



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



Francisco W.B. Aquino, Edenir R. Pereira-Filho*

Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, 13565-905 São Carlos, SP, Brazil

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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

* Corresponding author. Tel.: +55 16 3351 8092; fax: +55 16 3351 8350.

E-mail address: erpf@ufscar.br (E.R. Pereira-Filho).

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 a 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 – C₂H₂; Fuel flow 0.9 L min⁻¹; burner height 14.2 mm; wavelength 328.1 nm with D₂ 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].

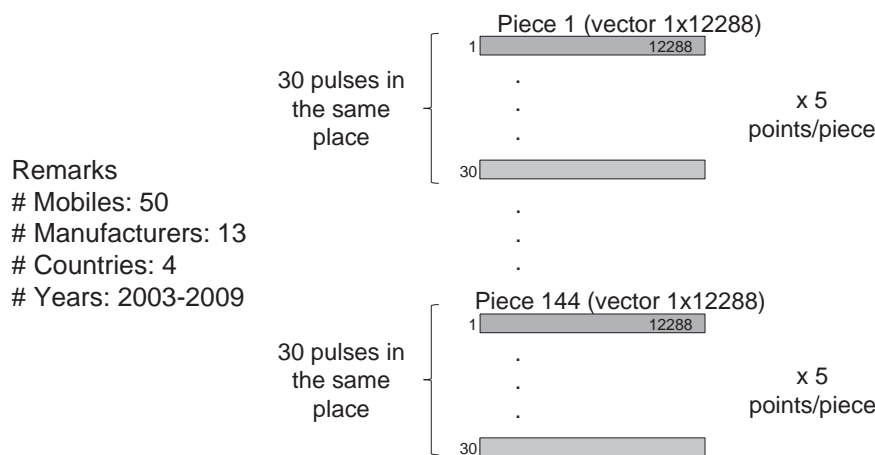
Soft Independent Modeling of Class Analogy (SIMCA) is a supervised method for classification purposes. In this classification model, a PCA is performed for each class and the number of principal components is selected individually for the classes under investigation. Then, a hiperbox is constructed involving 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

Table 1

Description of mobile phones (origin, coded manufacturer, predominant colors observed, and number of sub-samples).

Mobile phone identification	Origin country	Manufacturer	Predominant colors	Number of sub-samples	Mobile phone identification	Origin country	Manufacturer	Predominant colors	Number of sub-samples
1	Brazil	A	White	5	26	Brazil	K	Silver	3
2	Brazil	B	White, Pink	2	27	Brazil	B	Violet	4
3	Brazil	C	Silver, Blue	7	28	South Korea	C	Silver	3
4	Brazil	C	Black	2	29	China	L	Pink, White	3
5	China	D	Brown	2	30	Brazil	A	Black, Silver	2
6	South Korea	E	Black	2	31	Brazil	B	White	1
7	Mexico	F	Silver, Gray	3	32	Brazil	A	Black, Gray	4
8	China	G	Black, Silver	2	33	Brazil	A	Black	3
9	China	H	Black	3	34	South Korea	C	Silver	3
10	Brazil	G	Black	2	35	Brazil	A	Black	5
11	Brazil	G	Black	1	36	Brazil	F	Black, Silver	3
12	Brazil	C	Black, Gray	3	37	Brazil	C	Silver	5
13	Brazil	C	Black	2	38	Brazil	F	Black, Silver	5
14	Brazil	A	Silver	2	39	Brazil	B	Purple	4
15	Brazil	A	Black	2	40	Brazil	G	Gray, Silver	4
16	Brazil	B	Black	1	41	China	H	Blue, White, Black	4
17	Brazil	I	Silver	4	42	Brazil	G	Brown	5
18	Brazil	F	Gray, Blue	2	43	Brazil	F	Gray, White	2
19	Brazil	B	Black	1	44	Brazil	B	Black	2
20	Brazil	B	Black	1	45	Brazil	C	Black	2
21	Brazil	A	Black	1	46	Brazil	A	Silver	3
22	Brazil	B	Black	2	47	Brazil	C	Blue, Silver	6
23	Brazil	J	Black	2	48	Brazil	G	Black, Gray, White	3
24	Brazil	G	Black, Silver	2	49	Brazil	C	Silver, Gray	4
25	Brazil	G	Black, Silver	3	50	Brazil	C	Silver, Gray	2



Final matrix dimension: 21480 rows x 12288 columns

Fig. 1. Matrix data organization.

cross-validation. One of our objectives, for example, was to identify the origin of the samples. In this case, when the samples from Brazil, for example, were investigated, these samples were designated as class number 1 and the other samples (from China) as class 0. The main purpose of PLS-DA is to calculate a calibration model taking into consideration the emission spectra (matrix **X**) and the classes designation (matrix **Y**). During the model calculations the scores from both matrices are considered and the best number of latent variables (LVs) is selected for the situation that presents at the same time low classification error and high explained variance. In addition, these calculi can be done with or without cross-validation (CV). In the first case, one sample (one-leave-out) is separated from the rest of the matrix **X** and a model is calculated. Then the class of this sample that

was segregated is calculated using the model and an error is computed. This process is repeated for all samples and for several numbers of LV. In the case of without cross-validation, all samples are used to build the classification model [29].

3. Results and discussion

3.1. Assessment of repeatability from the LIBS measurements

Prior to the sample analysis, the repeatability of the LIBS system was evaluated. For this purpose, spectra of the same polymer piece (randomly chosen from the sample set) were

obtained over 10 subsequent days. On each day, 60 spectra were obtained from 20 laser shots at 3 distinct points. From these spectra, 14 emission lines were selected in an effort to cover the entire spectral range (186–1042 nm). The selected lines were (I and II mean atomic and ionic emission lines, respectively): Line 1=193.09 – C (I); Line 2=247.85 – C (I); Line 3=279.55 – Mg (II); Line 4=334.94 – Ti (II); Line 5=393.36 – Ca (II); Line 6=422.67 – Ca (I); Line 7=498.17 – Ti (I); Line 8=521.03 – Ti (I); Line 9=588.99 – Na (I); Line 10=656.28 – H (I); Line 11=742.36 – N (I); Line 12=766.49 – K (I); Line 13=824.23 – N (I) and Line 14=862.92 – N (I).

