Analysis of the polymeric fractions of scrap from mobile phones using laser-induced breakdown spectroscopy: Chemometric applications for better data interpretation

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ABSTRACT

Because of their short life span and high production and consumption rates, mobile phones are one of the contributors to WEEE (waste electrical and electronic equipment) growth in many countries. If incorrectly managed, the hazardous materials used in the assembly of these devices can pollute the environment and pose dangers for workers involved in the recycling of these materials. In this study, 144 polymer fragments originating from 50 broken or obsolete mobile phones were analyzed *via* laser-induced breakdown spectroscopy (LIBS) without previous treatment. The coated polymers were mainly characterized by the presence of Ag, whereas the uncoated polymers were related to the presence of Al, K, Na, Si and Ti. Classification models were proposed using black and white polymers separately in order to identify the manufacturer and origin using KNN (*K*-nearest neighbor), SIMCA (Soft Independent Modeling of Class Analogy) and PLS-DA (Partial Least Squares for Discriminant Analysis). For the black polymers the percentage of correct predictions was, in average, 58% taking into consideration the models for manufacturer and origin identification. In the case of white polymers, the percentage of correct predictions ranged from 72.8% (PLS-DA) to 100% (KNN).

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1. Introduction

Currently, the management of obsolete electronic equipment or the scrap originating from these devices, generally named as WEEE (waste electrical and electronic equipment) or e-waste, is of great concern in many countries [1,2]. Despite the advances arising from the implementation of norms, such as Directives 2002/95/EC [3] and 2002/96/EC [4] (created by the European Union), the different aspects related to the correct destination of e-waste are far from being fully developed, established and implemented in all countries [1,2,5,6].

In Latin American cities, this problem has not reached the same magnitude as observed in other cities such as Lagos (Nigeria), New Delhi (India), Guiyu and Taizhou (China) [1,2,7]; nevertheless, it is obvious that the general development of policies on e-waste management in this region is not ideal [1]. In this context, the Brazilian situation illustrates this problem. Brazil is the second largest producer of e-waste among emerging countries and

similarly to others, the complete recycling process of the e-waste does not occur properly. The exportation of printed circuit boards from Brazil to countries such as Canada, Belgium and Singapore, where they are recycled for precious metal refining, is an example of this issue [1,8].

On the other hand, the mechanical recycling of WEEE plastics, which represents around 20–25% by weight of WEEE (around 50% by volume) [9], is the main polymer recycling process performed in Brazil. In this technique the plastics are essentially selected by their type (not solely in Brazil), and aspects like their origin, previous use and possible contaminants are frequently unconsidered for economic or analytical reasons. This practice is undesirable since hazardous substances such as the toxic elements and the brominated flame retardants can remain in the recycled plastics engendering danger to its users or contaminating the environment [10].

Therefore, independent of the development level of the country, actions aimed at dealing with e-waste problems must be conducted during all stages of the electronic device cycle: (1) from its assembly using components either with the absence or low levels of hazardous substances, (2) to its disposal, and (3) finally to its recycling and the prevention of illegal commerce of its generated scraps. Therefore, it is

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clear that chemical analysis is a critical step in ensuring the success of each of these actions. In this regard, the development of green, fast, simple and inexpensive analytical methods is desirable [11].

The combination of all these attributes into a unique analytical methodology is not an easy task; however, the development of laser-induced breakdown spectroscopy (LIBS) during the past few years has led to major steps in this direction [12–14]. Some advantages of LIBS include the elimination of expensive gases for plasma formation and the possibility to achieve analysis without sample preparation protocols with minimal amount of material. However, the proposition of calibration procedures for quantitative analysis using this method is not trivial. Despite this challenge, LIBS has been successfully applied in a wide range of analyses (e.g., biomedical, industrial, forensics, environmental, geological and archeological) [12,13].

In plastics analysis, LIBS associated with chemometric tools has been used to identify the different polymer types found in diverse wastes (including the scraps of electronic devices) as well as to determine the brominated flame retardants (BFRs) and metals in these materials [15–19]. However, the use of LIBS to build chemometric models based on the spectral data of the polymers employed in electronic device manufacturing, which may assist in the characterization or traceability of this equipment and its scraps, is an application that remains to be further exploited.

Despite their relatively small size, mobile phones are significant contributors to the growth of electronic waste. This occurs in function of their short life span, which is reduced by the high number of models launched with new technologies and by the increasing number of consumers that quickly acquire new devices. Moreover, due to the relatively small size, mobile phones (or their broken components) can easily be added to the domestic waste or improperly exposed to the environment. This kind of disposal poses a serious problem once the hazardous elements or materials such as Ba, Ni, and carbon black [20–23] used in the assembly of these devices can pollute the air when burnt in incinerators or contaminate the soil and drinking water sources through leaching when buried in landfills [6,24].

