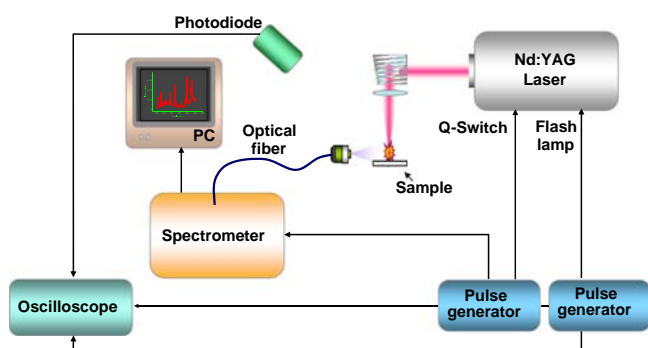


Fig. 1. Pictorial description of the LIBS equipment.

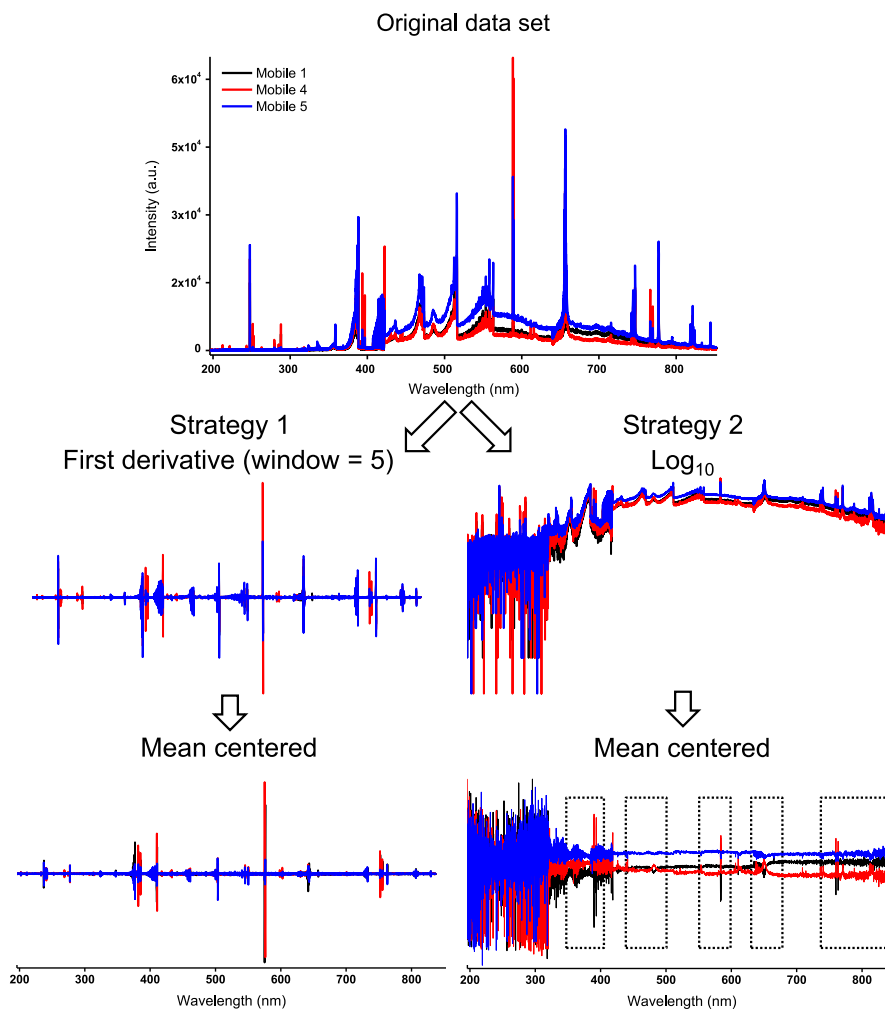


Fig. 2. Description of the data set mathematical treatment proposed. Two strategies were tested: use of first derivative and \log_{10} . The dotted squares depicted in the strategy 2 show the ranges of wavelengths used on the final discrimination study after PCA calculation.