All obtained spectra were grouped in a single matrix and normalized. The areas of each emission line were calculated and the relative standard deviations (RSDs) for the monitored lines were calculated and found to be between 11.5% and 27.5% with an average of 17.4%. Fig. 2 presents the RSD calculated for each line along the period monitored and Table 1S in the supporting information shows all calculated areas.

Considering that the J200 LIBS system has a sample chamber system, it is probable that ambient factors such as moisture or dust had no influence on the RSD range obtained. Thus, it is reasonable to expect that the more strong sources of this variation are the heterogeneity of the sample surface associated with intrinsic characteristics of LIBS spectroscopy where the formation of the plasma on the surface of a solid sample involves complex non-linear optical and physical phenomena [13,30].

According to Harmon et al. [30], these phenomena “depend[s] on a suite of interrelated factors that include the laser characteristics (wavelength, energy, and pulse duration), the degree of coupling of the laser energy to the sample surface, the atmosphere above the sample, the pressure of the environment in which the LIBS spark is formed, the nature of the material being analyzed, and the amount of material ablated.”

Concerning the surface characteristics of the white sample used in the repeatability evaluation test, this sample exhibited the same bright effect observed in Fig. 3a and b. Thus, it is important to point out that this effect was obtained by bright particles dispersed in the polymer. This condition can lead to the focalization of laser beam on the bright particles or in the opaque portion of the polymer during the analysis and increase the RSD values.

3.2. Aspects of black and white polymers of Brazilian and Chinese mobile phones

Spectral information from the 50 mobiles (144 fragments) were obtained using 5 points *per* sub-sample (see the number of sub-samples in Table 1) and in each point 30 pulses were made.

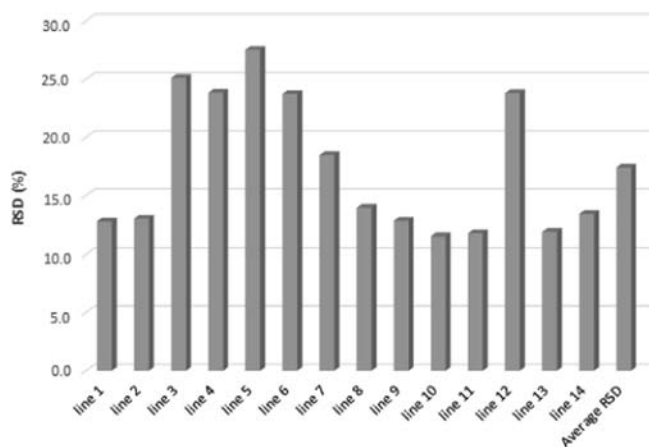


Fig. 2. RSD (%) of the monitored emission lines along 10 subsequent days.

This amount of pulses was established to ensure that information from all layers of samples was collected. This is justified since the polymers analyzed had a distinct pigmentation profile, some of which contained colors as a result of thin superficial pigmentation (see some examples in Fig. 3), while others showed pigmentation along all of their bulk. A third situation that was observed in some pieces was the presence of a transparent layer that seemed to have solely an esthetic function, such as providing shine to the polymer. Fig. 3 shows some examples of the craters observed in the samples with the characteristics mentioned above. The first panel (Fig. 3a)

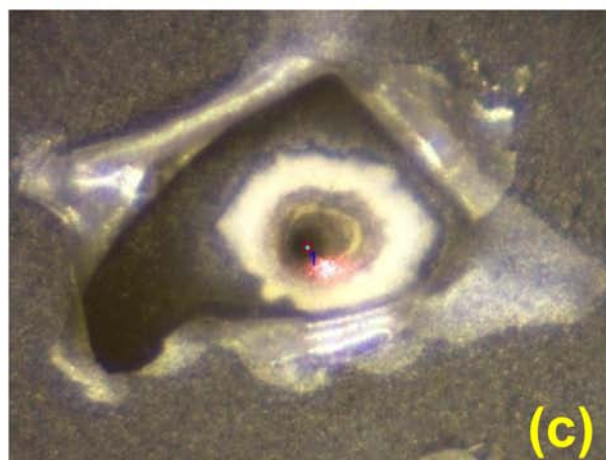
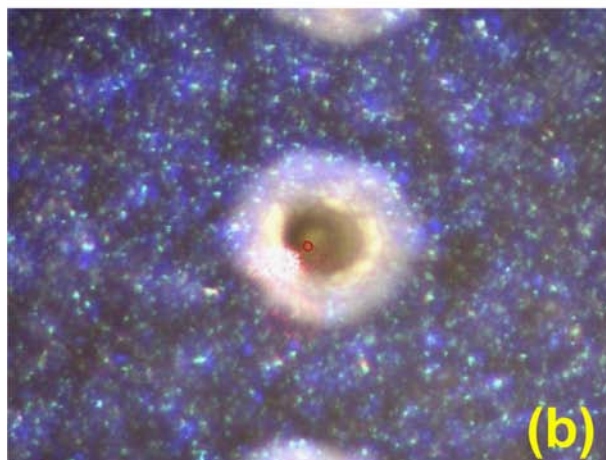
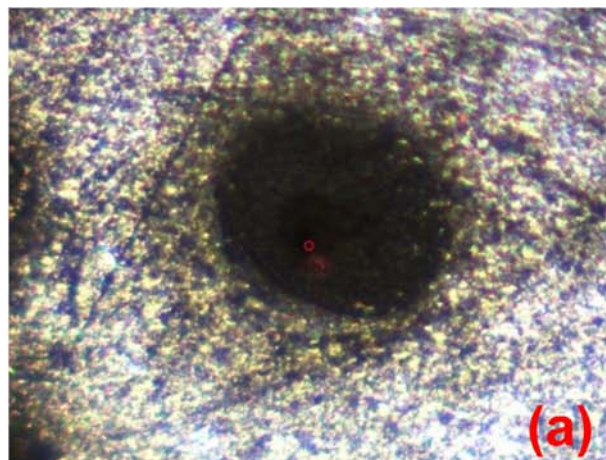


