



Use of laser-induced breakdown spectroscopy for the determination of polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) concentrations in PC/ABS plastics from e-waste



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ABSTRACT

Due to the continual increase in waste generated from electronic devices, the management of plastics, which represents between 10 and 30% by weight of waste electrical and electronic equipment (WEEE or e-waste), becomes indispensable in terms of environmental and economic impacts. Considering the importance of acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and their blends in the electronics and other industries, this study presents a new application of laser-induced breakdown spectroscopy (LIBS) for the fast and direct determination of PC and ABS concentrations in blends of these plastics obtained from samples of e-waste. From the LIBS spectra acquired for the PC/ABS blend, multivariate calibration models were built using partial least squares (PLS) regression. In general, it was possible to infer that the relative errors between the theoretical or reference and predicted values for the spiked samples were lower than 10%.

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1. Introduction

The worldwide demand for technical plastics and the consequent accumulation of these residues from end-of-life products are constantly increasing. In 2013, the global production of plastic was approximately 300 million tons, showing an increase of 4% from 2012 (Anuar Sharuddin et al., 2016). The same behavior is exhibited by waste from electrical and electronic equipment (WEEE or e-waste) (Vazquez and Barbosa, 2016), which is growing exponentially and contains large amounts of plastic materials (Aquino et al., 2016).

The technical plastic fraction of WEEE is composed by more than 15 different polymers. However, acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), and their blends are among the most important plastics used by the electronics industry (Buekens and Yang, 2014; Tarantili et al., 2010; Taurino et al., 2010), due to its good characteristics, which can be improved through the mixture of them. In PC/ABS blends, desirable features, such as the toughness and heat distortion temperature, are enhanced from PC, while ABS leads to better processability and

cost reduction. For these reasons, PC/ABS blends are widely used in important industries, such as the electronics and automotive (Buekens and Yang, 2014; Kuram et al., 2016).

Regarding the management of plastic residue, which often contains hazardous flame retardants (Aquino et al., 2016; Shao et al., 2016), the option to dispose these materials in landfills has become increasingly undesirable, due to the low sustainability, high cost, and decreasing available space (Ignatyev et al., 2014; Vazquez and Barbosa, 2016). In this context, the recycling of PC, ABS, and their blends has been a target of research and practical action in the last years (Balart et al., 2005; Barthes et al., 2012; Farzadfar et al., 2014; Hopewell et al., 2009; Jing-ying et al., 2012; Kuram et al., 2016; Liu and Bertilsson, 1999; Tarantili et al., 2010).

Concerning the analytical aspects, it is evident that precise knowledge of the amount of PC and ABS in their blends is very important, from the early steps of recycling (identification/classification) to the analysis of the obtained product. In addition, precise, simple, and fast analytical methods are required in quality control laboratories in industry and research or academic centers.

Several strategies have been employed to determine the composition of polymer blends of PC/ABS. The presence of both polymers in the blends can be confirmed using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), as

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two glass transition temperatures (T_g) are readily observed at 85–105 °C (ABS) and 150–155 °C (PC) (Adams et al., 1993; Babbar and Mathur, 1994). Mechanical analyses, such as impact and tensile tests, are also widely used (Krache and Debah, 2011; Kuczynski et al., 1994). However, these techniques are time consuming, require unusual sample preparation for an analytical chemistry laboratory, conditioning protocols prior to measurement, and present low analytical frequency. Near-infrared (NIR) has also been used to evaluate the proportion of PC and ABS in blends (Scaffaro et al., 2012); however, it is not suitable for the analysis of black plastic samples (Beigbeder et al., 2013; Maris et al., 2012; Masoumi et al., 2012; Roh and Oh, 2016). In this regard, laser-induced breakdown spectroscopy (LIBS) is an analytical technique that presents great potential for this application, due to the following advantages: high analytical frequency, portability, no or minimal sample preparation, and the possibility of hyphenation (Galbács, 2015; El Haddad et al., 2014).

LIBS is a multi-elemental technique in which a laser beam excites and intensively heats a small volume of the sample. The heated sample is converted to a gaseous plasma state and broken down into atoms, which produces a characteristic radiation of light. This light is analyzed spectrally, and through calibration, the intensity of the spectra indicates the concentration of the elements in the sample (Musazzi and Perini, 2014). However, some challenges are still present, such as the low availability of matrix-matched standards for quantitative analyses and pulse-to-pulse signal fluctuations that can lead to relative standard deviation (RSD) values higher than 10% (Aquino et al., 2016; Aquino and Pereira-Filho, 2015; Galbács, 2015).

Despite this, since 1998, a relative high number of publications have been presented methods for plastic identification using LIBS, particularly combining the use of different chemometric tools. Banaee and Tavassoli (2012), for instance, used a chemometric method based on discriminant function analysis (DFA) to identify polymers with slight differences among their spectra. Sattmann et al. (1998) used Artificial neural networks (ANNs) combined with LIBS with success to identify polymers. Lasheras et al. (2010) used with success the methods of normalized coordinates (MNC) and linear and rank correlation to identify polymers with very similar chemical compositions. Other chemometric tools such as soft independent modeling of class analogy (SIMCA), k-nearest neighbor (KNN) and partial least squares for discriminant analysis (PLS-DA) have been widely used in the identification and classification of polymers (Aquino et al., 2016; Aquino and Pereira-Filho, 2015; Costa et al., 2017). Determining the ratios of different emission lines and molecular bands associated with the use of principal component analysis (PCA), was a strategy found in the literature for identification and classification of polymers (Grégoire et al., 2011; Unnikrishnan et al., 2013; Xia and Bakker, 2014).

However, these above mentioned chemometric tools are limited to classification models proposition for the identification of samples according to their similarity. Thus, its application for quantitative analysis of PC and ABS in blends associated to chemometric tools is not reported in the literature. In this sense, partial least-squares (PLS) technique is often used for the analysis in multivariate calibration methods aiming quantitative analysis of various analytes (Mota et al., 2015; Viegas et al., 2016). PLS multivariate calibration is strongly used in combination with near-infrared (NIR) spectroscopy. Sulub and DeRudder (2013), for example, determining the concentration of polycarbonate and rubber in blends of these materials using PLS models NIR. Thus, the present study shows and discuss a new application of laser-induced breakdown spectroscopy (LIBS) using PLS for fast and direct determination of the amount of PC and ABS in blends of these materials obtained from samples of e-waste.

