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**Proposição de modelos de classificação e de calibração para polímeros presentes em resíduos eletrônicos empregando *laser-induced breakdown spectroscopy* (LIBS) e ferramentas quimiométricas**

Vinícius Câmara Costa\*

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**Orientador:** Prof. Dr. Edenir Rodrigues Pereira Filho

\*Bolsista: CAPES

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**Folha de Aprovação**


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Assinaturas dos membros da comissão examinadora que avaliou e aprovou a Defesa de Tese de Doutorado do candidato Vinicius Camara Costa, realizada em 29/07/2019:

  
Prof. Dr. Edenir Rodrigues Pereira Filho  
UFSCar

  
Prof. Dr. Caio Marcio Paranhos da Silva  
UFSCar

  
Profa. Dra. Ana Rita de Araujo Nogueira  
EMBRAPA

  
Prof. Dr. Marcelo Braga Bueno Guerra  
UFLA

  
Prof. Dr. Gilberto Batista de Souza  
EMBRAPA

“Porque dele, e por meio dele, e para Ele, são todas as coisas; a Ele, pois, a glória eternamente. Amém.” **Romanos 11:36**

“Ainda que a figueira não floresça, nem haja fruto na vide; o produto da oliveira minta, e os campos não produzam mantimento; as ovelhas sejam arrebatadas do aprisco, e nos currais não haja gado, todavia, eu me alegro no SENHOR, exulto no Deus da minha salvação”. **Habacuque 3:17,18**

Dedico esse trabalho a Jesus, minha esposa, família e amigos.

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**“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”**

Vinicius Câmara Costa, Francisco Wendel Batista de Aquino, Caio Marcio Paranhos da Silva and Edenir Rodrigues Pereira-Filho. *Waste Management* 70 (2017) 212 - 221

**“Calibration strategies for determination of the Pb content in recycled polypropylene from of the car battery using laser-induced breakdown spectroscopy (LIBS)”**

Vinicius Câmara Costa, Matheus Lima de Mello, Diego Victor Babos, Jeyne Pricylla Castro and Edenir Rodrigues Pereira-Filho. Submitted.

## LIST OF ACRONYNS

<b>ABS</b>	Acrylonitrile-butadiene-styrene
<b>ANN</b>	Artificial neural networks
<b>ASW</b>	Adjusting spectral weightings
<b>BR</b>	Brazil
<b>CCD</b>	Charge-coupled detector
<b>CF</b>	Calibration-free
<b>CN</b>	China
<b>DFA</b>	Discriminant function analysis
<b>DSC</b>	Differential scanning calorimetry
<b>FR</b>	Flame retardants
<b>HCA</b>	Hierarchical cluster analysis
<b>ICCD</b>	Intensified charge-coupled detector
<b>ICP-MS</b>	Inductively coupled plasma-mass spectrometry
<b>ICP OES</b>	Inductively coupled plasma optical emission spectrometry
<b>IS</b>	Internal standardization
<b>KNN</b>	K-nearest neighbor
<b>LIBS</b>	Laser-induced breakdown spectroscopy
<b>MEC</b>	Multi-energy calibration
<b>MMC</b>	Matrix-matching calibration
<b>MNC</b>	Methods of normalized coordinates
<b>MS</b>	Mass spectrometry
<b>Mt</b>	Million metric tons
<b>NIR</b>	Near-infrared
<b>OPG SA</b>	One-point gravimetric standard addition

<b>PA</b>	Polyamide
<b>PE</b>	Polyethylene
<b>PC</b>	Polycarbonate
<b>PCA</b>	Principal component analysis
<b>PCR</b>	Principal component regression
<b>PET</b>	Polyethylene terephthalate
<b>PLS</b>	Partial least squares
<b>PLS-DA</b>	Partial least squares discriminant analysis
<b>PP</b>	Polypropylene
<b>PS</b>	Polystyrene
<b>PU</b>	Polyurethane
<b>PVC</b>	Polyvinyl chloride
<b>RoHS</b>	Guidelines such as the restriction of hazardous substances
<b>SA</b>	Standard addition
<b>SAN</b>	Styrene acrylonitrile
<b>SIMCA</b>	Soft independent modelling of class analogy
<b>SOM</b>	Self-organizing maps
<b>TP CT</b>	Two-point calibration transfer
<b>USA</b>	United States of America
<b>WEEE</b>	Waste electrical and electronic equipment

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## RESUMO

PROPOSIÇÃO DE MODELOS DE CLASSIFICAÇÃO E DE CALIBRAÇÃO PARA POLÍMEROS PRESENTES EM RESÍDUOS ELETRÔNICOS EMPREGANDO *LASER-INDUCED BREAKDOWN SPECTROSCOPY* (LIBS) E FERRAMENTAS QUIMIOMÉTRICAS. Esta tese propõe o desenvolvimento de métodos analíticos para análise de polímeros provenientes dos resíduos de equipamentos elétricos eletrônicos (WEEE), por laser-Induced breakdown spectroscopy (LIBS). Os resultados apresentados nos capítulos 2 e 3 dessa tese foram desenvolvidos em colaboração com uma empresa de reciclagem de WEEE chamada REVERSA. No primeiro método proposto a LIBS foi usada para a identificação e classificação de seis polímeros e um total de 477 amostras foram analisadas. Modelos de classificação usando o *k-nearest neighbors* (KNN) e *soft independent modelling of class analogy* (SIMCA), foram usados para classificar os polímeros. Os modelos propostos apresentaram resultados satisfatórios para as amostras de validação, com exatidão de 98% para o KNN e 92% para o SIMCA. Além disso, os demais parâmetros de validação como sensibilidade, taxa de alarme falso e especificidade mostraram-se adequados. No segundo método a LIBS foi empregada para determinação dos constituintes policarbonato (PC) e acrilonitril-butadieno-estireno (ABS) nas blendas PC/ABS. Para isso foram construídos modelos de calibração multivariada usando *partial least squares* (PLS). Os modelos PLS obtidos para o PC e ABS apresentaram bons parâmetros analíticos, como: i) standard error calibration (SEC) de 3,4 (m/m%); ii) standard error of cross-validation (SECV) de 5,6 (m/m%); iii) coeficiente de correlação linear de 0,996; iv) número de variáveis latentes igual a 2; v) variância explicada de 70%. Para a validação dos modelos PLS foram analisadas blendas PC/ABS com concentrações desconhecidas de PC e ABS e as informações previstas pela LIBS estava em concordância com a técnica de referência. Um terceiro método foi desenvolvido em parceria com uma empresa de reciclagem de plásticos de baterias de carro. Esses plásticos estavam contaminados com Pb e objetivo foi avaliar diferentes estratégias de calibração em LIBS visando a determinação quantitativa deste analito. Estratégias de calibração multivariada e uma nova estratégia univariada foram propostas. A nova estratégia de calibração univariada foi denominada de transferência de calibração com dois pontos e os resultados apresentados foram satisfatórios. As ferramentas quimiométricas, incluindo planejamento experimental, métodos supervisionados para classificação, métodos não supervisionados e calibração multivariada foram empregadas durante o desenvolvimento dos métodos propostos nesta tese.

## ABSTRACT

PROPOSITION OF CLASSIFICATION AND CALIBRATION MODELS FOR POLYMERS PRESENT IN WASTE ELECTRICAL AND ELECTRONIC EQUIPMENTS (WEEE) EMPLOYING LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND CHEMOMETRIC TOOLS. This thesis proposes the development of analytical methods for the analysis of polymers from waste electrical electronic equipment (WEEE) by laser-Induced breakdown spectroscopy (LIBS). The results presented in the chapters 2 and 3 of this thesis were developed in collaboration with a recycling company of WEEE called REVERSA. In the first method proposed LIBS was used for the identification and classification of six polymers and a total of 477 samples were analyzed. Classification models using k-nearest neighbors (KNN) and soft independent modeling of class analogy (SIMCA) were used to classify the polymers. The proposed models presented satisfactory results for the validation samples, with accuracy of 98% for KNN and 92% for SIMCA. In addition, other validation parameters such as sensitivity, false alarm rate and specificity showed adequate. In the second method, the LIBS was employed to determination of the constituents polycarbonate (PC) and acrylonitrile-butadiene-styrene (ABS) in PC/ABS blends. For this were built multivariate calibration models using partial least squares (PLS). The PLS models obtained for the PC and ABS presented good analytical parameters as: i) standard error calibration (SEC) of 3.4 (w/w%); (ii) standard error of cross-validation (SECV) of 5.6 (w/w%); (iii) linear correlation coefficient of 0.996; (iv) number of latent variables equal to 2; (v) explained variance of 70%. For the validation of the PLS models PC/ABS blends with unknown concentrations of PC and ABS were analyzed, and the information provided by LIBS was in agreement with the reference technique. A third method was developed in collaboration with a plastics recycling company of car batteries. These plastics were contaminated with Pb and the objective was to evaluate different calibration strategies in LIBS for the quantitative determination of this analyte. Multivariate calibration strategies and a new univariate strategy were proposed. The new univariate calibration strategy was called a two-point calibration transfer and the results presented were satisfactory. The chemometrics tools including experimental desing, supervised methods for classification, unsupervised methods and multivariate calibration were employed during the development of the methods proposed in this thesis.

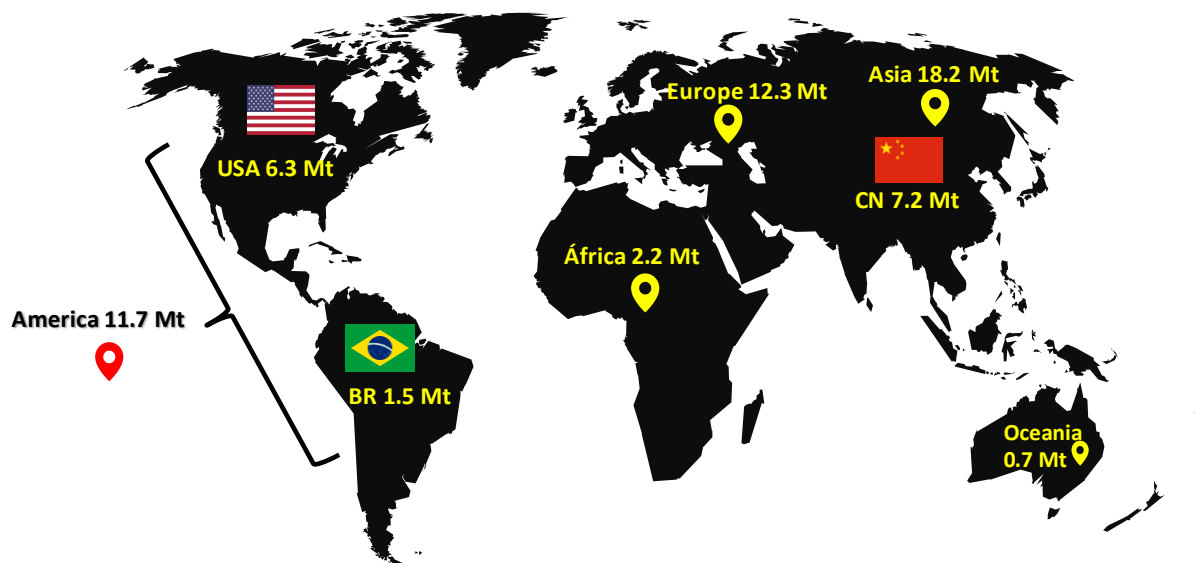
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# **Chapter 1 – Introduction**

## 1. Introduction

The widespread generation of large amounts of electronic waste is a significant problem in several countries. This type of material is normally designated as waste electrical and electronic equipment (WEEE) and is the type of solid waste that presents the fastest growing worldwide. In 2014 the global amount of WEEE produced was around 42 million metric tons (Mt) and in 2018 the generation was of 52 Mt. This scenario is worrying, taking into consideration that in just four years there was a growth of 20% in WEEE generation. Currently, the countries that most produce WEEE are China (CN) and the United States of America (USA), with a generation of 7.2 and 6.3 Mt, respectively. In this scenario, Brazil (BR) is in the sixth position with a production of 1.5 Mt, however it is the largest producer of the Latin America [1-4]. Figure 1 shows a summary of world production of WEEE.