Fig. 3. Examples of the different surface characteristics of polymers in the mobile phones exposed after laser ablation during LIBS analysis: (a) shiny black sample, (b) blue sample, and (c) thin film. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is related to a shiny black sample that presented pigmentation along its bulk (see dark crater). The second panel (Fig. 3b) is a blue sample where the pigmentation was observed only on the surface (see white crater). The last sample (Fig. 3c) revealed the presence of a thin film on its surface. This film, however, was destroyed by the successive laser pulses and a primer polymer was exposed.

Fig. 4 presents a general depiction of the LIBS spectra information obtained for the white and black polymers of the mobile phones. These colors were selected because they are present in majority of the mobiles collected (see Table 1). A quick look at these spectra reveals that LIBS analysis can provide valuable information, at least for samples of the same color.

Both the white and black polymers typically presented Na emission lines (588.9 and 589.5 nm) in the final region of the spectra (from 500 to 1000 nm), inferring good similarity between the plastic nature of the two samples. Table 2 summarizes the

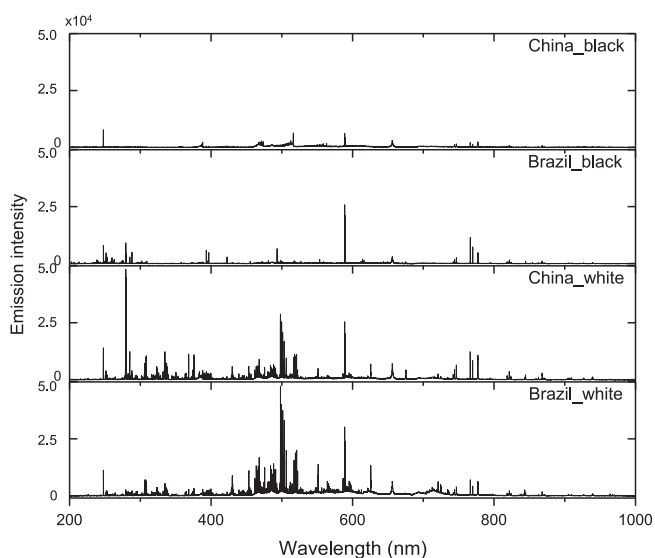


Fig. 4. Representative spectra for polymers from different mobile phones.

Table 2

More intense emission lines (I, atomic and II, ionic) associated with the observed elements in the analyzed polymers. Variable selection intervals A, B and C were used to build classification models for white and black polymers.

Chemical species	λ (nm)	Variable selection intervals
C ₂	469.75; 471.51; 473.70; 512.92; 516.52; 558.52; 563.54	C
C I	247.85	A, B and C
Zn I	213.85	–
Zn II	202.54; 206.42;	–
Si I	243.51; 250.69, 251.43; 251.61; 251.92; 251.42; 252.85; 288.15;	A, B and C
Fe I	361.87; 438.35	–
Fe II	238.20; 239.56; 240.48; 273.95; 274.64; 274.94; 275.57	–
Mg I	285.21	A and C
Mg II	279.55; 280.27;	A, B and C
Ba I	553.54	B and C
Ba II	455.40; 493.40; 614.17	B and C
Ca I	422.67; 518.88	A, B and C
Ca II	393.36; 396.84;	A, B and C
Ti I	498.17; 499.10; 499.95; 500.72; 501.41	A and B
Ag I	328.06; 338.28; 520.90; 546.55	B
Ag II	232.02; 233.14; 241.32; 243.78	–
CN	386.13; 387.08; 388;29	B, C
Ni I	341.47; 352.45;356.63; 361.93	–
Ni II	221.64; 227.02; 230.30; 239.45; 241.61	–
Na I	588.99; 585.59	A, B and C
H	656.28	A, B and C
N I	742.36; 744.23; 746.83; 821.63; 824,23	A, B and C
K I	766.49; 769.89	A, B and C
O I	777.19; 777.42; 777.54	A, B and C

emission lines observed in this study. No emission lines that were strictly associated with the pigments present in the samples were identified in this region. The Na and K lines can be attributed to the fact that these elements are present in the materials used in the production of polycarbonate ($[(C_{15}H_{16}O_2)_n]$) and ABS (*Acrylonitrile butadiene styrene*, $((C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z)$), the polymers most frequently employed in the manufacture of plastic housing for mobile phones and other electronic devices [31,32].

In contrast, the region from 200 to 500 nm presented remarkable differences among the polymers analyzed. For the black polymers of samples from China, a prevalence of C₂ emission lines was observed as a strong indication of the presence of carbon black (wavelengths: 469.75, 471.51, 473.70, 512.92, 516.52, 558.52 and 563.54 nm) [33,34], whereas a rich spectrum was observed for the Brazilian sample with emission lines from Zn (202.54, 206.42 and 213.85 nm), Si (250.69, 251.43, 251.61, 251.92, 252.41, 252.85, 263.12 and 288.15 nm), Fe (273.95, 274.64, 274.94 and 275.57 nm), Mg (279.55, 280.27 and 285.21 nm) and Ba (455.40, 493.40, 553.54, 614.17 and 854.2 nm). Additionally, CN and Ca lines were detected in both spectra. However, the CN emission lines were approximately 50% more intense in the Chinese sample than in the Brazilian sample, while the Ca emission lines were at least 400% more intense in the Brazilian sample.