2. Materials and methods

2.1. Laser-induced breakdown spectroscopy (LIBS)

LIBS spectra were obtained using a J200 LIBS system (Applied Spectra, Fremont, CA, USA) controlled by the Axiom 2.5 software (Applied Spectra). This instrument consists of a 1064 nm Nd:YAG laser and a 6-channel charge-coupled device (CCD) spectrometer recording spectra information from 186 to 1042 nm. Channel 1 goes from 186 to 309 nm, channel 2 from 309 to 460 nm, channel 3 from 460 to 588 nm, channel 4 from 588 to 692 nm, channel 5 from 692 to 884 nm and channel 6 from 884 to 1042 nm. The spectral resolution is <0.1 nm from UV to VIS and <0.12 nm from VIS to NIR. The Axiom 2.5 software from the same manufacturer controlled the operational parameters of the equipment. These parameters were the laser pulse energy, which ranging from 0 to 100 mJ, the gate delay - the time interval between the incidence of the laser pulse and the start of signal recording by the spectrometer - ranging from 0 to 2 μ s, and the spot size, ranging from 50 to 250 μ m. The Axiom 2.5 software also manages the movement of the sample, assisted by an automated XYZ stage and a 1280 \times 1024 complementary metal-oxide semiconductor (CMOS) color camera imaging system. The software at 1.05 ms establishes the gate width, which is the time interval that the spectrometer registers the emission signals.

2.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed on a Netzsch F3 200 Maia DSC (Netzsch-Gerätebau GmbH, Selb, Germany) instrument under nitrogen purge. Scanning analysis was carried out from 20 °C to 200 °C with heating and cooling rates of 20 °C·min⁻¹. The glass transition temperature (T_g) was determined during the second heating by the inflection method.

2.3. Blend and sample preparation

The multivariate calibration model was built using a set of 11 mixtures of PC/ABS in the following proportions: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100 (w/w%). These mixtures were prepared according to the following procedure:

- i) Individual dissolution of PC (polycarbonate Lexan 101, Sabic Company, Campinas, Brazil), ABS granule resin (Cyclocac EX 58 Sabic Company, Campinas, Brazil), and sample pieces in dichloromethane (p.a. ACS reagent, Sigma-Aldrich, St. Louis, MO, USA) until obtaining a 10% w/v solution.
- ii) Attainment of polymer/sample chips after dichloromethane evaporation, and spreading the solution on a glass plate under air flux at room temperature (25 °C).
- iii) Attainment of polymer/sample powder through grinding the chips in an analytical mill at 28,000 rpm, and subsequent sifting of the gross powder through a stainless-steel mesh sieve (0.5 mm).
- iv) All mixtures or sample pellets were prepared using 0.5 g of the respective powder material. This mass was added in an aluminum mold and heated in a thermopress at 200 °C for 10 min with a pressure of 0.4 metric tons. Additional details of this procedure are available in a previous publication (Aquino et al., 2016).

To evaluate the multivariate calibration model, 6 plastic samples containing only ABS (black and white pieces) obtained from scraps of a telephone, keyboards computer, two computer casings

and monitor were spiked with several amounts of PC. The amount of the spikes was calculated in order to distribute the samples along the lower, middle and highest intervals of the calibration range. After the sample spiking procedure, the 6 samples provided 11 different PC/ABS mixtures, which were prepared using the same procedure previously described. The choice to use a black piece was made in order to evaluate the behavior of the method for an unprepared sample, as black pigments (carbon black) are often troublesome in near-infrared (NIR) spectroscopy analysis (Beigbeder et al., 2013; Maris et al., 2012; Masoumi et al., 2012; Roh and Oh, 2016).

Additionally, 33 samples (from sample 7 to sample 39) with unknown PC and ABS concentrations were analyzed. These samples were directly subjected to LIBS analysis without the need for preparation. Moreover, polypropylene (PP, sample 37), polyethylene (PE, sample 38) and polystyrene (PS, sample 39) samples were analyzed in order to verify the robustness and specificity of PLS models for PC and ABS detection. The results were also compared through visual inspection of the thermogram obtained by DSC analysis. In addition, the analysis becomes much faster, since the sample need not be prepared.

2.4. Data collection and analyses

The conditions used for LIBS analyses in this study have been previously described by Aquino et al. (2016). Before each data collection the analyzed area was cleaned with laser pulses with 10 mJ laser pulse energy, and 200 μm spot size (Fluence around 32 mJ/cm^2). In each sample was performed a data collection in scan mode with the following laser operation setup: 10 Hz repetition rate, 75 mJ laser pulse energy, 0.5 μs delay time, 1.05 ms gate width, and 75 μm spot size (Fluence around 1700 mJ/cm^2). For each sample, approximately 600 spectra (in both sides of the samples) were obtained at different parts of the samples. The spectra were obtained in 6 lines, and in each one approximately 100 laser pulses were obtained. The following additional laser settings were used: a scan length of 18 mm, and a speed of 1.0 mm/s. The emission lines of the elements of interest were identified using the Aurora software (Applied Spectra).

After spectra acquisition, the workflow was as follows:

- i) Organization of data matrices (Microsoft Excel).
- ii) Preliminary data inspection performed using the Matlab software version 2009a (The Mathworks, Natick, MA) and a homemade routine “libs_treat” (Castro and Pereira-Filho, 2016); libs_treat was applied to detect eventual outlier spectra. In this case, for each sample (rows in the data matrix), the standard deviation, area, maximum and Euclidean norm were calculated. If an outlier was detected (e.g., standard deviation equal to 0), this spectrum was removed by the analyst, and then 12 normalization modes were automatically executed. This process was required because LIBS spectra are sensitive to several potential problems, including variations in the sample surface, the stability of the laser and the interaction between the laser and the sample.
- iii) Multivariate calibration model using Pirouette software version 4.5 (Infometrix, Bothell, WA). The calibration model was obtained by partial least squares (PLS) regression of the normalized sample data set. In the application of PLS, the data set was subdivided into 11 samples for calibration (the 11 mixtures PC/ABS) and 44 for validation: 11 mixtures that were prepared using the same procedure described for calibration data set and 33 samples without preparation. In this step the whole peak profile (12,288 variables) was initially used. The efficiency of the 12 normalization modes was assessed comparing the values of standard error of cal-

ibration (SEC) for the proposed models. The best results were those that presented the lowest SEC. Fig. 1 shows a pictorial description of steps for construction of the calibration models.