3. Results and discussion

3.1. Polymers exploratory analysis

For qualitative purposes, that is the goal of this study, typical Relative Standard Deviation (RSD) values ranged from 18% to 40%. These values were calculated taking the signals intensity at all wavelength range studied and the average number of replicates was 4. Otherwise, for quantitative purposes, the same calculation using 21 peak areas at relevant wavelengths was also performed and the RSD values ranged from 10% to 17% ($n=4$ in average). In both cases the RSD values were higher for surface measurements than for the bulk ones.

An initial exploratory analysis (Strategy 1, see Fig. 2) was performed using 38 spectra (from the surfaces and the bulk of the samples) and 8192 variables (197.146–852.190 nm). The first two PC's accounted 77% of the explained variable and Fig. 3 shows scores when the first derivate with 5 windows was applied. It can be seen that the silver and brown internal parts of mobiles 5 and 3, respectively, have a different composition when compared with the other polymeric pieces. On the other hand, it is possible to see also two different clusters, one related to all black and transparent parts of mobiles, no matter the mobile origin, and the other related to white parts (mobile 6).

After this initial exploratory analysis some particularities of the polymeric pieces are highlighted. Fig. 4 for instance shows the Si (4a) and Ti (4b) emission lines for the black pieces (mobiles 1–5). These pieces presented similar results and Si (4a) was observed in both the surface (black line) and the bulk (red line) parts of the polymers. On the other hand, Ti (4b) was only detected in the surface of the polymers. The brown part of mobile 3 was characterized by the presence of Ag (Fig. 5) only in the surface. The white polymers presented Ti (Fig. 6a), Al (b) and Ba (c) in the surface and bulk parts.

The silver part from mobile 5 presented intense Cr signal (Fig. 7) only in the inner part in contact with pieces of the mobile. Probably this part performs some special function in the mobile operation.

3.2. Manufacturers identification

Another possibility investigated was the manufacturer identification using LIBS emission spectra. In this case, only the black

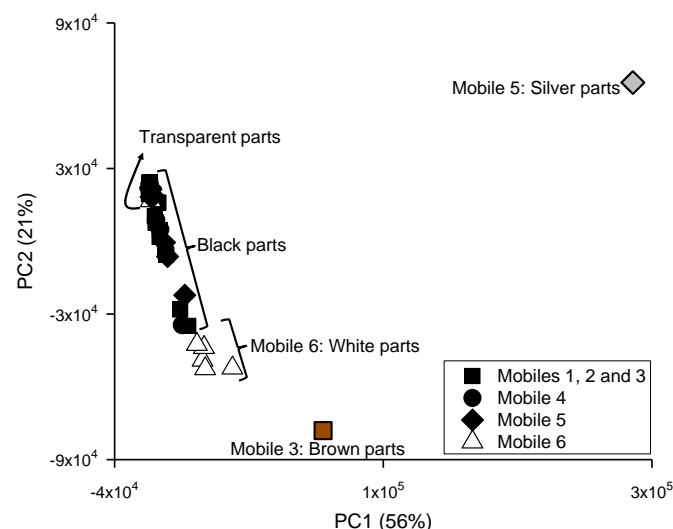


Fig. 3. Scores for PC1 versus PC2 for all pieces tested (black, white, transparent, brown and silver parts) from the mobiles studied. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