**FIGURE 1** Summary of world production of WEEE.

WEEE is basically composed of iron/steel (average 48%), polymers (average 21%), printed circuit boards (PCB, average 13%), flame retardants (FR, average 10%), glass (average 3%) and other materials (average 5%). Among the above mentioned WEEE components highlight the polymers. Scientific studies have reported at least 15 different types of polymers in WEEE. The most common are the acrylonitrile-butadiene-styrene (ABS), polyamide (PA), polycarbonate (PC), polyethylene (PE), polypropylene (PP), polystyrene (PS)

and styrene acrylonitrile (SAN) and blends PC/ABS [5-7]. Considering the large amount and complexity of the polymers generated from WEEE, adequate management is necessary for the correct disposal or recovery of these materials. One of the positive points of WEEE polymers is the fact that this material is thermoplastics, and when heated can be processed without any damage allowing them to be recycled. The goal of recycling is to return to the productive chain, reducing the amount of improperly disposed of post-consumer solid material [8].

In this sense, some methods for identification of polymers have been proposed, among which the following stand out: i) identification by means of codes, in which each polymer has a specific code. However, this method does not include the main polymers of WEEE; ii) identification by the density difference between the polymers in relation to water; iii) identification through of the burning characteristics (flame color, smell of vapor, vapor pH and flammability). In this case, characteristics are identified through the organoleptic properties that can be perceived by the human senses. Despite being rustic this method is very efficient and is the most used for identification of polymers in the recycling companies in Brazil [9]. Although the methods mentioned are widely used, they are laborious and time-consuming, which is not interesting for recycling companies. In this sense, several analytical techniques can be used for the chemical inspection of polymers from WEEE, aiming its identification and classification. Among the most often employed, there are mass spectrometry (MS) [10], near-infrared (NIR) [11], differential scanning calorimetry (DSC) [12], inductively coupled plasma mass spectrometry (ICP-MS) [13], and inductively coupled plasma optical emission spectrometry (ICP OES) [14]. Among these mentioned techniques, NIR and DSC are the most frequently used in the identification of polymers of WEEE. The main advantage of NIR is its portability, and some instruments have a library with spectra of several polymers, in addition have a high analytical frequency. These characteristics are desired by recycling companies. However, NIR is not suitable for the analysis of black plastic samples, which limits its application considering that most of the polymers of WEEE are black [15]. DSC is used to identify polymers mainly because of their accuracy, since the measurements are carried out in function of the glass

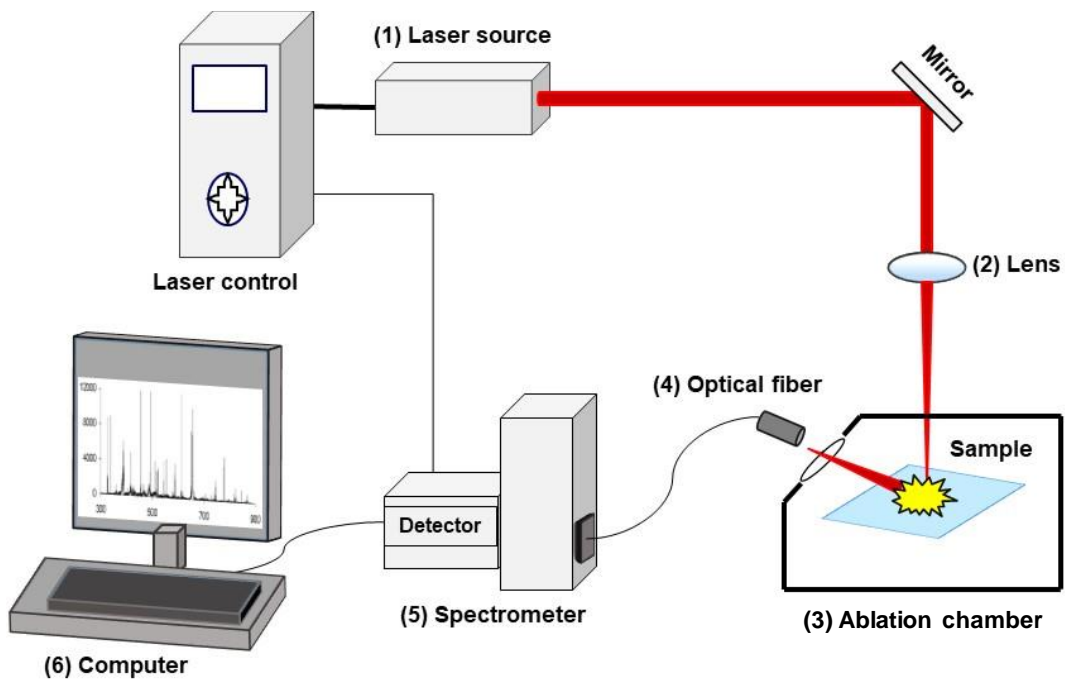
transition temperature specific for each polymer. However, these techniques have a low analytical frequency (2 samples per hour), which is not appropriate for routine analyzes, especially in recycling companies [16].

Another demand of the recycling companies is related to the proper management of PC/ABS blends. Differently of the other polymers (ABS, PA, PC, PE, PP, PS and SAN), the problems of the blends are not related to its identification, but in quantification the proportions between the PC and ABS constituents. This information is very important for recycling companies, because often the proper management and marketing of these blends depends on this data. Moreover, it is important to note that this information is not provided by the manufacturers. Some of the techniques used for identification of polymers can also be used for this purpose, among these stand out NIR and DCS. But as already mentioned, the NIR has limitations for analyzes of black plastics and the DSC has problems of low analytical frequency [15,16].

In this context, it is recurrent presentation of analytical techniques that are increasingly fast, which are suitability for direct use in an environmental factory, with minimum sample preparation and that solve issues such as the identification of polymers and the quantification of the constituents PC and ABS in blends. In this perspective, the technique laser-induced breakdown spectroscopy (LIBS) is an advantageous alternative and has particular characteristics that fulfill the aforementioned requirements.

LIBS is an optical emission spectroscopy technique that presents high energy laser source. The laser may have a duration of nano, pico or femto seconds. The energy of the laser pulse produces a high temperature plasma (in the order of 10,000 - 20,000 K) in the surface of the sample, causing the ablation, evaporation, atomization, ionization, and excitation, of the chemical species present in the sample. During relaxation of the excited atoms, ions and molecular fragments in the plasma emit radiations at specific emission lines. The emitted light is then collected, spectrally resolved and then detected by a charge-coupled detector (CCD) or intensified (I) CCD [17-19]. Figure 2 shows a typical scheme of a LIBS system, in which the main components are: (1) energy source; (2) lenses to focus the laser pulse on the sample

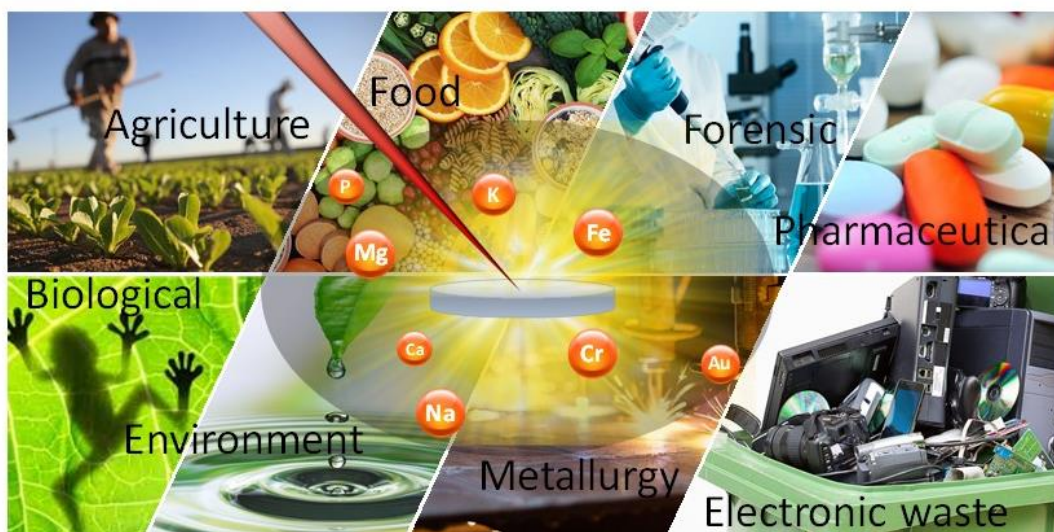
surface; (3) sample holder which can be mounted in an ablation chamber; (4) optical fiber responsible for the collection of radiation from plasma; (5) detection system (spectrometer/detector) and; (6) computer for precise control of temporal events, such as: laser pulse triggering and spectrum recording [19].