3. Results and discussion

3.1. General characteristics of LIBS spectra obtained for PC/ABS blends in different proportions

Fig. 2 shows LIBS spectra for different materials used in the multivariate calibration. Fig. 2a and b correspond to the PC/ABS (100/0 w/w%) and PC/ABS (0/100 w/w%) blends, respectively. Fig. 2c was obtained from sample 1, black telephone scrap that was 100% ABS (labeled identification), and was spiked with PC to provide a final mixture of PC/ABS of 50/50 w/w% (mixture 2), while Fig. 2d was acquired from sample 7, computer keyboard, and was analyzed as obtained (not prepared, nor spiked).

The four spectra in Fig. 2 represent samples at the extremes and around the center of the calibration range, and the main emission signals, indicated in Fig. 2 and listed in Table 1, are associated with the same elements, with the exception of Mg.

This indicates that the simple selection of a line or line ratios to generate a univariate calibration will hardly provide a satisfactory prediction of the PC and ABS content of the blend. Based on this, a multivariate calibration using PLS regression was performed. In PLS regression, all relevant variables are considered. This allows the identification of factors (linear combinations of the independent variables \mathbf{X}) that better fit one or more dependent variables \mathbf{Y} (response variables) (Geladi and Kowalski, 1986; Sjöström et al., 1983).

Using the PLS regression vectors, the evaluation of the most important emission lines, listed in Table 1, was possible for the development of the multivariate calibration model. In addition, the peak profiles for the most important emission lines (high regression vectors) are shown in Fig. 3a–i. Carbon emission lines (Fig. 3a and b) presented high regression vectors as expected. The molecular band of C2 (Fig. 3c) is important in differentiation between the polymers aromatic rings in PC and ABS. This differentiation is possible because PC has a more intense signal in relation to ABS and several studies have using this property to separate polymers (Anzano et al., 2008; Costa et al., 2017; Grégoirie et al., 2011). Emission lines related to CN (Fig. 3d), N (Fig. 3e), and O (Fig. 3f) presented also high regression vectors.

Calcium (Fig. 3g), present in the spectra, is commonly added to polymers in the form of calcium carbonate (CaCO_3). Calcium compounds can be used as pigments, fillers, reinforcement agents, stabilizers and flame retardants (Aquino and Pereira-Filho, 2015; Buekens and Yang, 2014; Kumar and Gupta, 2003). The Na signal (Fig. 3h) can be attributed to residual concentrations of sodium persulfate used as a water-soluble initiator during thermoplastic production (e.g., PC and ABS, which are widely used in electronic devices) by the emulsion polymerization technique (Kumar and Gupta, 2003). Na in the polymers can be also explained because NaOH is used in polycarbonate synthesis, as bisphenol A ($(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$) is treated with this base (Ebewele, 2000). The last emission line (Fig. 3i) is related to H 656.28 nm.

Additionally, emission lines were observed for Sb and Ti, which are very common in PC and ABS plastics (Aquino et al., 2016). The presence of Sb is strongly linked to antimony trioxide (Sb_2O_3), which is an inorganic flame retardant widely used in plastics employed in electronic devices (Buekens and Yang, 2014). The Ti lines are related to the white pigment, and surely, the main source is from the addition of titanium dioxide (TiO_2) (Kumar and Gupta, 2003).

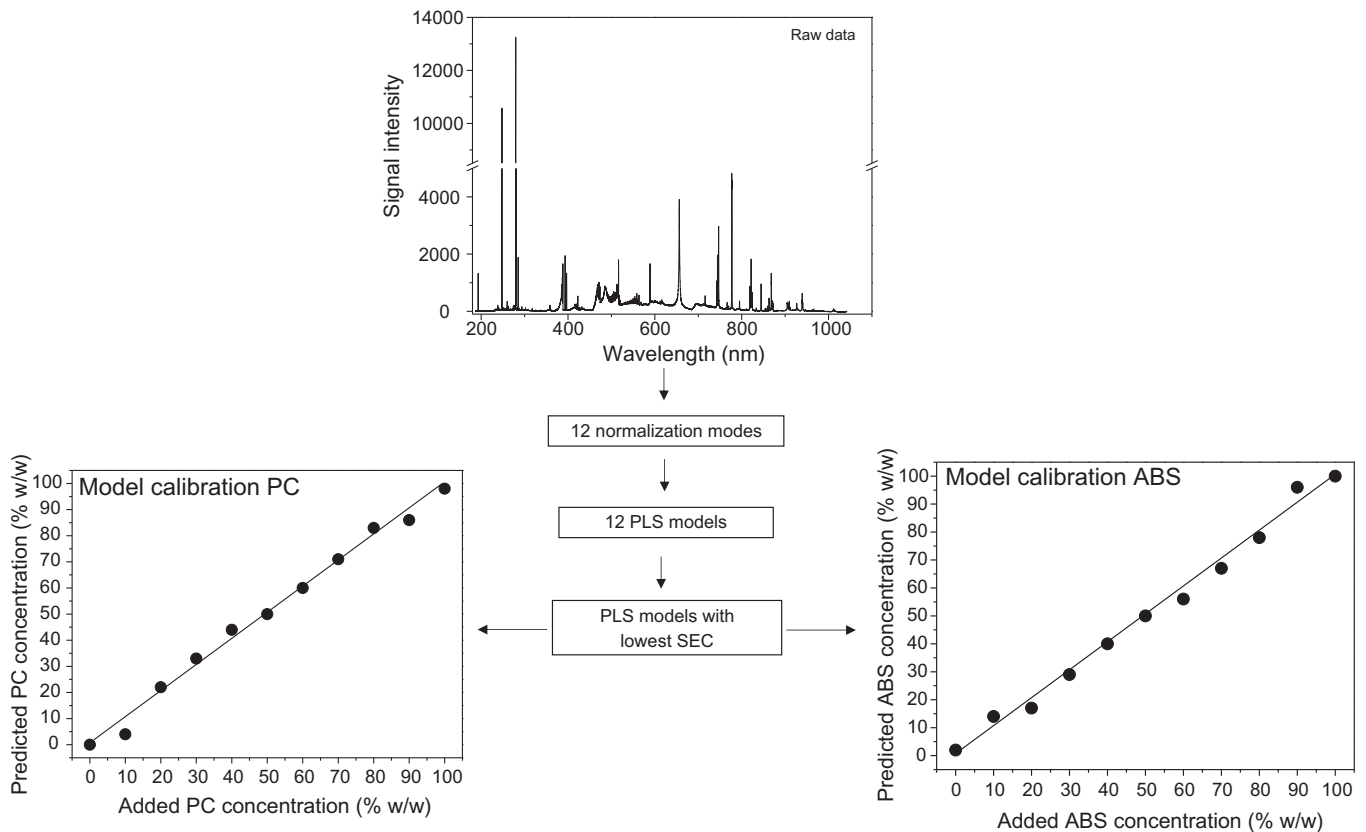


Fig. 1. Pictorial description of steps for signal normalization selection and construction of the calibration models.