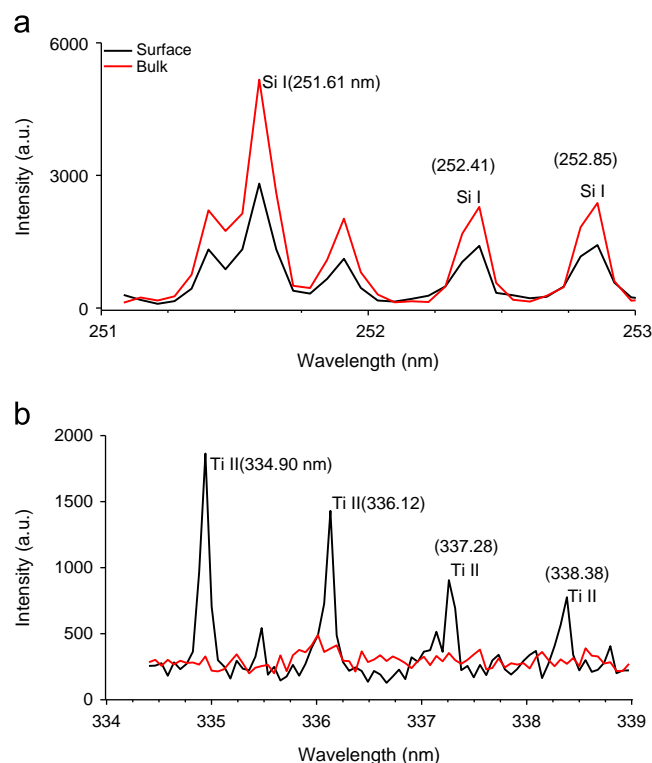


Fig. 4. Emission signals for Si (a) and Ti (b) obtained from black part. The black and red lines correspond to surface and bulk, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

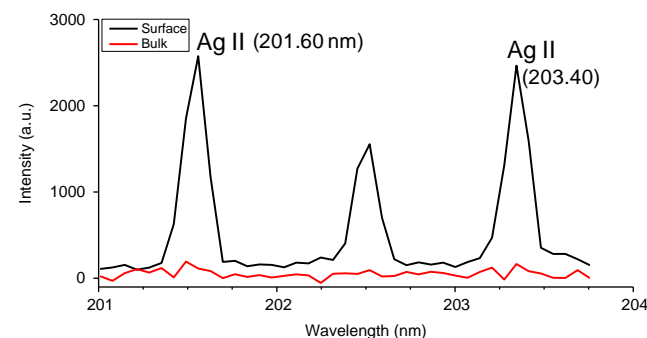


Fig. 5. Emission signals for Ag obtained from the brown part of mobile 3. The black and red lines correspond to surface and bulk, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pieces were analyzed and a matrix with 168 spectra from the bulk and 8192 variables was organized. The best manufacturers discrimination was obtained after using \log_{10} data transformation and mean centering pre-treatment (see Strategy 2 details in Fig. 2). An initial PCA was calculated and the loading values were used for variables selection. After that 3532 variables were selected.

Fig. 8 shows the scores (8a) and loadings (8b) plots when the black parts of 6 mobiles (mobiles 1, 2, 3, 4, 5 and 7) were studied. Three tendencies can be observed in Fig. 8a: (i) the black fragments from mobile 4 (red circles) were separated from the other pieces due to the high signals obtained for K I lines according to loadings values presented in Fig. 8b; (ii) mobiles 1, 2 and 3 were from the same manufacturer and their pieces were spread along PC1 with some samples presenting high values for this PC. These samples were mainly characterized by the presence of Na I, Ca II,