**FIGURE 2** Typical scheme of a LIBS system.

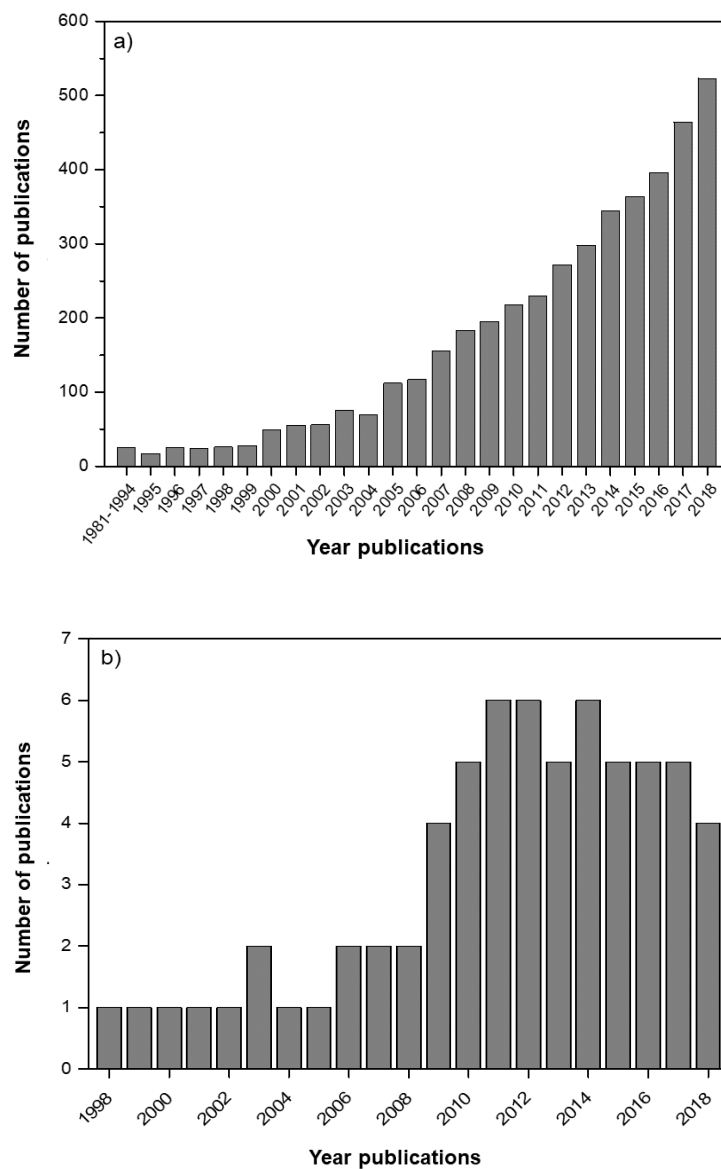
LIBS presents some advantages such as: (i) high analytical frequency; (ii) multielementary capability; (iii) direct analysis with minimal or no sample preparation; (iv) allows analysis under atmospheric conditions; (v) the instrumentation can have small size and portability; (vi) possibility of coupling with other analytical techniques; and (vii) can be implemented in online systems in several segments of the industry. These advantages combined with the simplicity of the technique make LIBS one of the most versatile examples already developed, and its consolidation can be seen in the applications in several fields of activity [20-29], as shown in Figure 3.





**FIGURE 3** Applications of the LIBS in different segments [19].

The growing interest using LIBS can be seen from the number of scientific publications in the last 30 years, as shown in Figure 4a. According to the Web of Science database, about 4500 papers were published during that period and the last 11 years (2008-2018) account for about 78% of total publications. These data exemplify the interest in using LIBS, being possible to find currently a wide variety of studies proposing innovations and improvements to the technique. Within of context LIBS and polymers it is also possible to find scientific publications. The first publication involving the theme was reported in 1998 [30], and since then about 65 publications can be found according to the Web of Science database, as shown in Figure 4b. Of the publications involving the topic, about 95% are related to qualitative analysis and only 5% focused on quantitative purposes. In addition, about 70% of the publications with the theme use the chemometric tools for interpretation of the data. These data show the importance of chemometrics in the advancement of methods involving LIBS. This tool is required because permits better interpretation of the large amount of generated data by LIBS, especially when using a large number of samples.



**FIGURE 4** Number of (a) LIBS publications and (b) LIBS and polymers publications.

Considering the demand of the companies of recycling by fast methods for the analysis of polymers, this PhD thesis had as goal use LIBS for this purpose. Chapters 2 and 3 of this thesis were developed in collaboration with the recycling company REVERSA in order to meet their main demands. REVERSA is an electronic waste management company, established at the city of Andradas, Minas Gerais, Brazil. In Chapter 2, we used LIBS in combination with chemometric tools to develop classification models for the main polymers found in WEEE. The highlight of this proposal in relation to existing publications is the large number of samples

(approximately 500). This allowed for obtaining robust and very accurate models. In Chapter 3 we used multivariate calibration models in combination with LIBS for the determination of concentration of the constituents PC and ABS in blends PC/ABS. It is important to highlight that this was the first scientific proposal showing this type of method. In Chapter 4, we used LIBS for the quantitative determination of Pb in recycled PP from car batteries. Although, the samples were not from WEEE, we decided to add this chapter to the thesis, since PP is one of the most found plastics in WEEE. Thus, in this chapter we evaluate different calibration strategies for the direct determination of Pb in PP samples recycled. Multivariate strategies were evaluated, in addition, a new univariate calibration strategy named two-point calibration transfer (TP CT) was proposed with success. The Chapter 5 presents a general conclusion about of the thematic LIBS and polymers and show an overview into the contributions of the results achieved in this thesis.

## **1.2 LIBS and polymers**

The increasing generation of polymers from WEEE is a problem of great industrial and environmental concern, and depending on the type of polymer or blend, certain industrial processes such as recycling and the production of new blends can be implemented. This scenario has attracted research with the goal of developing new simple and fast analytical methods for the analysis of these residues [16]. As already mentioned, LIBS can be a powerful analytical tool for this purpose due to their advantageous characteristics.

In this sense, we will present a review of the most relevant research involving the analysis of polymers of WEEE using LIBS. The first step for identifying polymers by LIBS is based on evaluation of specific emission lines corresponding to the original chemical constitution of the polymers. Commonly, the elements and molecular bands present in the original chemical composition of the polymers of the WEEE are C, N, O, H, CN and C<sub>2</sub>. However, other elements such as Al, Ba, Br, Ca, Fe, Mg, Na, P, S, Sb and Ti can also be found in large quantities because these are added to the polymers as additives in order to improve the properties of these materials [6,16].

The identification and classification of different polymers of WEEE using LIBS is highly challenging because: i) The variety of polymers found in the WEEE is very wide (up to 15 different types); ii) These materials can consist of mixtures of two or more polymers (blends); iii) They may contain different concentrations of FR (as high as 1% w/w) and additives; iv) They present similar original chemical compositions (mainly aromatic polymers). However, these problems can be minimized using chemometric tools associated with LIBS spectra [31,32].

In general, the polymers can be classified and identified based on the original LIBS spectra. In this sense, Sattmann et al. [30] proposed the combination of polymers and LIBS for the first time. In this study the authors used artificial neural network (ANN) combined with LIBS spectra to identify polymers with an accuracy of 93-96% for PE and PP and of >99% for polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Lasheras et al. [33] successfully used the methods of normalized coordinates (MNC) and linear and rank correlation in combination with LIBS spectra to identify eleven polymers with similar chemical compositions. In another study, Unnikrishnan et al. [34] used LIBS spectra and the selection of specific emission lines associated with principal component analysis (PCA) to classify four different classes of polymers (PE, PET, PP and PS). Spectra were recorded in the range 200 - 900 nm. From this spectral data, three small regions were chosen for the analysis based on the existence of characteristic spectral information related to C, H, CN. These regions were: Region 1 (R1) 245 - 260 nm, Region 2 (R2) 375 - 390 nm and Region 3 (R3) 485 - 500 nm. The R2 showed the best results when compared to others.

In study proposed by Aquino and Pereira-Filho [35] chemometric tools such as soft independent modeling of class analogies (SIMCA), k-nearest neighbors (KNN) and partial least squares for discriminant analysis (PLS-DA) in combination with spectral information from LIBS was used in the identification and classification of polymers from mobile phones. Classification models were proposed using black and white polymers separately to identify the manufacturer and origin. The proposed models for the manufacturer showed percentage of correct predictions ranging 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

analytical method proposed extends the applicability of the LIBS technique and open possibilities for polymer manufacturers identification.

Following this approach, Shameem et al. [36] proposed a LIBS–Raman system combined with PCA to identify four types of polymers (PE, PET, PP and PS). Atomic and molecular information of PE, PET, PP and PS were studied using plasma emission spectra and scattered signal obtained in the LIBS and Raman technique, respectively. The molecular information collected via Raman spectroscopy exhibits clearly distinct features for the transparent plastics (100% discrimination), whereas the LIBS technique shows better spectral feature differences for the colored samples. The study shows that the information obtained from these complementary techniques allows the complete classification of the plastic samples, irrespective of the color or additives.

Tang et al. [37] used LIBS combined with unsupervised learning algorithms of self-organizing maps (SOM) to discriminate between industrial polymers in the open air. Only the intensities of two molecular bands (CN and C<sub>2</sub>) and four atomic emission lines (C, H, N and O), were used. First, the SOM neural network with adjusting spectral weighting (ASW) was applied for a preliminary separation of 20 types of polymers. The results were obtained in the output space indicating that 18 polymers were separated, except for PC and PS. Afterwards, the K-means clustering algorithm was utilized to separate PC and PS. For 20 polymers, the accuracy of the industrial polymer classification was 99%.

All of the aforementioned studies used the range of LIBS spectra to identify the polymers. Although it is a widely used strategy in some cases, polymers cannot be identified from the raw LIBS spectra alone. In this case, the information about molecular spectral lines and the ratio of the molecular bands and the element lines can be used. This strategy is very interesting because it reduces the amount of variables and facilitates the manipulation of the data. This approach was employed for the first time by the group of Prof. Anzano from the University of Zaragoza (Spain). Anzano and his co-workers deserve special mention for their significant contributions to this particular application of LIBS and polymers [38,39].

Using this strategy Grégoire et al. [40], observed that the aromatic polymers (PS and PC) can be distinguished from aliphatic polymers (PE, PP and PA) using the emission lines related to ( $C_2$ , CN, H, C, N and O), the ratios of emission lines and molecular bands ( $H/C_2$ ,  $H/C$  and  $O/N$ ). In the aromatic group, the PC and PS showed a separation based on the  $C_2$  intensity and the  $O/N$  ratio; in the aliphatic group, PA could be distinguished from PE and PP, but PE could not be distinguished from PP, due to their similar chemical structures. In addition, the authors used PCA and partial least squares (PLS) to analyze the data.

Banaee and Tavassoli [41] used discriminant function analysis (DFA) combined with PCA to analyze five polymers (PET, PE, PVC, PP and PS). The authors used the following ratios among the emission lines and molecular bands:  $Cl/C$ ,  $C_2/C$ ,  $H/C$ ,  $O/C$ ,  $CN/C$ ,  $N/C$ ,  $CN/C$ ,  $N/C$ ,  $N/O$ ,  $C_2/C$ . The results of this study show that LIBS/DFA is a simple, low cost, accurate and fast method that can be used for identification and classification of polymers, showing an ability to correctly classify 99% of the polymers.

An approach combining LIBS and ASW with the use of the ratio of the emission lines and molecular bands was employed by Yu et al. [42]. This approach has been achieved through increasing the intensities of specific characteristic spectral lines that are important for polymer identification but are difficult to excite. Using the ASW method, the identification accuracy of all 11 polymers was increased to nearly 100%, while the accuracy of PE, PP, PC and polyurethane (PU) were only 98%, 74%, 90% and 98%, respectively, when the ASW method was not used. In this same perspective, Babier et al. [43] used the  $C_2/He$  and  $CN/He$  ratios associated with PCA to discriminate among four different plastics (PS, PP, ABS and PC/ABS).