The stability of the blend signals was confirmed over thirty days. The first analysis was performed on the day of mixtures production, the second was carried out after 15 days, and the third on the thirtieth day. The RSDs for the signals over the full spectrum varied from 8 to 19%. All analyses were performed in triplicate, and the number of laser pulses per mixture in each analysis was 600. The signal to background ration (SBR) and signal to noise ratio (SNR) for C I 193.09 emission line was 116 and 101, respectively.

3.2. PLS models for the prediction of PC and ABS in plastics produced from their blends

The spectral profile obtained by LIBS presents high complexity due to the abundance of emission lines for several elements, in addition, presents problems of repeatability of signals. In LIBS analysis, these reported limitations are usually caused by the complexity of the interaction between the laser and the sample (particularly with physically or chemically heterogeneous samples). Fluctuations in laser-plasma interactions includes the rate of ablation and plasma characteristics, or differences in instrumental settings (i.e., laser pulse energy, integration gate time, focal length and detector settings), as well as differences in the number of accumulated pulses (Tognoni and Cristoforetti, 2016). To overcome the signal fluctuations and sample matrix variations, were employed 12 normalization modes of signal after obtained around 600 spectra for each sample: signal average (Norm_1), signal normalized by individual norm and then averaged (Norm_2), normalized by area (Norm_3) and by maximum (Norm_4) and then averaged, signal sum (Norm_5), signal sum after normalization by individual norm (Norm_6), area (Norm_7) and maximum (Norm_8) and signal average (Norm_9 and Norm_11) and sum (Norm_10 and Norm_12) after normalization by C signals

(I 193.09 and I 247.85 nm). Additional details about normalization modes are available in publication of Castro and Pereira-Filho (2016). The lowest SEC was the criteria to select the best normalization to obtain the calibration models. SEC values were calculated according to Eq. (1):

$$SEC = \sqrt{\frac{(y_i - \hat{y}_i)^2}{n - 1}} \quad (1)$$

where y_i is the reference concentration PC and ABS and \hat{y}_i is the predicted concentration for dataset calibration and n is the number of samples.

In this step, the 11 PC/ABS blends were used: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100 w/w%. Initial models were calculated using the entire spectral range (186–1042 nm). Later, other models were calculated excluding the range from 278.01 to 281.78 nm in order to disregard the most intense Mg emission lines (see Fig. 2). This change in relation to the first model was performed to take into account that Mg is not present in PC or ABS molecules. Mg in the form of compounds, such as magnesium hydroxide and hydromagnesite, is used as a flame retardant, and its concentration in the samples can change according to the polymer application (Hornsby, 2001; Laoutid et al., 2009; Morgan and Gilman, 2013; Visakh and A Rao, 2015). Thus, keeping the interval of the LIBS spectra where the Mg lines are the most intense in the model can reduce its accuracy. Fig. 4 shows the comparison among the 12 normalization modes, and the best result (lowest SEC) was obtained with signal normalized by individual area and sum over n pulses (Norm_7). A horizontal red line was inserted in this figure in order to compare the results. As can be observed, the SEC value for PC or ABS was around 3% and using only the signal average (Norm_1) the SEC value was 2-fold higher.