From the analysis of a set of 50 mobile phones, this study aims to demonstrate that the combination of LIBS with chemometric strategies can provide a simple and useful tool (proposition of classification models) for the classification of the origin and manufacturer of polymeric scraps of these devices.

These classification models can be used in circumstances where determination of the traceability of these products is necessary. Examples of these situations are the investigations of illegal WEEE commerce, piracy and smuggling. In addition, this methodology can also be applied in cases where the chemical profile (fingerprint) of these scraps is an important factor for the correct choice of their management.

2. Materials and methods

2.1. LIBS set-up and samples

The experiments were performed using an Applied Spectra (Fremont, California – USA) J200 commercial LIBS managed by the Axiom 2.5 software. This instrument is equipped with an ablation chamber with an HEPA air cleaner to purge ablated particles, an automated XYZ stage and a 1280×1024 CMOS color camera imaging system. The Nd:YAG laser was employed at 1064 nm, delivering a maximum of 100 mJ in a single laser pulse with 8 ns duration at a frequency of 10 Hz. The plasma light emission was guided into an optical fiber bundle coupled with a 6-channel CCD spectrometer with a spectral window from 186 to 1042 nm, resulting in spectra composed of 12,288 points (variables). The Aurora software (Applied Spectra) was employed for the identification of the emission lines.

The complete set of samples consisted of 50 broken or obsolete mobile phones. After the manual disassembly, the phones provided 144 polymeric sub-samples. The number of sub-samples from each phone depended on the quantity of different polymers that had visually distinct characteristics, such as color, coating with film or covered with a rubber material. A description of the mobile phones can be found in Table 1.

2.2. Flame Atomic Absorption Spectrometry set-up

Silver determinations were carried out using a Thermo iCE 3000 Atomic Absorption Spectrometer operated at the analytic conditions recommended for this analyte according to the manufacturer instructions: Fuel – C_2H_2; Fuel flow 0.9 L min^{-1}; burner height 14.2 mm; wavelength 328.1 nm with D_2 background radiation correction.

2.3. Data set collection and chemometric evaluation

For all polymer fragments, 5 points were randomly selected upon which 30 laser pulses per point were performed. These samples were directly analyzed without any chemical pretreatment. A surface cleanup was performed using a single pulse with 20% of the total laser power in a 250 µm spot. After this procedure, the spot size was reduced to 125 µm and the pulse sequence was conducted with 100 mJ of power (100%), a gate delay of 1 µs and a gate width of 1.05 ms. From the analysis of 144 polymer fragments, more than 20,000 spectra were obtained. The raw data were normalized by the individual norm and mean-centered. Afterward, the data set was organized into a matrix (Fig. 1) from which the chemometric analyses were performed or derived. Matlab 2009a (The Math Works, Natick, USA) and Pirouette 4.5 (Infometrix, Bothell, USA) were used for the data processing.

The first chemometric inspection performed was a Principal Component Analysis (PCA) [25]. This chemometric tool is one of the most used for exploratory analysis and its objective is to project the data set in a smaller number of variables named as Principal Component (PC). With this small number of variables the data set is then represented by two separate and complementary matrices: scores and loadings. The scores plot provides information about the samples and it is possible to observe clusters and outlier samples. The loading plot shows the most important variables for sample characterization. With these two informations it is possible to make variables selection in order to identify specific characteristics for a particular group of samples [26].

In the proposition of classification models, four chemometric strategies were used. The first one was K-nearest neighbor (KNN) that calculates the Euclidean distance between samples whose classes are previously known (training data set). If one neighbor is selected for each sample it is observed which class this neighbor belongs to. For example, if the first neighbor of a specific sample belongs to a hypothetical class A, then this sample also belongs to class A. This approach is repeated for 1, 2 up to K neighbors and the number of neighbors selected is that presented by the lower classification error [27].

Soft Independent Modeling of Class Analogy (SIMCA) is a supervised method for classification purposes. In this classification model, a PCA is performed for each class and the number of principal components is selected individually for the classes under investigation. Then, a hiperbox is constructed involving samples of each class (training data set). The classification of samples outside the model occurs through its projection on the scores and the distance established between each class [28].

The Partial Least Squares for discriminant analysis (PLS-DA) was also used in this study for determining a classification model that creates a correlation between samples that belong to a class and all others. The calculation was performed with and without