The quantitative analysis in WEEE polymers by LIBS is a major problem. The polymer matrix is very complex, in addition LIBS exhibits severe problems with calibration, and the use of the information acquired by a laser system in combination with reference techniques is mandatory in several cases. Some elements that are considered hazardous, emerging contaminants and environmental pollutant agents can be added in the polymer matrix as FR (as high as 1% w/w). Guidelines such as the Restriction of Hazardous Substances (RoHS)

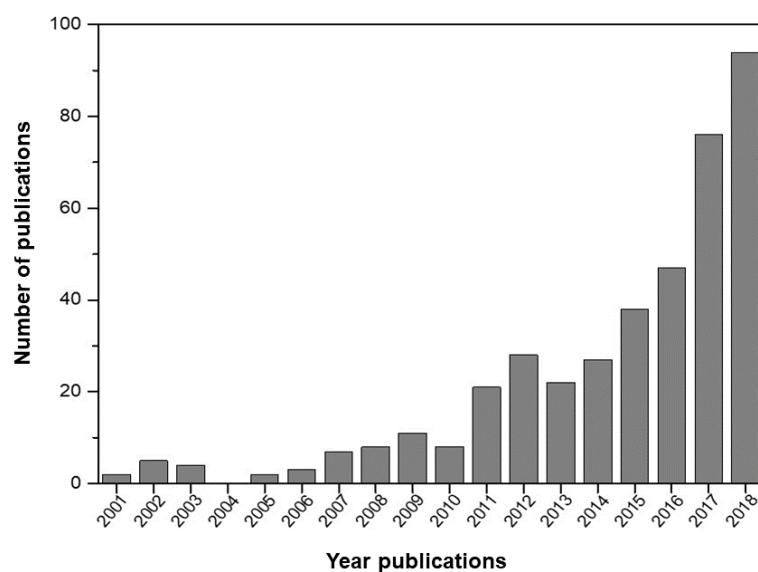
Directive D.2002/95/EC [44] stipulate the maximum permissible concentrations of these elements in WEEE. To address this problem, Aquino et al. [45] proposed a new method for directly determining Sb in PC/ABS blends using LIBS. A calibration curve (Sb: 0 to 2.6% w/w) was prepared and analyzed using LIBS and more than 10,000 spectra were obtained. Carbon (247.85 nm) and Sb (259.80 nm) signals were recorded and normalized by their individual norm values. The best results were obtained when C was used as the internal standard and the Sb concentration observed in the samples ranged from 0.15 to 0.68% (w/w). Standard addition tests were performed, and the recoveries ranged from 63 to 83%.

### **1.3 LIBS and chemometrics**

In analytical chemistry, the term "chemometrics" was introduced by Svante Wold in 1971, to describe the use of mathematical models and statistical principles. Currently, chemometrics is defined as a science that employs a multidisciplinary approach, which also includes mathematics and statistics, and has become indispensable for modern researchers in analytical chemistry [46].

LIBS spectra are very complex, due to some factors related to signal-to-noise ratio, such as: laser energy fluctuations, ablation rate and laser-plasma coupling. These factors directly reflect in precision of the measures, causing high standard deviation values. These drawbacks makes impossible a wide application of the LIBS in the field of the analytical chemistry. In the last years some of these difficulties have been overcome with combination between LIBS and chemometrics. In addition, the chemometrics is fundamental for interpretation of the large amount of generated data by LIBS [47].

In this sense, the use of chemometrics is practically indispensable in LIBS analysis. Figure 5 shows how the use of LIBS associated with chemometric tools has been growing over the years. According to the Web of Science database, since 2001, about 375 scientific articles using some type of chemometric tool were published, accounting about 10% of the total LIBS publications. Moreover, since 2011 the number of publications with the term has growing significantly, and the trend is that this number will continue to increase.



**FIGURE 5** Number of publications involving LIBS and chemometrics.

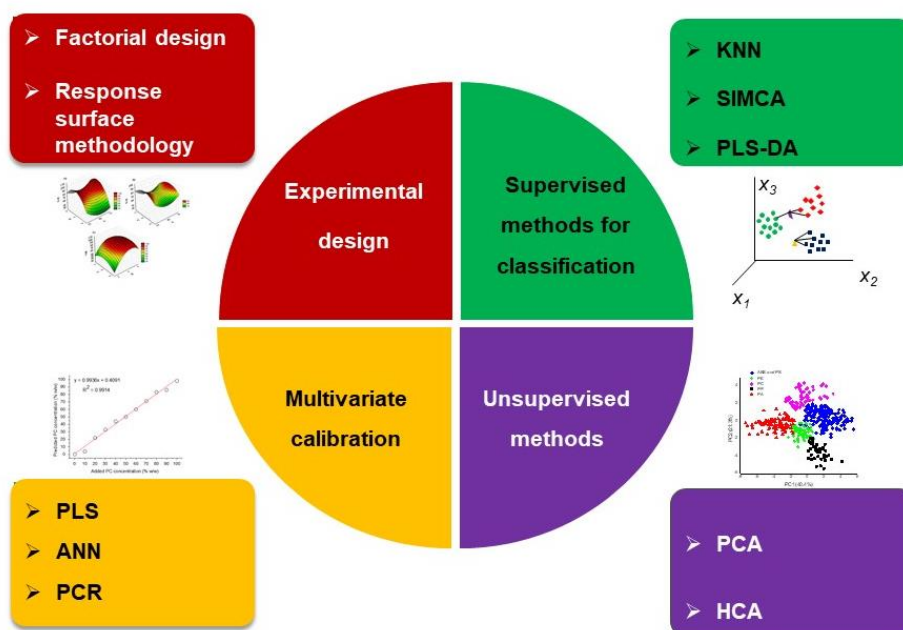
Before, the application of any chemometric tool, the data need to be transformed to reduce the influence of sample surface morphology or microheterogeneity [48]. This transformation is even more important for the direct analysis of solid samples. Several types of transformations, such as the use of digital filters [49] and the application of normalizations based on Euclidean norm, signal area or height [50,51] have been reported. This process is 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 [47]. Our research group used mainly the data normalizations strategy to minimize above mentioned problems and used for the first time in the quantitative analysis metal alloys [51]. Subsequently, these normalizations were applied successfully for qualitative and quantitative analysis of a wide range of samples [52-57].

The chemometrics can be divided into four areas, as shown in Figure 6: (i) experimental desing; (ii) supervised methods for classification; (iii) unsupervised methods; and (iv) multivariate calibration. All the mentioned areas are widely used in the development of analytical methods by LIBS. Experimental design is very employed for optimization of the instrumental parameters in LIBS, and the most used tools are factorial design and response



surface methodology [51,53,55,56]. The supervised methods of pattern recognition using the chemometric tools, SIMCA, KNN and PLS DA are widely used in LIBS. The use of these tools is indispensable when the goal is to employ the spectral information from LIBS to propose classification models. The mentioned tools were employed with successfully in proposition of classification models in metal alloys [51], leather [58] and cosmetics [59].

Unsupervised methods such as PCA and hierarchical cluster analysis (HCA) are also employed for interpretation of the LIBS data [46]. According to Porinzka et al. (2018) [60], the first step in interpretation LIBS data for a large sample set is the application of the PCA. Moreover, according to the authors, the PCA is the chemometric tool most used in LIBS data. Another chemometric approach widely used in LIBS analysis is the use of multivariate calibration. The main tools of multivariate calibration used in LIBS are ANN [61], PLS [62], and principal component regression (PCR) [63].



**FIGURE 6** Representative scheme of the main areas of chemometrics.

As can be observed is wide the applications of the chemometrics tools for interpretation of LIBS data. Despite extract and maximize useful information and to improve the precision of qualitative and quantitative analysis, the chemometric universe applied to LIBS still requires a

greater improvement, aiming to obtain good performance of the technique in several fields of application.

#### **1.4 Approaches for quantitative analysis by LIBS**

LIBS is an analytical technique established for qualitative analysis purposes, aiming the identification of chemical elements in a wide variety of samples [16,18]. However, for quantitative analysis it requires considerable efforts, mainly due to severe matrix effects and difficulties in obtaining compatible solid standards for calibration, which can compromise precision and accuracy of the measures, making difficult a broader application of LIBS [19].

To overcome the problems aforementioned, several calibration strategies have been reported in the literature over the years to improve the precision and accuracy of the measurement in LIBS [19]. Among the calibration strategies employed in LIBS, the matrix-matching calibration (MMC) is more employed. In MMC method the calibration standards are matched with sample matrix, usually using certified reference materials (CRMs), or a set of samples with reference values as calibration standards. In this case, matrix effects can be minimized when the physical properties of the calibration standards closely match those samples being analyzed. Despite its advantages, MMC is not able to correct for spectral interferences. In addition, obtaining reference values for some analytes by other techniques may be difficult in some cases (*e.g.* for samples of difficult decompositions like glass) and when there is a small set of samples or CRMs [64].

Other effective alternative to minimize the main limitations associated with LIBS, is the use of calibration by standard additions (SA) [19]. In SA, a constant amount of sample is added to the blank and all calibration standards, ensuring that both samples and standards are subjected to the same conditions, thus minimizing matrix effects. The limitations of this calibration approach include its inability to correct for spectral interferences and the requirement for large amounts of sample. In addition, SA may be considered cumbersome since a calibration curve with a few calibration standards (typically four or five standards) must be prepared for each individual sample [64].

The internal standardization (IS) is another calibration alternative for minimizing signal bias due to fluctuations in instrumental operational conditions, sampling errors, and, to a lesser extent, matrix effects [45,65]. However, choosing an appropriate internal standard specie is not a trivial task since it must go through similar plasma temporal processes as the analytes, which is usually challenging in LIBS. In addition, IS is not able to overcome some of the severe matrix effects observed in LIBS analyses [19].

Calibration-free LIBS (CF-LIBS) uses the intensities of emission lines and some plasma properties (e.g. plasma electron density and temperature), which are calculated from the Boltzmann distribution, to determine the analyte concentration in the sample. In this case, only a CF-LIBS algorithm is required, with no need for a calibration curve or matrix-matched standards. For this strategy to be employed it is necessary local thermodynamic equilibrium in the plasma generated in the analysis of the samples [19,66].

Recently, Babos et al. [55] proposed a new calibration strategy called multi-energy calibration (MEC). The MEC uses only two calibration standards, for each sample, and various emission wavelengths of the analyte with different sensitivities to determine its concentration in the sample. Both calibration standards are prepared using the same amount of sample, which contributes to efficiently minimize the matrix effect. The standard 1 is composed of 50% w/w of sample and 50% w/w of an appropriate blank, while the standard 2 is composed of 50% w/w of sample and 50% w/w of a reference standard containing the analytes. Some limitations of this method are related to the difficulty of choosing an appropriate blank and homogenization of standards [67]. In another study, Babos et al. [68] proposed a calibration strategy called one-point gravimetric standard addition (OP GSA). Similarly, to MEC calibration, OP GSA uses only two calibration standards. However, in this strategy an analytical curve is constructed with only one point.