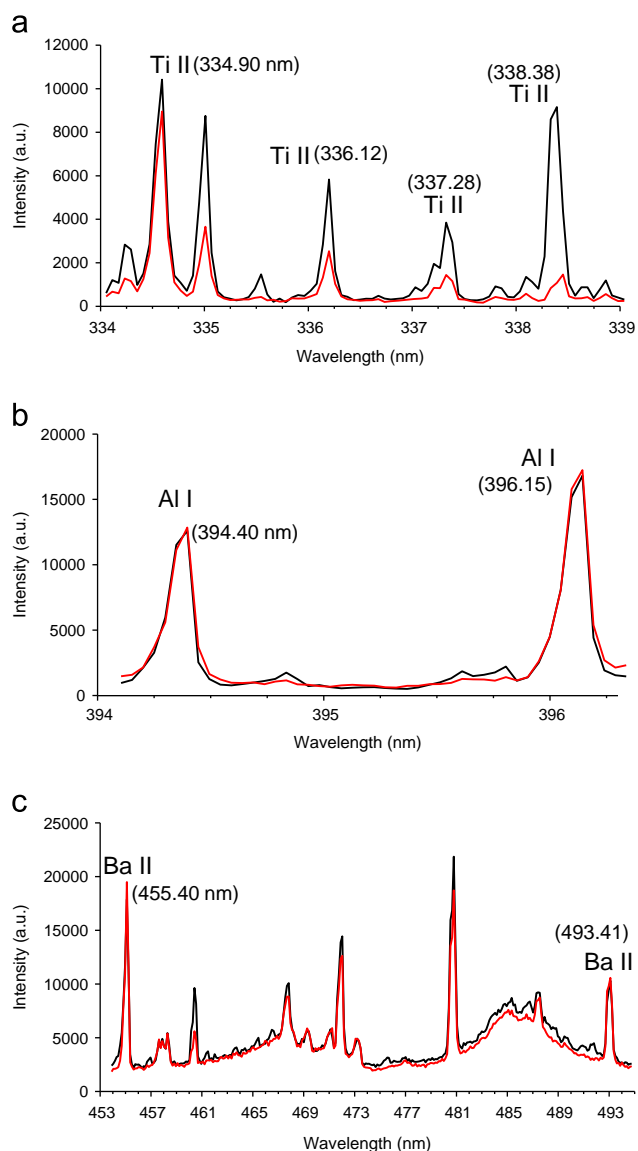


Fig. 6. Emission signals for Ti (a), Al (b) and Ba (c) obtained from the white part. The black and red lines correspond to surface and bulk, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

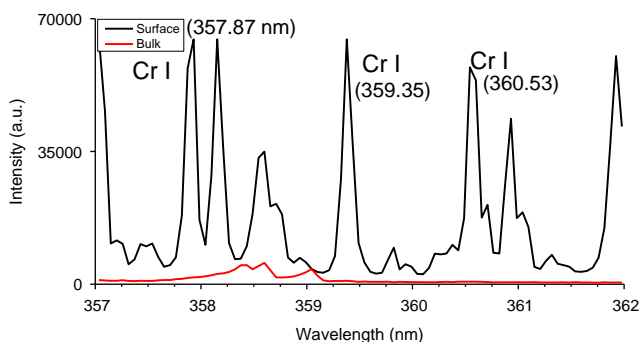


Fig. 7. Emission signals for Cr obtained from the silver part of mobile 5. The black and red lines correspond to surface and bulk, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

C₂ I and CN I lines; (iii) mobiles 5 and 7 were clustered at negative values of PC1 and, in this case, these samples were mainly correlated to N I and O I lines.