In both spectra of the white polymers, emission lines were observed from Ca (393.36, 396.84, 422.67 and 518.88 nm), Mg (279.55, 280.27, 285.21, 383.2 and 383.8 nm), Si (250.69, 251.43, 251.61, 251.92, 252.41, 252.85, 263.12 and 288.15 nm) and Ti (the 5 most intense signals from over 50 observed were found at 498.17, 499.10, 499.95, 500.72 and 501.41 nm). Although the Brazilian sample spectrum is characterized by strong emission intensities for the Ti lines (a set of lines between 450 and 520 nm), the Chinese sample spectrum exhibited a significantly higher contribution from other lines within the UV region.

3.3. Analysis of the coated polymers

Some mobiles presented a rigid coating on their internal surface that appeared to be a ceramic material with beige and

golden colors. Emission lines (see Fig. 5) were strongly observed for Ag (the 5 most intense signals from over 25 observed were found at 243.78, 328.06, 338.28, 520.90 and 546.55 nm) in the beige coating, whereas Fe, Ni and Si emission lines were predominantly observed in the golden coating. According to literature, these metals are often deposited as thin layers over the surface of the polymeric pieces of electronic devices to act as a shield against electromagnetic interference that can compromise the equipment performance [35,36]. Common to both layers, but with different emission intensities, was the presence of C, CN, Ca, Na, H, N, K and O emission lines.

Encouraged by these distinct profiles, a Principal Components Analysis (PCA) was performed using the total profile of the spectral information collected for all the samples (matrix 21,480:12,288). In the experimental part, 143 sub-samples had 5 points and 30 pulses per point and 1 sub-sample had 1 point and 30 pulses (total of 21,480 spectra). The data set was normalized and mean-centered. The first four principal components were selected and analyzed. These four PCs accounted for 60% of the explained variance and a higher number of PCs did not improve

this value. The main characteristics that were observed were related to the presence of the coatings. By visualizing the score values for PC3 (11.8%) and PC4 (6.8%), a remarkable difference was observed between the coated and uncoated samples (see scores plot in Fig. 6a). Fig. 6b presents the loadings plot for PC3 in different emission lines, where the distinction between the samples is mainly a result of Si, Al, Ti, Na, K (characteristic of the uncoated samples, positive loading values), and Ag (related to the coated samples, negative loading values).

Concerning the Ag presence in the coated polymers (mainly in function of its economic value) a quantitative evaluation of its content in one sample randomly selected from the cluster of beige coated polymers was performed (Fig. 6a). For this, 0.250 g of small pieces of coated polymer were leached (in triplicate) according to the procedure described by Yamane et al. [37]. The Ag content in the solution resulting after the leaching process was determined by Flame Atomic Absorption Spectrometry (FAAS). The average content of Ag determined in this sample was 206 mg kg⁻¹. Although this value comes from a single sample, an aspect that cannot be overlooked is the fact that concentrations of this order probably can be easily detected by LIBS systems. As can be observed in Fig. 7, which presents the two most intense emission lines for Ag in the analyzed sample, the ratio of emission noise/intensity is approximately 1:170 at 520.90 nm and 1:188 at 546.55 nm. This situation illustrates how the LIBS technique can be a powerful tool for prospection of valuable metals and control in the recycle centers of e-waste. The polymers with other colors did not present remarkable characteristics in the emission spectra. For this reason, the experimental part was focused in the white and black polymers.

3.4. Chemometric analysis of black and white polymers of Brazilian and Chinese mobile phones

A second PCA was calculated for the white samples only (1500 spectra), and a selection of variables was performed (matrix 1500:1,104). This variable selection was necessary to improve the resolution of the clusters obtained from a first PCA where all variables (12,288 wavelengths) were considered. The criterion adopted for the variable selection was the highest (intensities absolute values higher than 0.03) for loadings of PC2 (principal component along the clusters were segregated).

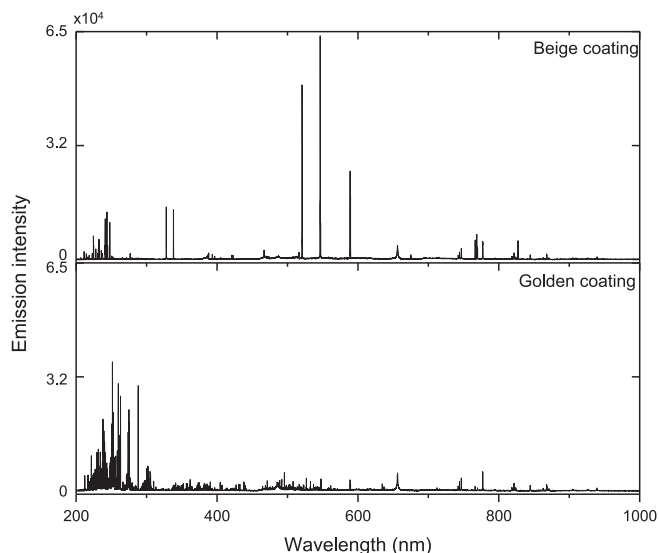


Fig. 5. Representative spectra for coated polymer samples located on the internal surfaces of the mobile phones.