Multivariate calibration strategies also provide measurements with satisfactory precision and accuracy in LIBS. One of the main advantages of these methods is the possibility of proposing a calibration model in the presence of the interferents, provided that they are present in the calibration set used to construct the model. In addition, some intrinsic limitations

of each multivariate method must be known so that erroneous conclusions are not obtained in the calibration of the method [19,61,62,63].

As can be seen, the calibration strategies applied in LIBS are varied and each has its advantages and limitations. The choice of the employed calibration strategy in the analytical method to be developed will depend on the intrinsic properties of the sample analyzed and knowledge of the advantages and limitations of each strategy.

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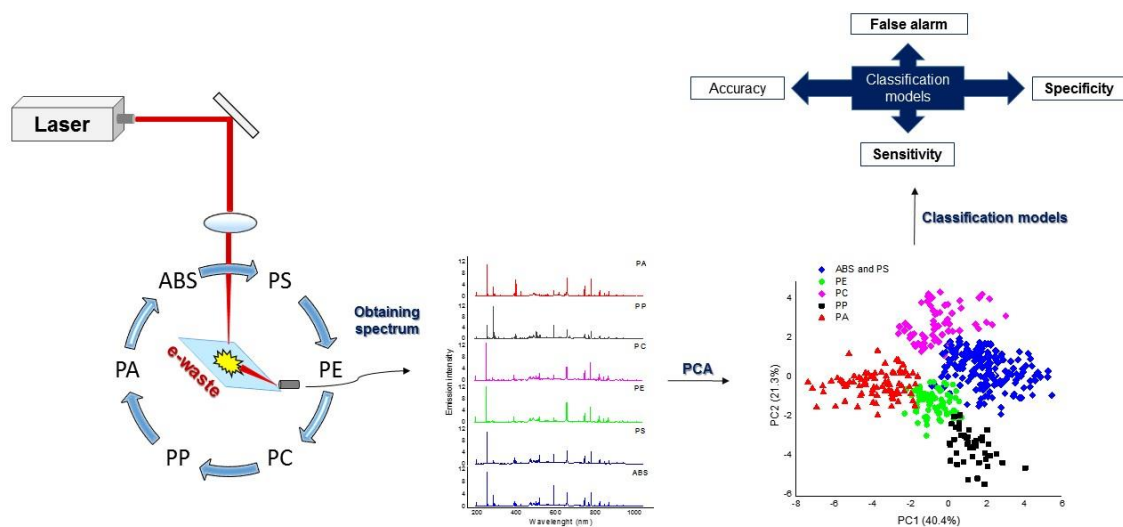
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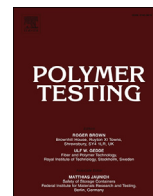
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## **Chapter 2 – Published Results**

2.1 Identification and classification of polymer e-waste using laser-induced breakdown spectroscopy (LIBS) and chemometric tools. *Polymer Testing* 59 (2017) 390-395.

Graphical Abstract





## Analysis Method

## Identification and classification of polymer e-waste using laser-induced breakdown spectroscopy (LIBS) and chemometric tools



Vinicius Câmara Costa <sup>a</sup>, Francisco Wendel Batista Aquino <sup>a</sup>, Caio Marcio Paranhos <sup>b</sup>,  
Edenir Rodrigues Pereira-Filho <sup>a,\*</sup>

<sup>a</sup> Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip code 13565-905, São Carlos, SP, Brazil

<sup>b</sup> Laboratório de Polímeros, Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip code 13565-905, São Carlos, SP, Brazil

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## ABSTRACT

In the recycling of polymer e-waste, there is a pressing need for rapid measurement technologies for the simple identification and classification of these materials. The goal of this work was to instantly identify e-waste polymers by laser-induced breakdown spectroscopy (LIBS). The studied polymers were acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), polyethylene (PE), polycarbonate (PC), polypropylene (PP), and polyamide (PA). Emission lines were selected for C (247), H (656), N (742 + 744 + 747), and O (777), as well as the molecular band of C2 (516), and the ratios of the emission lines and molecular band were utilized. Classification models, k-nearest neighbors (KNN) and soft independent modeling of class analogy (SIMCA), were used to rank the polymers. Both constructed models gave satisfactory results for the validation samples, with average accuracies of 98% for KNN and 92% for SIMCA. These results prove the predictive analytical capabilities of the LIBS technique for plastic identification and classification.

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## 1. Introduction

Electronic segments are considered as the world's largest and fastest growing industry [1]. Associated with this rapid growth in electrical and electronic applications, a relatively new type of waste stream, termed waste electronic and electrical equipment (WEEE or e-waste), has become a major area of concern worldwide [2]. During the last three decades, the amount of e-waste generated has increased dramatically, and this trend is currently projected to keep increasing for the next several years [3,4].

A recent report by United Nations University estimated that approximately 42 million metric tons (Mt) of e-waste was generated in 2014 and that 50 million Mt will be generated in 2018 [4]. Electronic waste is a type of solid waste with the fastest growth in the world, mainly due to the rapid obsolescence of equipment (2–3 years or less). Its composition is complex, and the amount of polymer e-waste is estimated to be between 10 and 30% by weight (average 21%) and varies according to the type of device [5,6].

Polymers that constitute e-waste are diverse, and at least 15 different types exist. Among the most commonly used are acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC), high-impact polystyrene (HIPS), polypropylene (PP) and polyethylene (PE) [7–9].

Considering the large amount and complexity of polymers that can be generated from e-waste, adequate management is necessary for the correct disposal or recovery of these materials. In this sense, the process of recycling is presented as an attractive alternative [6]. The goal of recycling is to return polymeric waste to the productive chain, reducing the amount of improperly disposed of post-consumer solid material. Therefore, recycling is a solution to this problem, and the first step is the identification and classification of the polymer composition in a given e-waste.

Several techniques are used to identify polymers. Among the most often employed are mass spectrometry (MS) [10,11], infrared spectrometry (IR) [12], thermal analysis [13,14], inductively coupled plasma-mass spectrometry (ICP-MS) [15] and inductively coupled plasma optical emission spectrometry (ICP OES) [16]. Among these mentioned techniques, IR is one of the most frequently used in the identification of polymers [12]; however, it is not suitable for the

\* Corresponding author.

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

analysis of black plastic samples [17]. Thermal analysis is commonly used but is destructive [12] and presents a low analytical frequency. Other techniques such as ICP-MS and ICP OES normally require time-consuming or extensive sample preparation routines and are destructive in order to turn the solid sample into a homogeneous aqueous solution [18]. In this regard, laser-induced breakdown spectroscopy (LIBS) is an analytical technique that presents great potential for this application (high analytical frequency, portability, no or minimal sample preparation, and the possibility of hyphenation) [19–22].

Laser-induced breakdown spectroscopy is primarily an elemental analysis technique that is applied in several fields [23–25], such as qualitative and quantitative samples analysis. However, molecular materials are almost entirely atomized when exposed to the intense laser radiation that is sufficient for breakdown. This implies that limitations exist in the application of LIBS to the identification of compounds because of the loss of molecular information in the plasma, especially for organic compounds that only contain mostly carbon and hydrogen, as well as oxygen and nitrogen [17,26]. These limitations can be addressed using statistical chemometric tools. Many research groups are working to identify polymeric materials using LIBS, particularly through the use of different chemometric tools [17].

Several studies in the scientific literature conducted to identify plastics employed different strategies combining LIBS and chemometric tools. Determining the ratios of different emission lines and molecular bands [27,28] is a strategy found in the literature. Methods of normalized coordinates (MNC) and linear and rank correlation were applied to identify polymers with very similar chemical compositions [29]. A complete analysis of several polymers was made using principal component analysis (PCA) [30,31]. A chemometric method based on discriminant function analysis (DFA) was used to discriminate polymers with slight differences between their spectra [32]. 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 [33]. Artificial neural networks (ANNs) combined with LIBS have been used with success to identify polymers [34].

In this context, this study presents an alternative method for the identification and classification of six polymer types most commonly found in e-waste. The studied polymers were acrylonitrile-butadiene-styrene (ABS), polystyrene (PS), polyethylene (PE), polycarbonate (PC), polypropylene (PP) and polyamide (PA). Initially, PCA was applied in an exploratory analysis, and SIMCA and KNN were later applied for the proposition of classification models based on the LIBS spectra. These classification models can be used for the recycling of e-waste polymers, contributing to the management of these wastes by different industrial segments.

## 2. Experimental

### 2.1. Instrumentation

#### 2.1.1. Laser-induced breakdown spectroscopy (LIBS)

LIBS spectra were obtained on a J200 LIBS system (Applied Spectra, Fremont, CA, USA) using the control software Axiom 2.5 (Applied Spectra). This system consisted of a nanosecond Nd:YAG laser (Quantel Ultra, Bozeman, MT, USA) that provided up to 100 mJ of energy, a 6-channel CCD spectrometer with a fixed gate width of 1.05 m in a spectral window from 186 to 1042 nm and an x–y–z translational ablation chamber with a 1280–1024 CMOS color camera imaging system. The emission lines of the elements of

interest and the internal standards were identified using Aurora software (Applied Spectra).

#### 2.1.2. Differential scanning calorimetry (DSC)

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

### 2.2. Samples

A total of 477 recyclable polymers derived from e-waste possessing different characteristics (colors, sizes and precedence) were used. These polymers contained several additives that were mineral, metallic, or organic. The organic additives involved the presence of oxygen, nitrogen, or carbon that did not originate from the polymer chain. These elements can jeopardize the classification of polymers. For this study, six types of polymers were used that represent the most commonly found polymers in e-waste. The studied polymers were divided into the following classes: (1) ABS and PS, (2) PE, (3) PC, (4) PP, and (5) PA. For the calibration set, 277 samples were used, and 200 samples were used for the validation set. For additional evaluation of models 15 samples of polymers were supplied by a polymer e-waste recycling company. These samples were identified through the company's routine method, which consisted of burning the polymers followed by identification by the human senses.

### 2.3. Optimization of the instrumental conditions of LIBS

A Doehlert design [35] was used to optimize the experimental LIBS variables. The variables and their respective levels were as follows: a laser energy of 50, 63, 75, 88, and 100 mJ, delay time of 0, 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0  $\mu$ s and spot size of 50, 100, and 150  $\mu$ m. A total of 15 experiments were performed in triplicate, considering the central point. The experiments for the optimization of the conditions were performed using four classes of polymers (polyethylene PE, polycarbonate PC, polypropylene PP and polyamide PA).