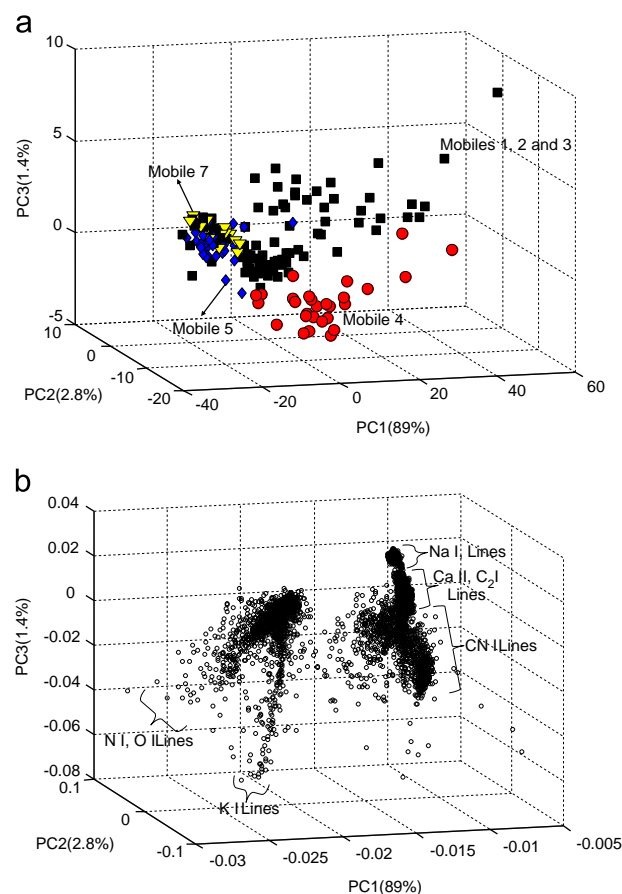


Fig. 8. 3D view of the scores (a) and loadings (b) plots for the black polymers studied from 6 mobiles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

According to the results presented it is possible to conclude that few lines are responsible for polymers characterization and also typical constituents of organic components (C, O, N and CN) are important for their distinction.

3.3. PCB's characterization

The same procedure described for the collection of spectra in the polymers was used for the PCBs. In this type of samples the bulk part is much richer in analytical signals than the surface (Fig. 9). Cu, Ba, Si and Mg were observed in the bulk part. Probably these elements have insulation properties and the presence of Cu in PCBs seems obvious due to the electrical connections. In surface analysis, Ba, Si and Mg signals were also appreciable; however, Cu signal was almost negligible (see Fig. 9).

3.4. WEEE and LIBS outlook

The use of LIBS for WEEE investigation opens some perspectives to generate a fast and reliable panorama of the WEEE composition. In addition, the LIBS system can be miniaturized and portable devices are nowadays available in the market. When compared with the procedures already described in the literature and recommended by the legislations, such as acid digestion [11] or use of the samples in the form of slurries [18] in combination with spectroanalytical techniques like ICP MS and ICP OES (ICP optical emission spectrometry), the combination of LIBS and WEEE analysis is also attractive because the initial steps related to sample preparation are drastically shortened. On the other hand, the LIBS technique for quantitative analyses presents some

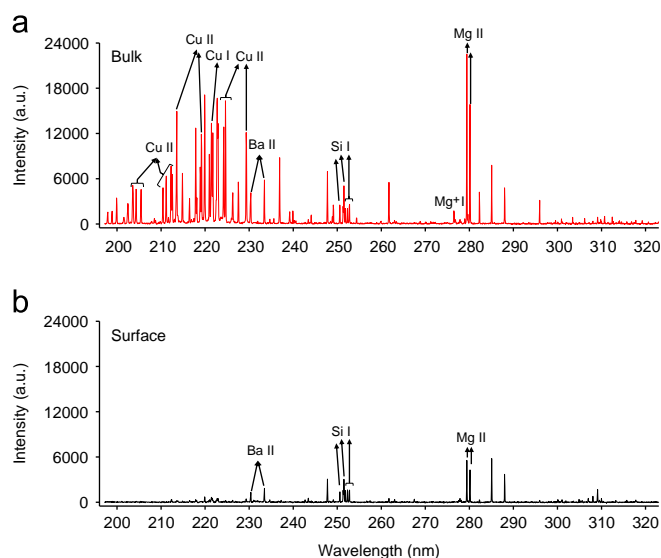


Fig. 9. Emission spectra obtained from the PCB's from bulk (a) and surface (b).

challenges, such as the use of solid standards, matrices effects, and the laser interaction with different materials. In addition, when compared with X-ray fluorescence (XRF) the LIBS system does not require a vacuum system for detecting light elements (C, N, and O) and by using a single pulse inorganic and organic fingerprints can be obtained. Finally, due to the emission spectra complexity and the huge quantity of data that can be obtained in just one pulse the use of chemometric tools is sometimes mandatory in order to deal with the data and extract useful information from them.

The combination of LIBS and chemometric strategies provided better data interpretation and visualization. In addition, the whole spectra profile was used and not only the inorganic elements but also the organic components can help in the manufacturer identification. This study opens possibilities for e-waste characterization providing information for supporting recycling procedures and also identification of counterfeit.

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