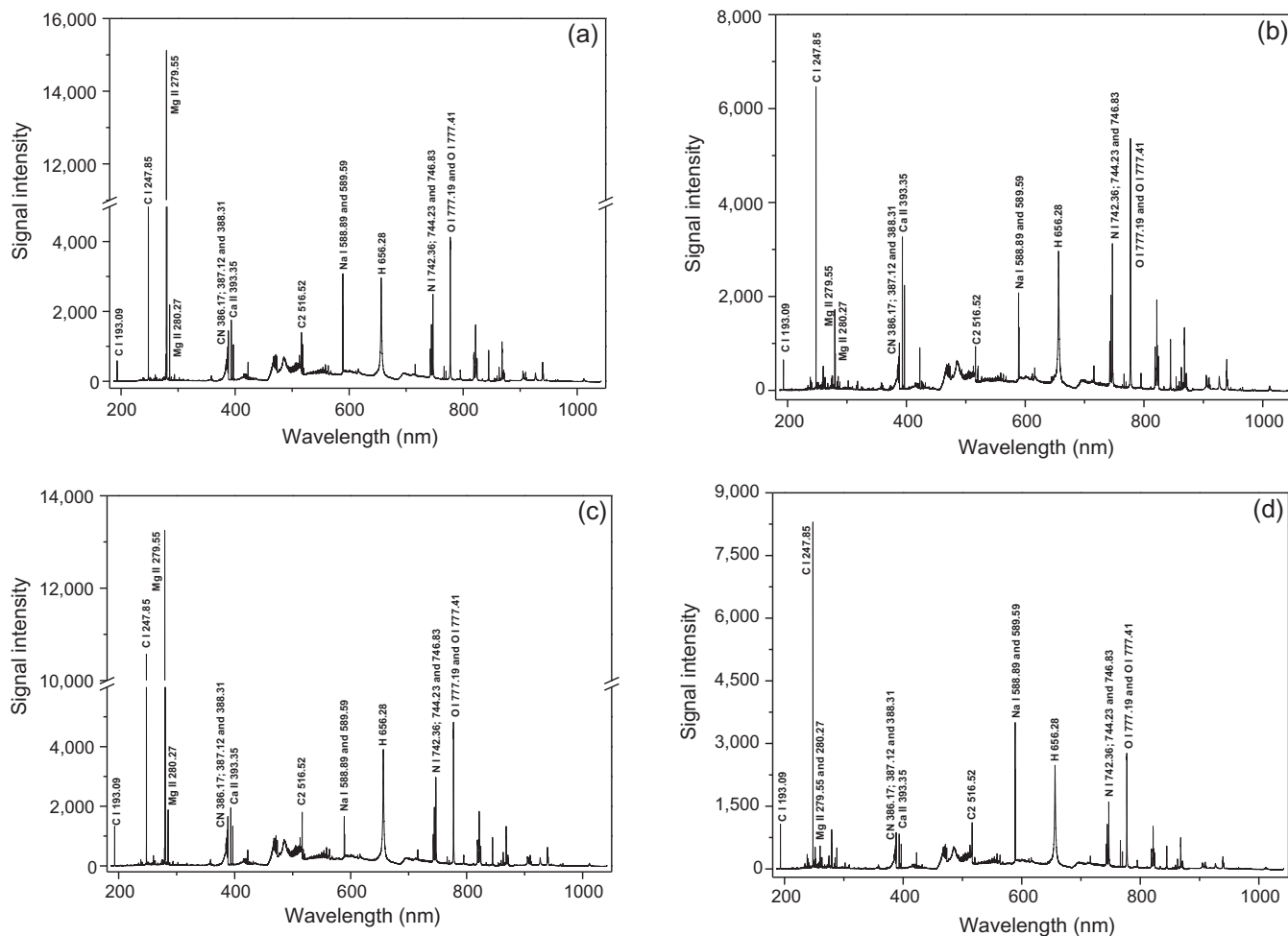


Fig. 2. LIBS emission spectra for the 100% w/w PC (a), 100% w/w ABS (b), sample 1 spiked to provide a PC/ABS 50/50 w/w mixture (c), and sample 7 without spiking (d).

Table 1

More intense emission lines (I, atomic and II, ionic) associated with the observed elements in the spectra shown in Fig. 2.

Chemical species	λ (nm)
^a C ₂	469.74; 471.50; 473.70; ^a 516.52; 558.54 and 563.55
^a C I	^a 193.09 and ^a 247.85
Sb II	259.08
Sb I	252.85
Ca I	422.67
^a Ca II	^a 393.35 and ^a 396.82
Ti I	498.17; 499.10; 499.95; 500.72; 501.41; 517.37; 519.29 and 521.03
^a CN	^a 386.17; ^a 387.12 and ^a 388.31
^a Na I	588.99 and 589.59
H	656.28
^a N I	742.36; 744.22 and 746.83
K I	766.48; 769.89
^a O I	^a 777.19; ^a 777.41 and 777.53

^a Emission lines that presented high regression values.

Table 2 shows the correlations obtained between the predicted and expected values for PC (0.996) and ABS (0.996) and the figures of merit for the calculated PLS models. Standard error of calibration (SEC) and cross-validation (SECV) were 3.4–5.6%, respectively, and in both models 2 latent variables (LV) were used with almost 70% of explained variance.

To verify the applicability of the results obtained with the PLS models, a reference method, DSC, was used to verify the presence of PC and ABS in the constructed mixtures blends. DSC is a robust analysis widely employed to identify polymer matrices and also quantitative estimation of polymer blends (Ehrenstein et al., 2004) in especially PC/ABS blends (Greco et al., 1994; Santana et al., 1998).

The DSC thermograms for all mixtures blends in the calibration model presented in Fig. 5 show two glass transitions. The only exceptions are Fig. 5a (PC/ABS = 100/0) and Fig. 5k (PC/ABS = 0/100), which present only one glass transition. The glass transition temperatures were estimated as the half-step temperature related to the change in heat capacity. The higher glass transition temperature of 145 °C (T_{g1}) is attributed to first blend component, polycarbonate (PC), and the lower glass transition temperature of 110 °C (T_{g2}) is attributed to the second blend component, acrylonitrile-butadiene-styrene (ABS). It is observed that the profiles obtained from the thermograms are concordant with the results presented in Table 2.

3.3. Application

To validate the PLS models, the 11 mixtures obtained from samples 1 to 6, listed in Table 3, were analyzed. For a better interpretation of these data, the relative error between the concentrations predicted by the combination of LIBS and the PLS model was calculated and added according to Eq. (2):