### 2.4. Data collection and chemometric evaluation

For data treatment, twelve different normalization modes were tested to compensate for signal variations and sample matrix differences [36]. The best results were those normalized by the individual norm and averaged over  $n$  pulses. The data set was organized using Microsoft Excel, and a routine developed in Matlab 2009 (MathWorks, Natick, USA) was used for data normalization. Aurora software (Applied Spectra) was employed for the identification of emission lines, and Pirouette 4.5 (Infometrix, Bothell, USA) was used to calculate the data classification models. The data set was organized into a matrix with 477 rows and 10 columns, in which the rows represented the polymer samples and the columns represented the variables.

For all polymer fragments, 5 points were randomly selected, upon which 10 laser pulses *per point* were performed. A previous surface cleanup had been performed using a single pulse of 10 mJ and with a 200  $\mu$ m spot size. After this procedure, the optimized conditions were used. Initially, PCA was performed to evaluate whether LIBS could differentiate the classes of polymers investigated. Variable selection was based on the intensity ratios of selected elemental lines and molecular bands: C (247), H (656), N (742 + 744 + 747), O (777) and C2 (516). After this selection, two



classification models for the identification and classification of polymers were proposed: KNN and SIMCA.

### 3. Results and discussion

#### 3.1. Optimization of LIBS

In order to evaluate the conditions of the LIBS instrumental parameters, the interclass distance (ICD) from the SIMCA classification model was used with the goal of identifying an experimental condition that reflected a high ICD, i.e., high discrimination among the polymers investigated. Six interclass distances (PE<sub>x</sub>PC, PE<sub>x</sub>PS, PE<sub>x</sub>PA, PC<sub>x</sub>PS, PC<sub>x</sub>PA, PS<sub>x</sub>PA) were calculated and converted to a geometric average in order to obtain a committed experimental condition. To obtain dependable results, the quality of the mathematical model was evaluated, i.e., if the model can satisfactorily describe the behavior of the experimental values. To assess the quality of the model, the lack of fit was verified. If the mathematical model presents a good fit to the experimental data, the mean square lack of fit ( $MS_{lof}$ ) should reflect only the random errors inherent to the system. Additionally, the mean square pure error ( $MS_{pe}$ ) should also be an estimate of these errors, and it is assumed that these two values are not significantly different. Thus, it was possible to use the *F* distribution to assess whether there was any significant difference between these two means. The quality of the model was tested by analysis of variance (ANOVA). Thus, for the considered model, there was no lack of fit because  $MS_{lof}/MS_{pe}$  (0.33) was lower than  $F_{table}$  (19.16). After evaluation of the model, the best experimental conditions (high interclass distances) were represented by the central point: laser energy of 75 mJ, delay time of 0.5  $\mu$ s and spot size of 100  $\mu$ m.

#### 3.2. Selection of emission lines and molecular bands for analysis

A typical spectrum of each polymer analyzed is presented in Fig. 1. As expected, carbon and hydrogen had spectral lines with high intensity. Additionally, molecular bands for C2 can be observed. Other lines observed were related to N, O, Ca, Na, Mg and Ca. The emission intensity ratios of the molecular bands of C2, as well as C, H, O and N, were the parameters required for the identification of organic compounds. Under the experimental conditions, atmospheric nitrogen and oxygen may have influenced the spectra obtained. Therefore, signals of nitrogen and oxygen could appear in the spectra but were not present in the polymers. A better approach would be to use an inert atmosphere composed of helium or argon, for example. However, our objective was to analyze polymer e-waste in real conditions of a recycling company, in which is not possible use an inert atmosphere.

Variable selection was based on the intensity ratios of emission lines and molecular bands commonly used for the qualitative identification of polymers [30,31]. The emission lines of C (247), H (656), N (742 + 744 + 747), and O (777) and the molecular band of C2 (516) were used to calculate the theoretical ratios, which are shown in Table 1. After analyzing this table, several observations are apparent: the polyamide (PA) polymer, for instance, was mainly characterized by a high C(247)/C2(516) ratio, and the C2(516)/N(742 + 744+777) ratio was high for ABS and PS.

#### 3.3. Exploratory analysis using PCA

With the obtained data matrix (277 samples and 10 variables), PCA analysis was conducted with the autoscaled data. Initially, PCA was generated with six classes of polymers (ABS, PS, PE, PC, PP and PA); however, it was not possible to obtain separation between ABS and PS. This separation difficulty was due to the similarity between

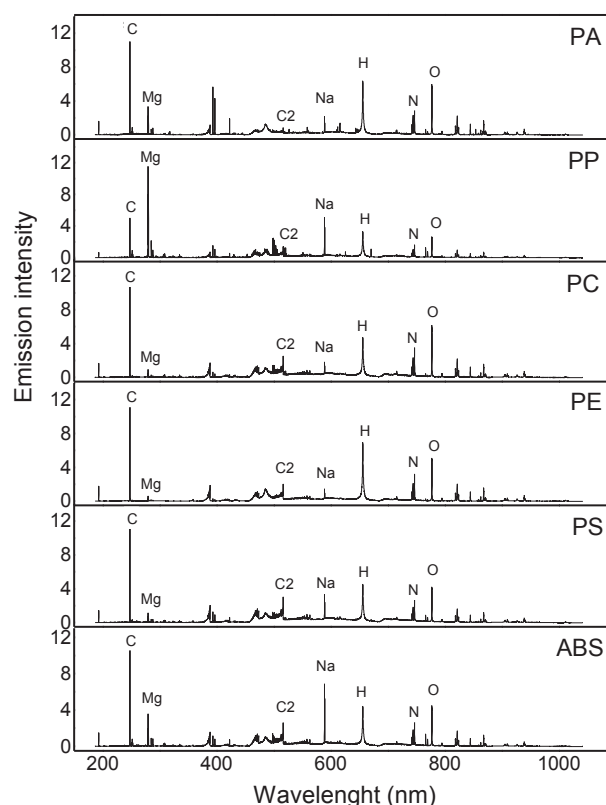


Fig. 1. Representative spectra of the analyzed polymers: ABS, PS, PE, PC, PP and PA.

the styrene repeating unity found in both of these polymers. Therefore, these two polymers were grouped into a single class, and PCA with five classes was newly generated. Five classes were analyzed, assessing the ratios of the emission lines of C (247), H (656), N (742 + 744 + 747), and O (777) and the molecular band of C2 (516). The scores and loadings of first three principal components were evaluated, and Fig. 2a presents the score plot for PC1xPC2 for different samples, with 61.3% of the explained variance. Fig. 2b presents the loading plot for PC1xPC2 using different ratios of the emission lines and molecular band.

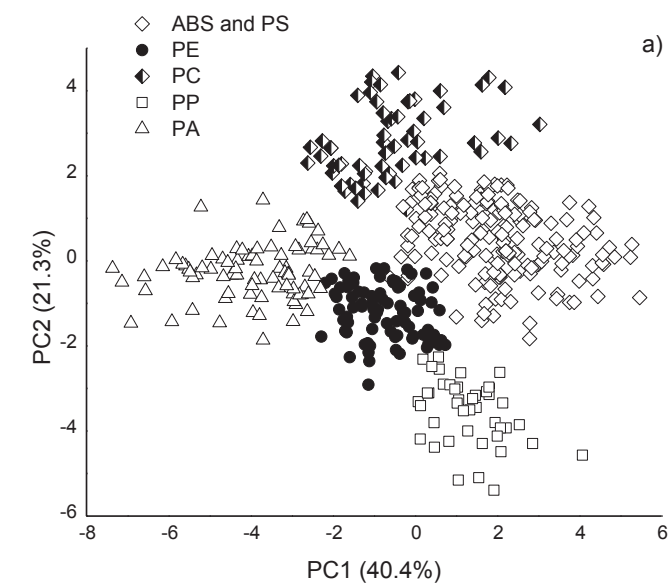
In Fig. 2a, there is separation between the five classes of polymers in our study. The aliphatic polymers (PE, PP and PA) are separated from the aromatic polymers (ABS, PS and PC). This differentiation was possible because the C2 signal was lower for the aliphatic polymers [29].

#### 3.4. Classification model proposition

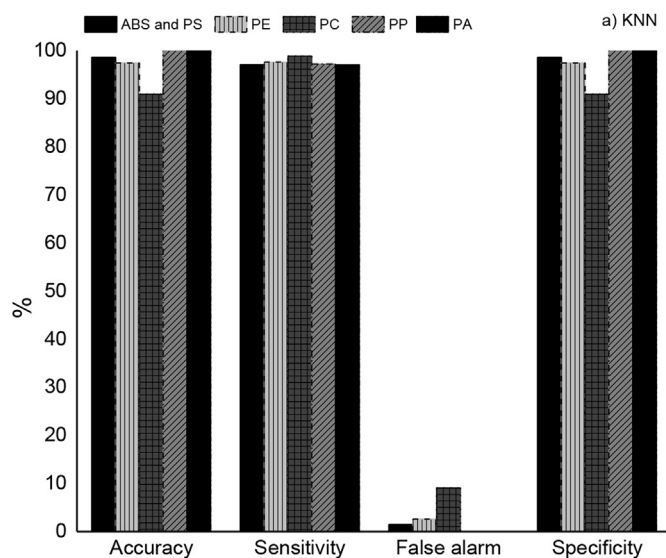
Fig. 3 shows the figures of merit for the proposed classification models. Five classes of polymers were studied, and two classification models were proposed for each class: KNN and SIMCA. In the case of KNN, three neighbors were selected for the five classes. For SIMCA, the number of principal components was 2 or 3 for the five classes considered. The data set was divided into calibration (277) and validation (200) samples, and Fig. 3 shows the accuracy, sensitivity, false alarm rate and specificity calculated for validation data set in each model. Between the two models, KNN presented the best results, with an accuracy of 91–100%. In the case of SIMCA, the accuracy ranged from 89 to 92%.