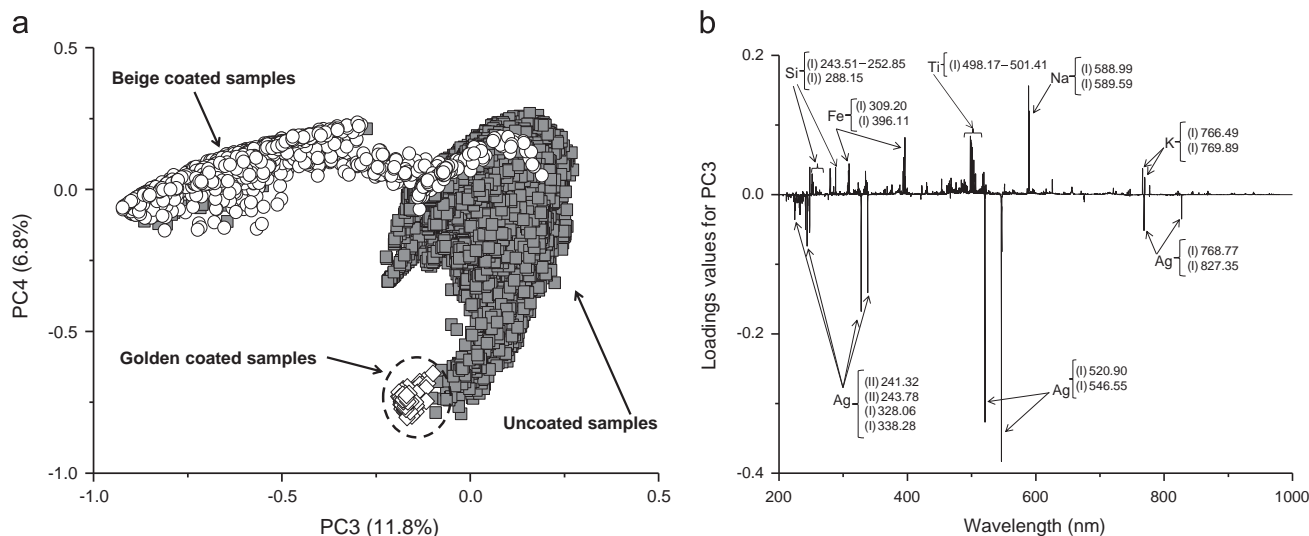


Fig. 6. Scores plot (a) and loadings plot (b) for the coated and uncoated polymers located on the internal surfaces of the mobile phones.

Fig. 8a and b presents the scores and loadings plots, respectively. In Fig. 8a, a clear separation among the mobiles from Brazil (mobiles named as 1 A, 2B, 31B, 43 F, and 48 G, see details in Table 1) and China (mobiles named as 29 L and 41 H, see details in Table 1) is observed. Additionally, the 6 different manufacturers appeared to be clustered. Mobiles 2B and 31B were from the same manufacturer but of different models. Mobile 1A was split into two categories: external (1 A_e) and internal (1 A_i). The white samples were mainly characterized by the presence of Ti, N, O, Mg, Na and K emission lines.

Concerning the presence of Na and K, these signals can be attributed to residual concentrations of potassium or sodium persulfate used as water-soluble initiator during thermoplastics (e.g., polycarbonate and ABS which are widely used in mobile phones) production by the emulsion polymerization technique [38]. Another possible source of residual Na in polymers found in mobile phones is NaOH used in the polycarbonate synthesis when the Bisphenol A ((CH₃)₂C(C₆H₄OH)₂) is treated with this base [39]. On the other hand, even the polymers had undergone some clean-up process to remove the residues of these substances, these elements can be originated from the additives used in the polymer formulation. In this sense, in the data set of this study it was possible to detect signals of Na and K also in the bulk of the sample (in this case after 20 pulses).

Regarding Ca, calcium carbonate (CaCO₃) is one of the most important sources of this element in polymers. The calcium compounds can be used as pigment, filler, reinforcement agent, stabilizer and as flame retardant [38–40]. The presence of Mg is strongly linked to Mg(OH)₂ which is an inorganic flame retardant widely used in plastics employed for electronic devices production [41]. The titanium dioxide (white pigment) surely is the main source of Ti detected in the analyzed samples [42].

It is also important to observe that scores for PC1 (43.6%) reflect the variation along the bulk of the samples. For most of the samples, the first 15 pulses are remarkably more heterogeneous (note that the symbols are less clustered) than the last 15 pulses (more clustered pulses). Due to this behavior exhibiting a tendency for all of the samples (except for sample 48 G), this is a factor that needs to be considered when classifying samples of diverse colors.

Regarding the pattern exhibited for sample 48 G, two hypotheses can be discussed. The first is that the sample exhibits a similar composition from the surface till its bulk. The second one is that the surface layer is much thinner in relation to the bulk (in this case thin pigmentation layer).

The evaluation of these hypotheses should consider the fact that the heterogeneity of the samples is observed mainly along PC1 (scores distributed from the values positive to negative values

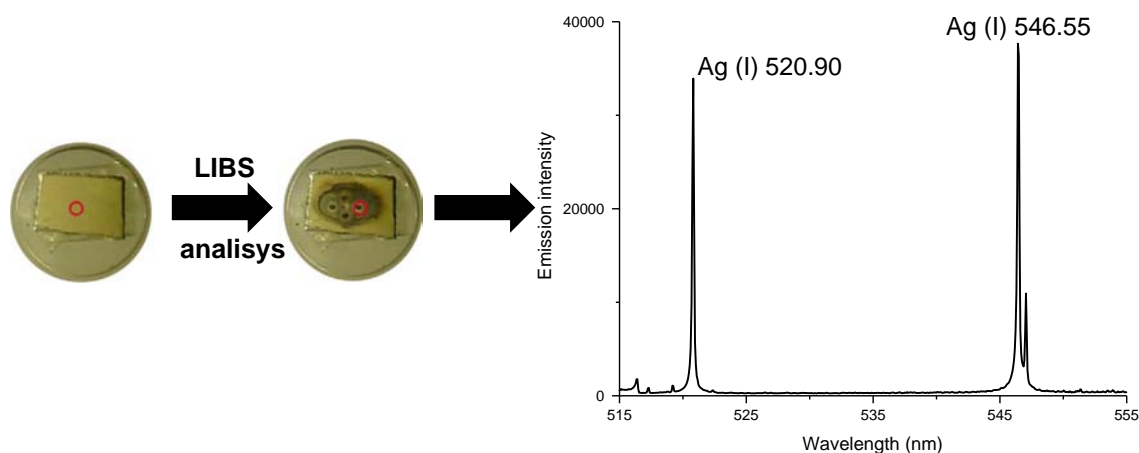


Fig. 7. Pictorial description of Ag analysis in the coated polymer samples.