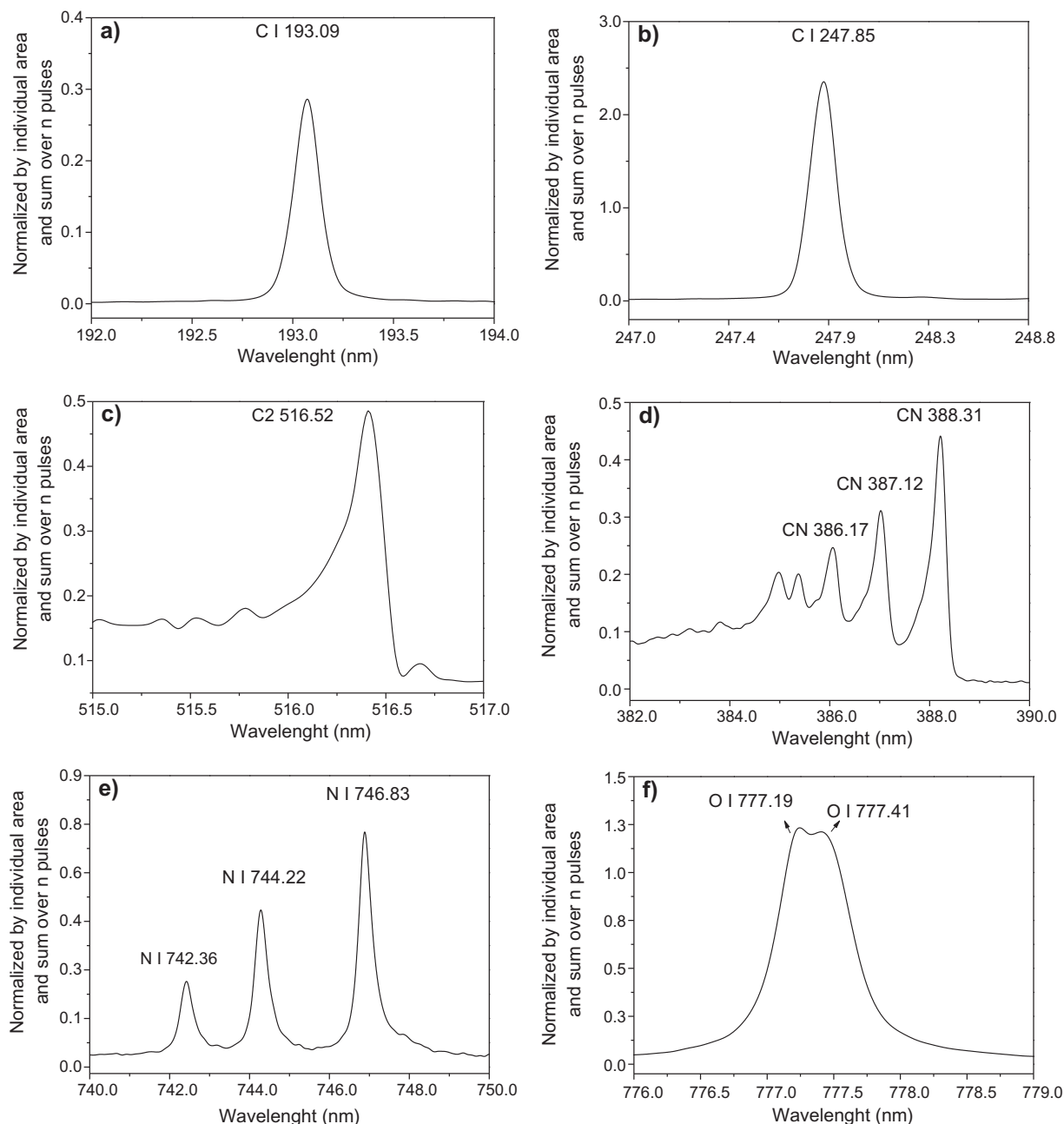


Fig. 3. Signal profiles of the most important emission lines selected by PLS regression vectors: C I 193.09 (a); C I 247.85 (b); C2 516.52 (c); CN 386.17, 387.12 and 388.21 (d); N I 742.36, 744.22 and 746.83 (e); O I 777.19 and 777.41 (f); Ca II 393.35 and 396.82 (g); Na I 588.99 and 589.59 (h); and H 656.28 (i).

$$\text{Relative error\% (LIBS, Added)} = \frac{\text{LIBS}_{\text{Predicted}} - \text{Added}_{\text{value}}}{\text{Added}_{\text{value}}} \times 100 \quad (2)$$

The results are presented in Table 3, where negative numbers represent that the polymer content predicted by the PLS model is lower than the theoretical (reference) value added to the sample. In general, it is possible to infer that the differences between the theoretical and predicted values are on average lower than 10%, except for mixtures originating from samples 1 and 4. A possible explanation for this difference is that this material (samples 1 and 4) may not be 100% ABS, mainly because this is a recycled plastic. Despite it being labeled pure ABS, it is relatively common that recycled plastics present residual amounts of other plastics. Since the morphology of ABS is based on a con-

tinuous phase of styrene-acrylonitrile copolymer (SAN) and a microdispersed elastomeric phase of polybutadiene, thermooxidative degradation can significantly affect the chemical nature of these phases in the recycling processes (Karahaliou and Tarantili, 2009).

In addition, regarding samples 1 and 4, at least theoretically, another factor that can contribute to the difference between the predicted and obtained results is a variation in the proportions of the monomers that compose ABS, making them different than those of the ABS used in the construction of the PLS models.

A point that needs to be highlighted is that the standard deviations were consistently lower than 5% and the Relative Standard Deviation (RSD) values are lower than 10% in all cases ($n = 3$). This is very good behavior, since the LIBS technique usually presents standard

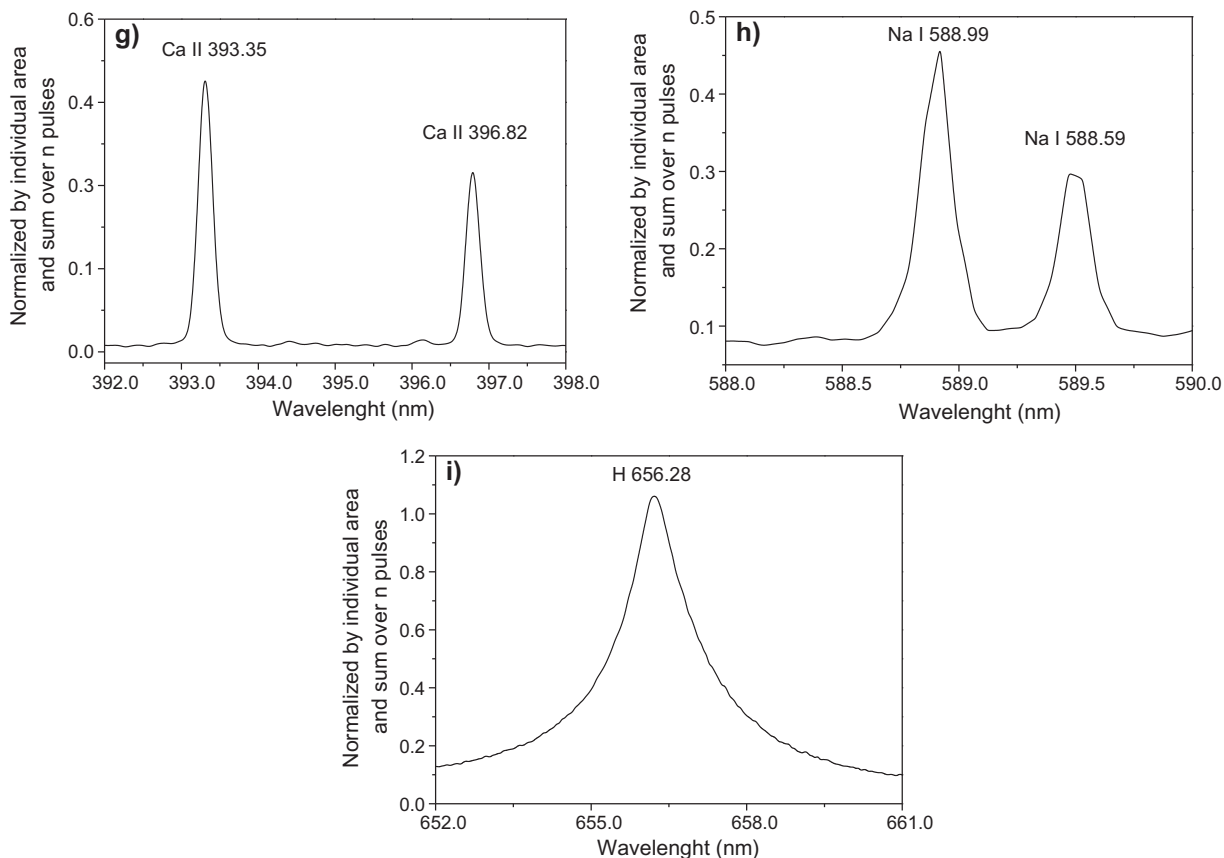


Fig. 3 (continued)