**Table 1**  
Polymers used and their average and range ratios.

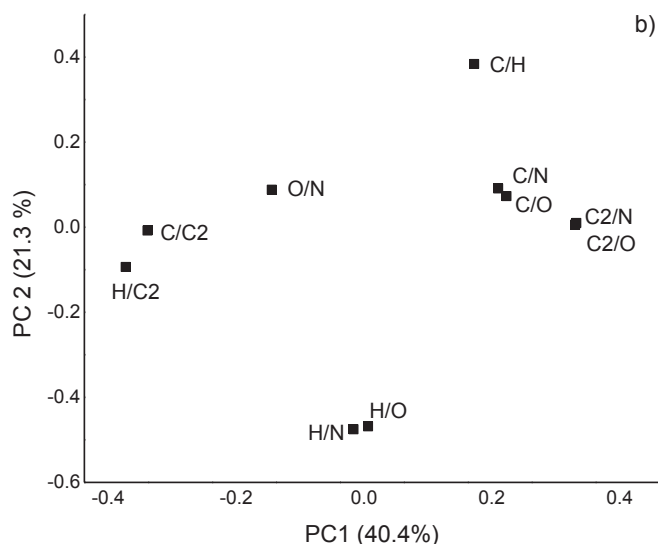
Variable	Evaluated ratio	ABS and PS		PE		PC		PP		PA	
		Average Ratio	Range Ratio	Average Ratio	Range Ratio	Average Ratio	Range Ratio	Average Ratio	Range Ratio	Average Ratio	Range Ratio
1	C(247)/H(656)	2.8	1.3–4.2	1.8	0.9–2.5	3.0	1.4–5.1	1.6	0.5–2.5	1.9	0.7–3.1
2	C(247)/C2(516)	5.2	2.2–10.3	8.6	2.5–12.5	7.6	2.8–16.8	6.0	1.1–20.6	23.9	7.8–49.1
3	C(247)/N(742 + 744+747)	4.5	2.0–7.4	3.9	1.7–6.0	3.9	1.9–7.8	3.6	0.9–6.2	3.2	1.2–5.6
4	C(247)/O(777)	2.7	1.2–4.6	2.3	1.0–3.7	2.1	1.1–4.1	2.1	0.5–3.9	1.8	0.7–3.2
5	H(656)/C2(516)	1.9	1.0–3.0	4.7	2.3–6.3	2.6	0.9–4.5	3.5	1.4–8.8	13.5	3.8–32.7
6	H(656)/N(742 + 744+747)	1.7	1.3–2.1	2.1	1.9–2.4	1.3	0.8–1.7	2.2	1.5–2.9	1.7	1.2–2.3
7	H(656)/O(777)	1.0	0.8–1.3	1.3	1.1–1.4	0.7	0.5–0.9	1.3	0.9–1.6	1.0	0.6–1.3
8	C2(516)/ N(742 + 744+777)	1.0	0.6–1.7	0.5	0.3–0.8	0.6	0.3–1.0	0.7	0.2–1.4	0.15	0.05–0.45
9	C2(516)/O(777)	0.6	0.3–1.0	0.3	0.2–0.5	0.3	0.1–0.6	0.4	0.1–0.8	0.09	0.03–0.26
10	O(777)/N(742 + 744+747)	1.7	1.6–1.8	1.7	1.6–1.8	1.8	1.7–1.9	1.7	1.6–1.9	1.8	1.6–2.1



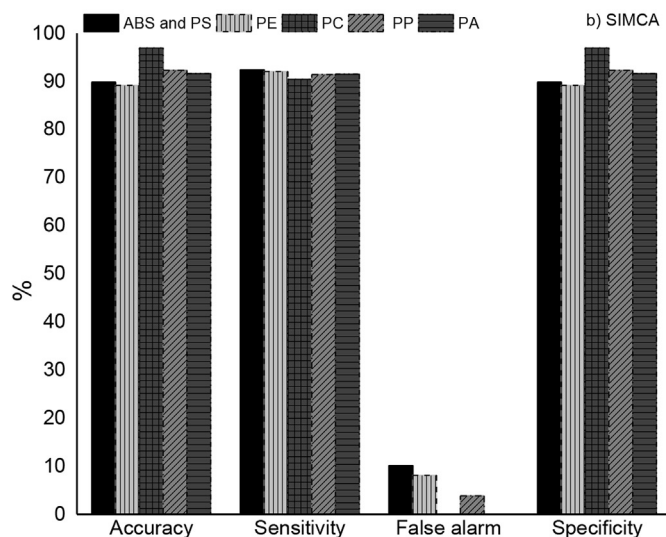
a)



a) KNN



b)



b) SIMCA

**Fig. 2.** (a) Score and (b) loading plots for PC1xPC2 of the analyzed polymers.

**Fig. 3.** Accuracy, sensitivity, false alarm rate and specificity obtained for the (a) KNN and (b) SIMCA models.

**Table 2**  
Identification of samples by the recycling company, DSC and proposed models.

Sample	Recycling company	DSC	KNN	SIMCA
1	ABS	ABS	ABS or PS	ABS or PS
2	PPO/PS <sup>a</sup>	PPO/PS <sup>a</sup>	ABS or PS	Not predicted
3	POM <sup>b</sup>	PE	PE	Not predicted
4	PS	PE	PE	PE
5	ABS	PS	ABS or PS	ABS or PS
6	ABS	ABS	ABS or PS	ABS or PS
7	PC	PC	PC	PC
8	ABS	ABS	ABS or PS	ABS or PS
9	ABS	ABS	ABS or PS	ABS or PS
10	PS	PS	ABS or PS	ABS or PS
11	PS	PS	ABS or PS	ABS or PS
12	ABS	ABS	ABS or PS	ABS or PS
13	PS	PS	ABS or PS	ABS or PS
14	PC	PC	PC	PC
15	PS	PS	ABS or PS	ABS or PS

<sup>a</sup> Blend of poly(phenylene oxide)/polystyrene.

<sup>b</sup> Polyoxymethylene.

### 3.5. Identification of samples by recycling company, DSC and proposed models

The 15 samples provided by the recycler were initially identified by the KNN and SIMCA models and then analyzed by DSC, which is a reference technique based on the principles of thermal analysis. All samples were identified by their DSC glass transition temperature ( $T_g$ ) except samples 3 and 4, which were identified by their fusing temperature. Table 2 shows the results obtained from DSC, KNN, SIMCA and the results provided by the company when conventional identification was used.

The results were consistent for most samples; however, there were discrepancies between the results of samples 2, 3, 4 and 5. According to the recycling company, sample 2 was a blend of poly(phenylene oxide)/polystyrene, which is consistent with the results obtained from DSC. However, using KNN, the predicted class was 1 (ABS or PS), and the SIMCA model did not predict any of the studied classes. The KNN model is deterministic and thus predicted the sample to be Class 1. However, the model was not calibrated to identify the sample in question. On the other hand, the SIMCA model is probabilistic and did not predict this sample class because the model had not been calibrated to identify that type of polymer. Samples 3 and 4 were identified by the recycling company as polyoxymethylene (POM) and PS, respectively. These results were not consistent with those obtained from DSC and KNN, which showed that these samples belonged in class 2 (PE). The SIMCA model did not predict sample 3 but predicted sample 4 to be PE, which agrees with the results of DSC and KNN. Sample 5 was identified by the recycling company as ABS; DSC identified this sample as PS, and the KNN and SIMCA models classified this sample in Class 1 (ABS or PS). A limitation of KNN and SIMCA models is that it is not possible to discriminate between ABS and PS samples.

## 4. Conclusion

LIBS together with discriminant function analysis were used for the identification and classification of five groups of the most commonly used polymers in the electronics industry. Classification models (KNN and SIMCA) were developed using the theoretical ratios of the emission lines and molecular bands obtained from LIBS. The predictive abilities of the models were similar, showing that these two models can be used to identify and classify the investigated polymers. The results show that LIBS combined with chemometric tools is a simple, inexpensive, accurate and fast method that can be used for the identification and classification of

e-waste polymers.

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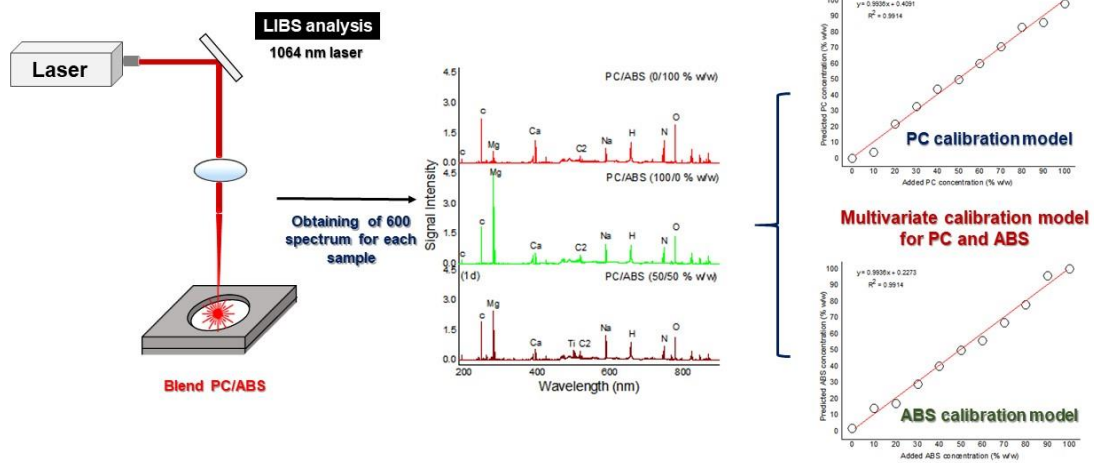
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## **Chapter 3 – Published Results**

3.1 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. *Waste Management* 70 (2017) 212 - 221.

### Graphical Abstract







# 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



Vinicius Câmara Costa<sup>a</sup>, Francisco Wendel Batista Aquino<sup>a</sup>, Caio Marcio Paranhos<sup>b</sup>,  
Edenir Rodrigues Pereira-Filho<sup>a,\*</sup>

<sup>a</sup> Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip Code 13565-905, São Carlos, SP, Brazil

<sup>b</sup> Laboratório de Polímeros, Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip Code 13565-905, São Carlos, SP, Brazil

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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

\* Corresponding author at.

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

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  $\mu$ s, and the spot size, ranging from 50 to 250  $\mu$ 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<sup>-1</sup>. 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  $\mu\text{m}$  spot size (Fluence around 32  $\text{mJ}/\text{cm}^2$ ). 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  $\mu\text{s}$  delay time, 1.05 ms gate width, and 75  $\mu\text{m}$  spot size (Fluence around 1700  $\text{mJ}/\text{cm}^2$ ). 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 **X**) that better fit one or more dependent variables **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 ( $\text{CaCO}_3$ ). 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 ( $\text{Sb}_2\text{O}_3$ ), 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 ( $\text{TiO}_2$ ) (Kumar and Gupta, 2003).