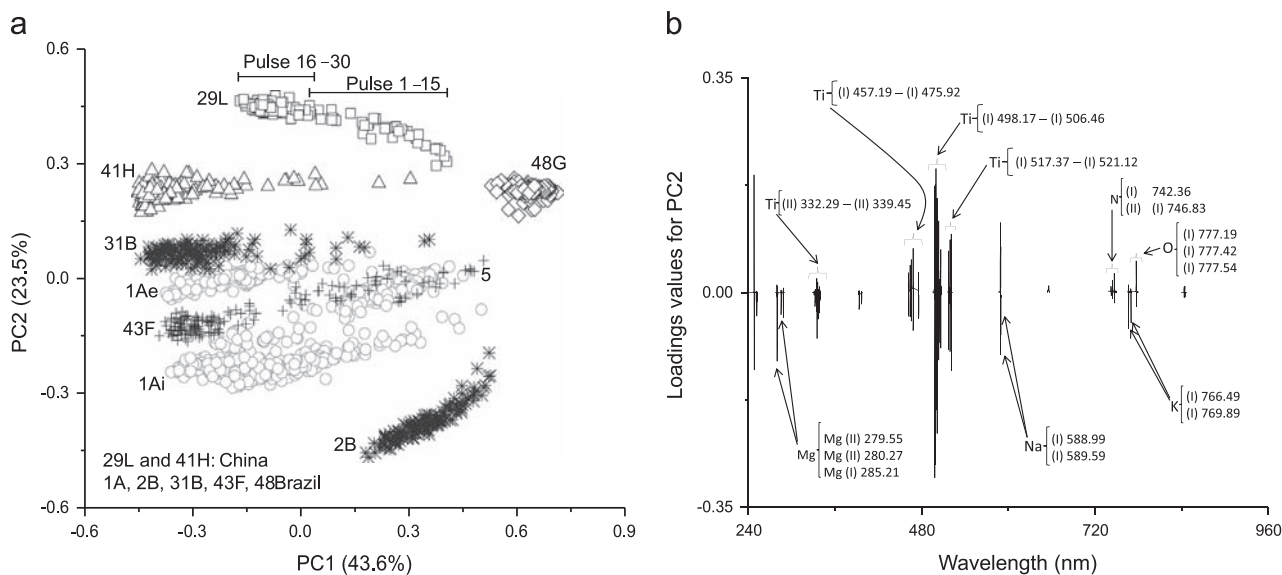


Fig. 8. Scores plot (a) and loadings plot (b) for the white polymers from the mobile phones from Brazil and China.

of PC1), and sample 48 G has scores only in the positive part of PC1. Thus, an observation in loadings plot of this PC1 (see Fig. 1S of supporting information) can lead to a better understanding of its behavior.

In this way, PC1 loadings plot shows that Ti has a great influence on the negative values of PC1, in opposition to this the Ca, Mg, H and C have positive values of PC1. Considering both aspects and the fact of high loadings not necessarily indicating a higher concentration of analyte, a suitable explanation of sample 48 G behavior is that its pigmentation layer is too thin in relation to the bulk. This justifies the short distribution along the PC1 axis.

One of the most appreciable advantages of LIBS is the ability to conduct analyses in small areas [13]. This advantage was exemplified in the graphical abstract of this manuscript where the sampled area was solely a number in the keyboard of a mobile phone. This characteristic does not limit the possibilities of applying this technique for other goals, such as determining the origin of a sample. In this study sample 41 H was correctly classified as originating from China using the white color of the numbers printed on its keyboard.

In this sense, the data from the white mobiles were used to build classification models to identify the manufacturer and the origin. Three chemometric techniques for classification were tested using Pirouette 4.5 software: KNN (K-nearest neighbor), SIMCA and PLS-DA (Partial Least Squares for Discriminant Analysis). The least technique was used with and without cross-validation. The data were also normalized and mean-centered. For the manufacturers, the percentage of correct predictions ranged from 80% (for PLS-DA) to 99% (for KNN). In the case of origin, the percentage of correct predictions ranged from 98% (for SIMCA) to 100% (for KNN). The KNN technique thus presented the best results with 1 neighbor for both models. Sample 1 A was correctly predicted even using spectral information from the external or internal polymers.

A third PCA was calculated based on loading selection criteria (highest absolute values) with the purpose of comparing the models generated from the white samples (variable selection named as A, see Table 2) against the models from the black (variables selection named as B – 2210:2367 and C – 2210:2192, see Table 2) polymer samples. Additionally, one more model was built for the black polymers of this data set, however, with the spectral ranges used in our previous communication (variable selection named as C, see Table 2) [15]. These additional models were built aiming to compare the percentage of correct classifications provided for each sample and the sensitivity of the obtained models. In the sensitivity evaluation, the ratio between the total of correct classifications provided for all classes divided by the total of the samples (correct and incorrect classifications) was considered [43].

As can be observed in Table 3, which summarizes the results obtained for each model, the KNN technique followed by SIMCA provided the best results for the prediction of the manufacturer and the origin of the samples analyzed in terms of the average of the percentage of correct classifications and sensitivity. On the other hand, the use or not of cross-validation did not cause significant differences in the performance of the models generated with PLS-DA. Therefore, this technique looks more suitable in situations where the object of analysis presents white polymers.