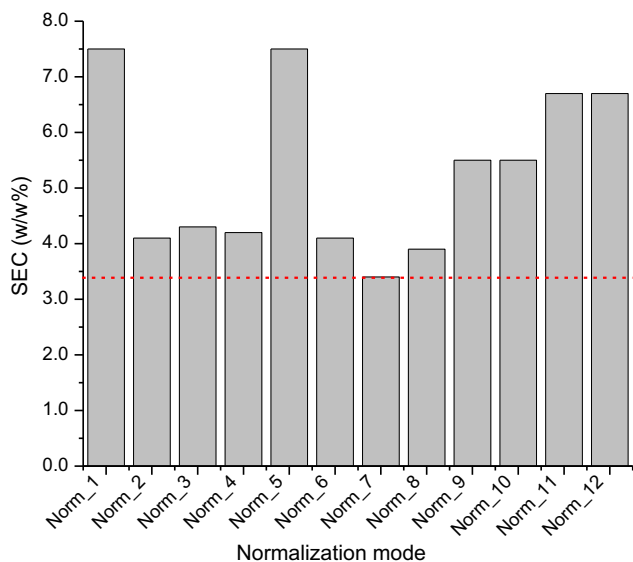


Fig. 4. Standard error of calibration (SEC) using the normalization modes (from Norm_1 to Norm_12) proposed to obtain calibrations models for PC and ABS.

deviations higher than 10% (Aquino et al., 2016; Aquino and Pereira-Filho, 2015; Galbács, 2015).

In addition, 33 samples (see Table 4), which had an unknown PC/ABS content, were analyzed as obtained (not spiked), and its predicted PC and ABS content was obtained using LIBS and the PLS model. The results were also compared through visual inspection of the thermogram obtained by DSC analysis.

Table 2

Predicted PC and ABS concentrations (w/w%) of samples in the calibration data set and figures of merit for the PLS models.

PC/ABS Reference concentrations (expected)	PC Predicted concentrations	ABS Predicted concentrations
100/0	97	3
90/10	86	14
80/20	83	17
70/30	71	29
60/40	60	40
50/50	50	50
40/60	44	56
30/70	33	67
20/80	21	79
10/90	5	95
0/100	0	100
SEC (w/w%)	3.4	3.4
SECv (w/w%)	5.6	5.6
R ²	0.996	0.996
LV	2	2
Explained variance (%)	69.3	69.3

These results prove the feasibility of the LIBS method as a useful and fast alternative for the determination of the PC and ABS content in their blends. Table 4 shows 33 samples that were analyzed without preparation. As can be observed there is a good concordance between the results obtained with DSC and those with the PLS model. Sample 8, for instance, presented only one T_g value in DSC and it was related to ABS. The PLS model predicted 1 and 99% for PC and ABS, respectively. Samples 37, 38 and 39 were identified as PP, PE and PS, respectively, when DSC was used. The PLS models predicted inconsistent values (negative and higher than

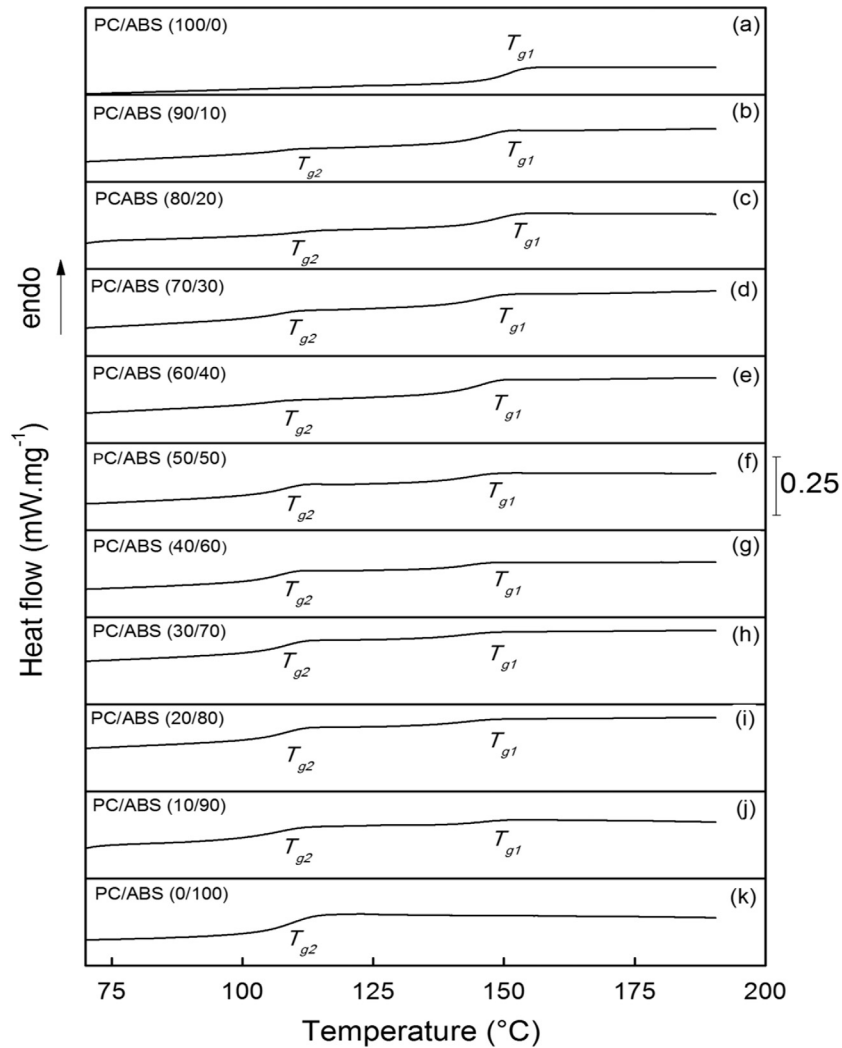


Fig. 5. DSC thermograms obtained for the calibration model with different concentrations of PC and ABS (w/w%): 100/0 (a); 90/10 (b); 80/20 (c); 70/30 (d); 60/40 (e); 50/50 (f); 40/60 (g); 30/70 (h); 20/80 (i); 10/90 (j); and 0/100 (k).