To check this scenario, the same variable selection (spectral ranges of LIBS spectra from black polymers) as was used in our previous work [15] (variable selection named as C, see Table 2) was applied to the black polymers of this new sample set (2210:2192). The resulting models showed the respective average correct classifications and sensitivity (in parentheses): KNN – 1 neighbor 92.8 (93.8); SIMCA 82.4 (71.3); PLS-DA without cross-validation 17.1 (29.5) and PLS-DA with cross-validation 16.0 (27.3) for the prediction of manufacturers and for the origin

Table 3

Average percentage of correct classifications and sensitivity for the models built from white and black polymers.

Technique	Manufacturers		Origin	
	% of correct classification	Sensitivity	% of correct classification	Sensitivity
White polymers models (variable selection A), Matrix=1500:1104				
KNN (1 neighbor)	99.5	99.2	100	100
SIMCA	95.9	95.1	98.0	98.5
PLS-DA without cross-validation	73.2	78.7	98.8	98.0
PLS-DA with cross-validation (leave-one-out)	72.8	78.4	98.8	98.0
Black polymers models (variables selection B), Matrix=2210:2367				
KNN (1 neighbor)	100	100	100	100
SIMCA	84.7	74.5	86.9	73.8
PLS-DA without cross-validation	15.0	25.2	33.5	81.3
PLS-DA with cross-validation (leave-one-out)	15.5	25.9	33.5	81.4
Black polymers models (variables selection C [15]), Matrix=2210:2192				
KNN (1 neighbor)	92.8	93.8	100	100
SIMCA	82.4	71.3	86.8	76.0
PLS-DA without cross-validation	17.1	29.5	32.1	82.6
PLS-DA with cross-validation (leave-one-out)	16.0	27.3	32.2	82.7

(in parentheses) the results were: KNN – 1 neighbor 100 (100); SIMCA 86.8 (76.0); PLS-DA without cross-validation 32.1 (82.6) and PLS-DA with cross-validation 32.2 (82.7). These numbers essentially reflect the same performance as of the previous models of black polymers.

Despite the lower performance exhibited by the PLS-DA models from the black polymers (mainly for manufacturers' classification), we highlight the improvement of LIBS application in the analysis of polymers from mobile phone scraps, since in practically all mobiles it is possible to find black or white pieces. Furthermore, it is more than reasonable to expect that this methodology can be used in the analysis of scraps from other e-waste, since the polycarbonate, ABS and their blends present in most of the mobile phones are also widely used for the manufacture of electronics.

4. Conclusions

In this study, a procedure combining LIBS and chemometric tools for the analysis of e-waste samples obtained from obsolete or broken mobile phones was described. A strategy for the recording and treatment of data was also presented in which the elements related to the different types of samples were highlighted. Additionally, the proposed classification models demonstrated good predictive ability (excepted for PLS-DA). The analytical method proposed herein extends the applicability of the LIBS technique and open possibilities for polymer manufacturers' identification.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.10.051>.