Table 3

Added and found concentrations of PC and ABS in the PC/ABS blends (average \pm standard deviation, $n = 3$).

Samples	Mixtures prepared	PC added reference	PC predict concentrations	Relative error (%) between added and predicted concentrations (see Eq. (2) for details) ^a
Sample 1 (ABS black mobile phone)	1	20	24 \pm 1.5	20
	2	50	46 \pm 3.2	-8.0
Sample 2 (ABS black computer casing)	1	60	63 \pm 4.7	5.0
	2	50	54 \pm 3.7	8.0
	3	70	69 \pm 2.5	1.4
Sample 3 (ABS white computer casing)	1	40	43 \pm 4.1	7.5
	2	50	53 \pm 2.9	6.0
	3	60	62 \pm 0.8	3.3
Sample 4 (ABS white computer monitor)	1	10	12 \pm 1.5	20
Sample 5 (ABS white computer keyboards)	1	40	43 \pm 2.5	7.5
Sample 6 (ABS white computer monitor)	1	80	77 \pm 6.0	3.5

^a Relative error for PC predicted concentration (LIBS and PLS).

SEC) for PC and ABS. The thermograms obtained for the analyzed samples can be seen in the supplementary material.

4. Conclusion

The results presented in this study clearly demonstrate the capability of LIBS combined with PLS as a fast and quasi-non-

destructive tool for determining the PC and ABS content in their blends originating from plastic scraps of e-waste and other sources. In addition, LIBS can supply relevant information on the metallic composition in these samples with analytical frequency of 20 samples per hour. An example of this is the investigation of species related to flame retardants, such as Mg, Al, and Sb, pigments or additives. With the information provided in this study a

Table 4
Predict concentrations (%) of PC and ABS in the PC/ABS blends by PLS models (average \pm standard deviation, $n = 3$) and conclusion after DSC analyses.

Samples	Reference information obtained after DSC analysis	PC predict concentrations (%)	ABS predict concentrations (%)
Manufacturer labeled composition and sample description			
Sample 7 (PC/ABS blend white computer keyboards)	PC/ABS	47 \pm 2.1	53 \pm 2.1
Sample 8 (PC/ABS blend black notebook casing)	ABS	1.0 \pm 12	99 \pm 12
Sample 9 (PC/ABS blend black notebook casing)	ABS	5.0 \pm 3.0	95 \pm 3.0
Sample 10 (PC/ABS blend black notebook casing)	PC/ABS	63 \pm 2.0	37 \pm 2.0
Sample 11 (PC/ABS blend black notebook casing)	ABS	4.0 \pm 1.8	96 \pm 1.8
Sample 12 (PC/ABS blend black notebook casing)	ABS	6.0 \pm 2.1	94 \pm 2.1
Sample 13 (PC/ABS blend black computer screen)	PC/ABS	60 \pm 0.8	40 \pm 0.8
Sample 14 (PC/ABS blend gray mobile phone)	ABS	0.0 \pm 0.8	100 \pm 0.8
Sample 15 (PC/ABS blend gray calculator casing)	PC/ABS	25 \pm 5.2	76 \pm 5.2
Sample 16 (PC/ABS blend white mobile phone)	PC	99 \pm 1.9	1.0 \pm 1.9
Sample 17 (PC/ABS blend black computer screen)	PC/ABS	47 \pm 1.5	52 \pm 1.5
Sample 18 (PC/ABS blend gray computer keyboards)	PC/ABS	46 \pm 1.5	54 \pm 1.5
Sample 19 (PC/ABS blend black computer casing)	ABS	0.0 \pm 5.0	100 \pm 5.0
Sample 20 (PC/ABS blend black TV screen)	PC/ABS	73 \pm 5.8	27 \pm 5.8
Sample 21 (PC/ABS blend black calculator casing)	PC/ABS	36 \pm 3.0	64 \pm 3.0
Sample 22 (PC/ABS blend white computer keyboards)	PC/ABS	77 \pm 4.3	63 \pm 4.3
Sample 23 (PC/ABS blend white computer keyboards)	PC/ABS	31 \pm 4.7	69 \pm 4.7
Sample 24 (PC/ABS blend black computer keyboards)	PC/ABS	47 \pm 1.5	53 \pm 1.5
Sample 25 (PC/ABS blend black TV screen)	PC/ABS	71 \pm 2.4	29 \pm 2.4
Sample 26 (PC/ABS blend black computer screen)	PC/ABS	76 \pm 1.4	24 \pm 1.4
Sample 27 (PC/ABS blend white computer keyboards)	PC/ABS	39 \pm 2.8	61 \pm 2.8
Sample 28 (PC/ABS blend black calculator casing)	PC/ABS	49 \pm 4.3	51 \pm 4.3
Sample 29 (PC/ABS blend gray calculator casing)	PC/ABS	18 \pm 1.9	82 \pm 1.9
Sample 30 (PC/ABS blend blue mobile phone)	PC	100 \pm 1.4	0.0 \pm 1.4
Sample 31 (PC/ABS blend black calculator casing)	PC/ABS	41 \pm 1.5	59 \pm 1.5
Sample 32 (PC/ABS blend black TV screen)	PC/ABS	70 \pm 2.4	30 \pm 2.4
Sample 33 (PC/ABS blend white computer keyboards)	PC/ABS	45 \pm 6.5	55 \pm 6.5
Sample 34 (PC/ABS blend black notebook casing)	PC/ABS	12 \pm 1.9	88 \pm 1.9
Sample 35 (PC/ABS gray notebook casing)	PC/ABS	42 \pm 5.0	58 \pm 5.0
Sample 36 (PC/ABS blend black computer screen)	PC/ABS	30 \pm 5.2	70 \pm 5.2
Sample 37	PP	–65	165
Sample 38	PE	–71	171
Sample 39	PS	–19	119

PP, Polypropylene; PE, polyethylene; PS, polystyrene.

All DSC thermograms are presented in supplementary material.

LIBS system can be adapted in a conveyor belt providing a faster technical plastic identification or quantification. In addition, portable system can be used in fast identification.

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