References

- [1] C.R. Oliveira, A.M. Bernardes, A.E. Gerbase, *Waste Manag.* 32 (2012) 1592–1610. <http://dx.doi.org/10.1016/j.wasman.2012.04.003>.
- [2] S. Sthiannopkao, M.H. Wong, *Sci. Total Environ.* 463–464 (2013) 1147–1153. <http://dx.doi.org/10.1016/j.scitotenv.2012.06.088>.
- [3] Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment, Brussels, 2003, pp. 19–23.
- [4] Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on Waste Electrical and Electronic Equipment (WEEE), Official Journal of the European Union Brussels, 2003, pp. 24–38.
- [5] A. Sepúlveda, M. Schluep, F.G. Renaud, M. Streicher, R. Kuehr, C. Hagelüken, et al., *Environ. Impact Assess. Rev.* 30 (2010) 28–41. <http://dx.doi.org/10.1016/j.eiar.2009.04.001>.
- [6] K. Hibbert, O.A. Oguseitan, J. Hazard. Mater. 278C (2014) 1–7. <http://dx.doi.org/10.1016/j.jhazmat.2014.05.089>.
- [7] I. Labunska, S. Hammad, M. Wang, D. Santillo, P. Johnston, *Environ. Sci. Technol.* 48 (2014) 5555–5564. <http://dx.doi.org/10.1021/es500241m>.
- [8] A.E. Gerbase, C.R. Oliveira, *Quim. Nova* 35 (2012) 1486–1492. <http://dx.doi.org/10.1590/S0100-40422012000700035>.
- [9] I. Dalrymple, N. Wright, R. Kellner, N. Bains, K. Geraghty, M. Goosey, et al., *Circuit World* 33 (2007) 52–58. <http://dx.doi.org/10.1108/03056120710750256>.
- [10] N. Lubick, *Environ. Sci. Technol.* 46 (2012) 3607–3608. <http://dx.doi.org/10.1021/es300731n>.
- [11] E.S. Beach, Z. Cui, P.T. Anastas, *Energy Environ. Sci.* 2 (2009) 1038. <http://dx.doi.org/10.1039/b904997p>.
- [12] F. Anabitarte, A. Cobo, J.M. Lopez-Higuera, *ISRN Spectrosc.* 2012 (2012) 1–12. <http://dx.doi.org/10.5402/2012/285240>.
- [13] D.W. Hahn, N. Omenetto, *Appl. Spectrosc.* 66 (2012) 347–419. <http://dx.doi.org/10.1366/11-06574>.
- [14] H. Xia, M.C.M. Bakker, *Talanta* 120 (2014) 239–247. <http://dx.doi.org/10.1016/j.talanta.2013.11.082>.
- [15] M. Ángel Aguirre, M. Hidalgo, A. Canals, J.A. Nóbrega, E.R. Pereira-Filho, *Talanta* 117 (2013) 419–424. <http://dx.doi.org/10.1016/j.talanta.2013.09.046>.
- [16] S. Barbier, S. Perrier, P. Freyermuth, D. Perrin, B. Gallard, N. Gilon, *Spectrochim. Acta Part B At. Spectrosc.* 88 (2013) 167–173. <http://dx.doi.org/10.1016/j.sab.2013.06.007>.
- [17] N. Huber, R. Viskup, T. Linsmeyer, H. Scherndl, J. Heitz, J.D. Pedarnig, *Proc. SPIE* (2010), <http://dx.doi.org/10.1117/12.855048> (77260G–1–77260G–8).
- [18] M.N. Siddiqui, M.A. Gondal, M.M. Nasr, *Bull. Environ. Contam. Toxicol.* 83 (2009) 141–145. <http://dx.doi.org/10.1007/s00128-009-9749-x>.
- [19] S. Grégoire, M. Boudinet, F. Pelascini, F. Surma, V. Detalle, Y. Holl, *Anal. Bioanal. Chem.* 400 (2011) 3331–3340. <http://dx.doi.org/10.1007/s00216-011-4898-2>.
- [20] S.-R. Lim, J.M. Schoenung, *J. Hazard. Mater.* 177 (2010) 251–259. <http://dx.doi.org/10.1016/j.jhazmat.2009.12.025>.
- [21] N.R. Lakshimsetty, *J. ChemTech Res.* 6 (2014) 1343–1353.
- [22] F. Geng, J. Hua, Z. Mu, L. Peng, X. Xu, R. Chen, et al., *Environ. Res.* 120 (2013) 27–32. <http://dx.doi.org/10.1016/j.envres.2012.08.007>.
- [23] W. Lin, W. Huang, T. Zhu, M. Hu, B. Brunekreef, Y. Zhang, et al., *Environ. Health Perspect.* 119 (2011) 1507–1512. <http://dx.doi.org/10.1289/ehp.1103461>.
- [24] R.K. Kaushal, A.K. Nema, *Waste Manag. Res.* 30 (2012) 1169–1177. <http://dx.doi.org/10.1177/0734242x12454697>.
- [25] S. Wold, K. Esbensen, P. Geladi, *Chemom. Intell. Lab. Syst.* 2 (1987) 37–52. [http://dx.doi.org/10.1016/0169-7439\(87\)80084-9](http://dx.doi.org/10.1016/0169-7439(87)80084-9).
- [26] P.M. Santos, E.R. Pereira-Filho, *Anal. Methods* 5 (2013) 3669. <http://dx.doi.org/10.1039/c3ay40561c>.
- [27] R.G. Brereton, *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*, John Wiley & Sons, Ltd., Chichester, United Kingdom, 2003.
- [28] J.H. Kalivas, in: S.D. Brown, R. Tauler, B. Walczak Ferré (Eds.), *Comprehensive Chemometrics Chemical and Biochemical Data Analysis*, vol. 3, Elsevier, Oxford, 2009.
- [29] M. Barker, W. Rayens, *J. Chemom.* 17 (2003) 166–173. <http://dx.doi.org/10.1002/cem.785>.
- [30] R.S. Harmon, R.E. Russo, R.R. Hark, *Spectrochim. Acta Part B At. Spectrosc.* 87 (2013) 11–26. <http://dx.doi.org/10.1016/j.sab.2013.05.017>.
- [31] K.J. Lee, Y.J. Lee, Y.R. Choi, J.S. Kim, Y.S. Kim, S.B. Heo, *Anal. Chim. Acta* 758 (2013) 19–27. <http://dx.doi.org/10.1016/j.aca.2012.10.047>.
- [32] E. Stenvall, S. Tostar, A. Boldizar, M.R.S. Foreman, K. Möller, *Waste Manag.* 33 (2013) 915–922. <http://dx.doi.org/10.1016/j.wasman.2012.12.022>.
- [33] M. Wang, *Carbon Black Science and Technology*, second ed., CRC Press, New York, 1993.
- [34] S.S. Harilal, R.C. Issac, C.V. Bindhu, V.P.N. Nampoori, C.P.G. Vallabhan, *J. Phys. D Appl. Phys.* 30 (1997) 1703–1709. <http://dx.doi.org/10.1088/0022-3727/30/12/003>.
- [35] S.M. Yang, Y.Y. Chang, Y.C. Hsieh, Y.J. Lee, *J. Appl. Polym. Sci.* 110 (2008) 1403–1410. <http://dx.doi.org/10.1002/app.28806>.
- [36] S. Geetha, K.K.S. Kumar, C.R.K. Rao, M. Vijayan, D.C. Trivedi, E.M.I. Shielding, *J. Appl. Polym. Sci.* 112 (2009) 2073–2086. <http://dx.doi.org/10.1002/app.29812>.
- [37] L.H. Yamane, V.T. de Moraes, D.C.R. Espinosa, J.A.S. Tenório, *Waste Manag.* 31 (2011) 2553–2558. <http://dx.doi.org/10.1016/j.wasman.2011.07.006>.
- [38] A. Kumar, R.K. Gupta, *Fundamentals of Polymer Engineering*, second ed., Marcel Dekker, New York, 2003.
- [39] R.O. Ebewele, *Polymer Science and Technology*, CRC Press, New York, 2000.
- [40] A.B. Morgan, J.W. Gilman, *Fire Mater.* 37 (2013) 259–279. <http://dx.doi.org/10.1002/fam.2128>.
- [41] S.V. Levchik, E.D. Weil, *J. Fire Sci.* 24 (2006) 137–161.
- [42] S.F. Taghinejad, M. Behrouzi, S. Asiaban, *J. Appl. Polym. Sci.* 124 (2011) 2016–2021. <http://dx.doi.org/10.1002/app>.
- [43] Pirouette Multivariate Data Analysis Software, n.d.