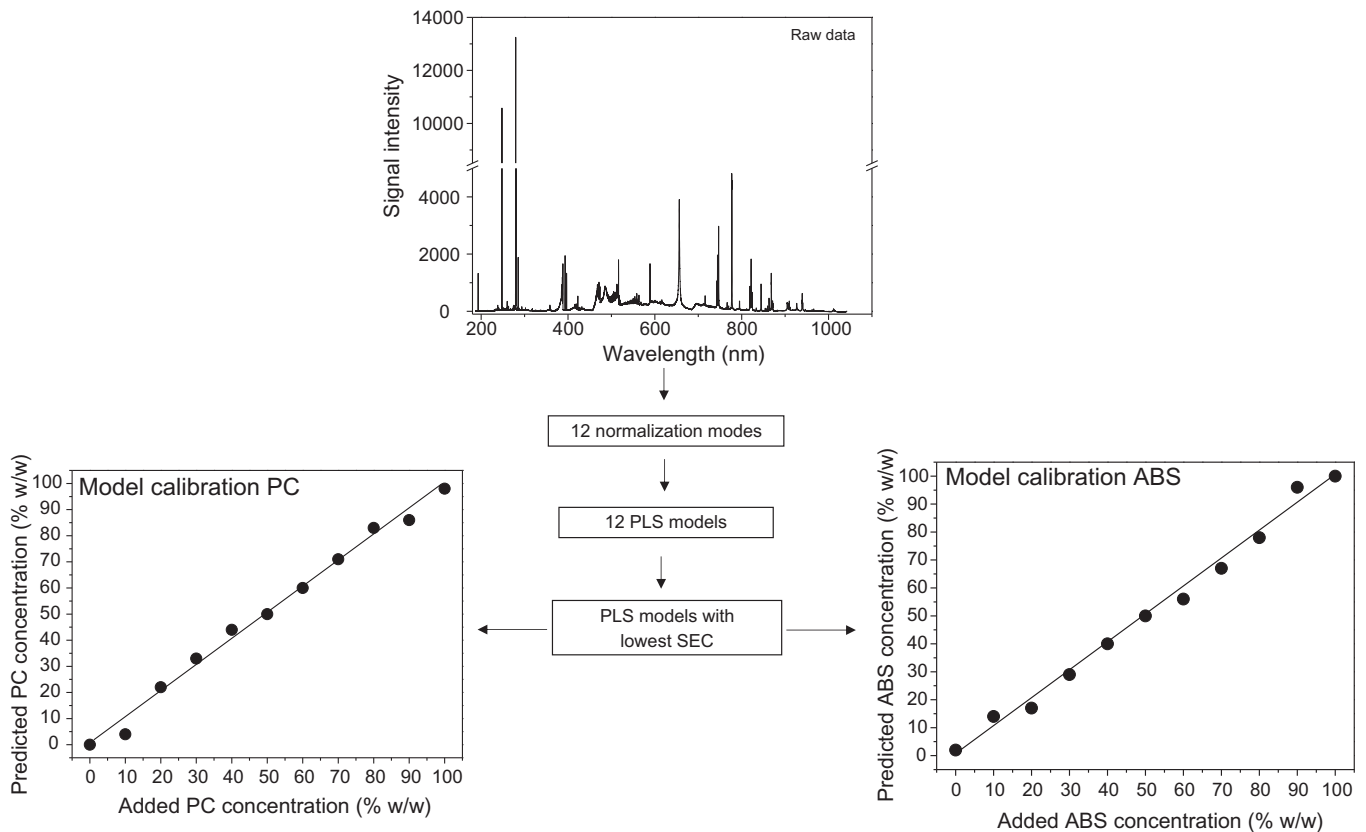


Fig. 1. Pictorial description of steps for signal normalization selection and construction of the calibration models.

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):

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

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 Arao, 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.

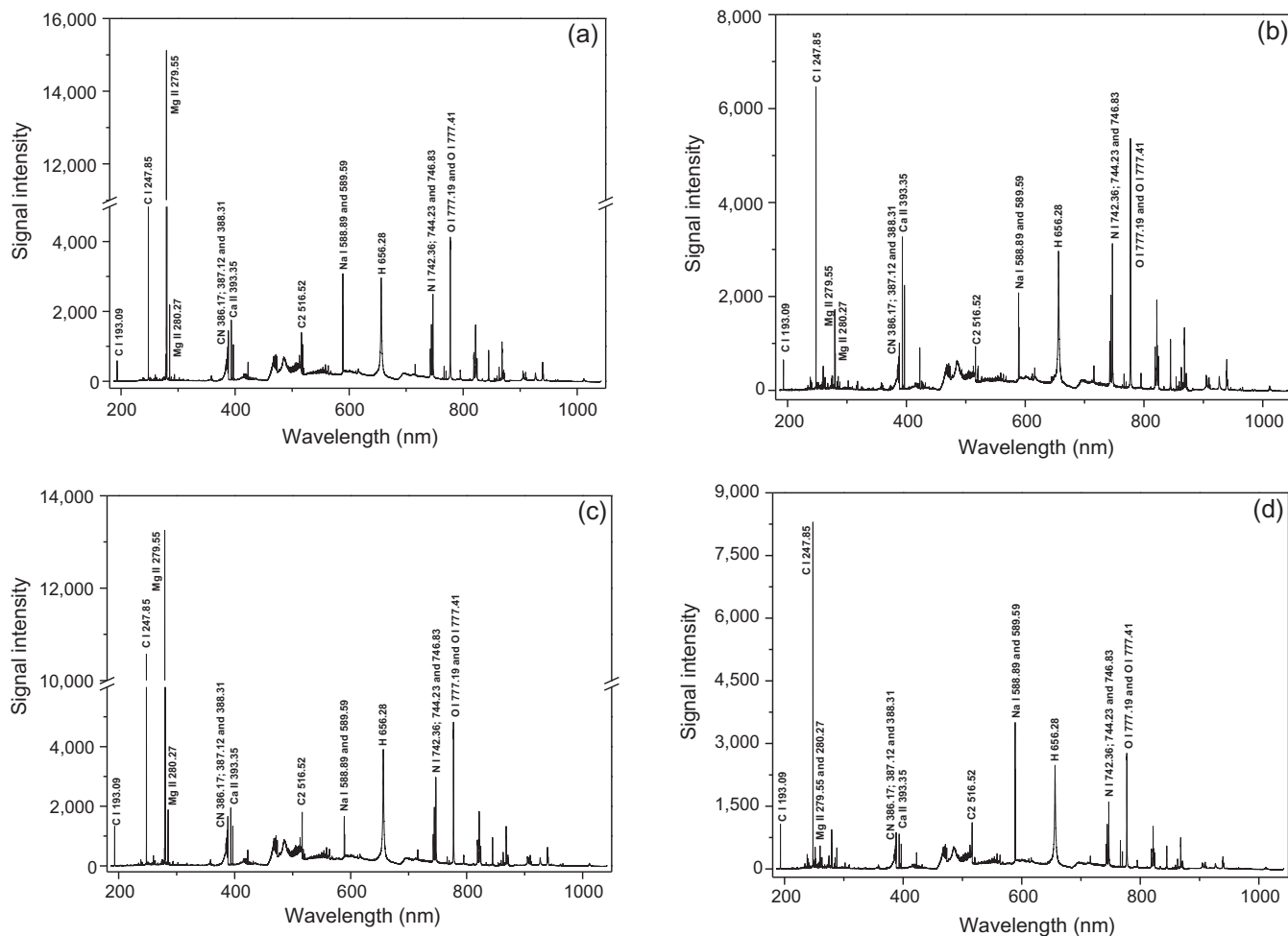


Fig. 2. LIBS emission spectra for the 100% w/w PC (a), 100% w/w ABS (b), sample 1 spiked to provide a PC/ABS 50/50 w/w% mixture (c), and sample 7 without spiking (d).

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

<sup>a</sup> Emission lines that presented high regression values.

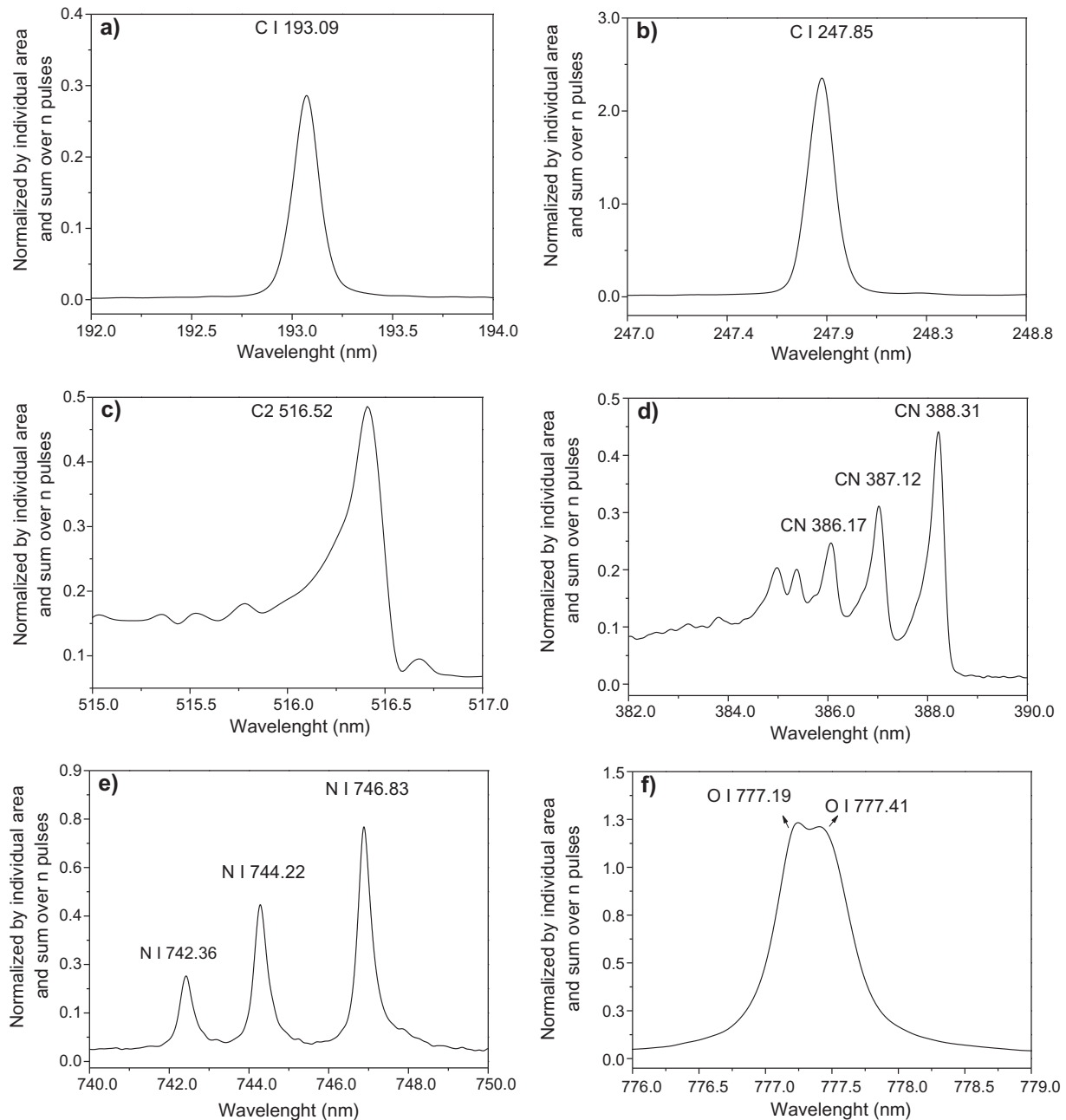
Table 2 shows the correlations obtained between the predicted and expected values for PC (0.996) and ABS (0.996) and the figures of merit for the calculated PLS models. Standard error of calibration (SEC) and cross-validation (SECV) were 3.4–5.6%, respectively, and in both models 2 latent variables (LV)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

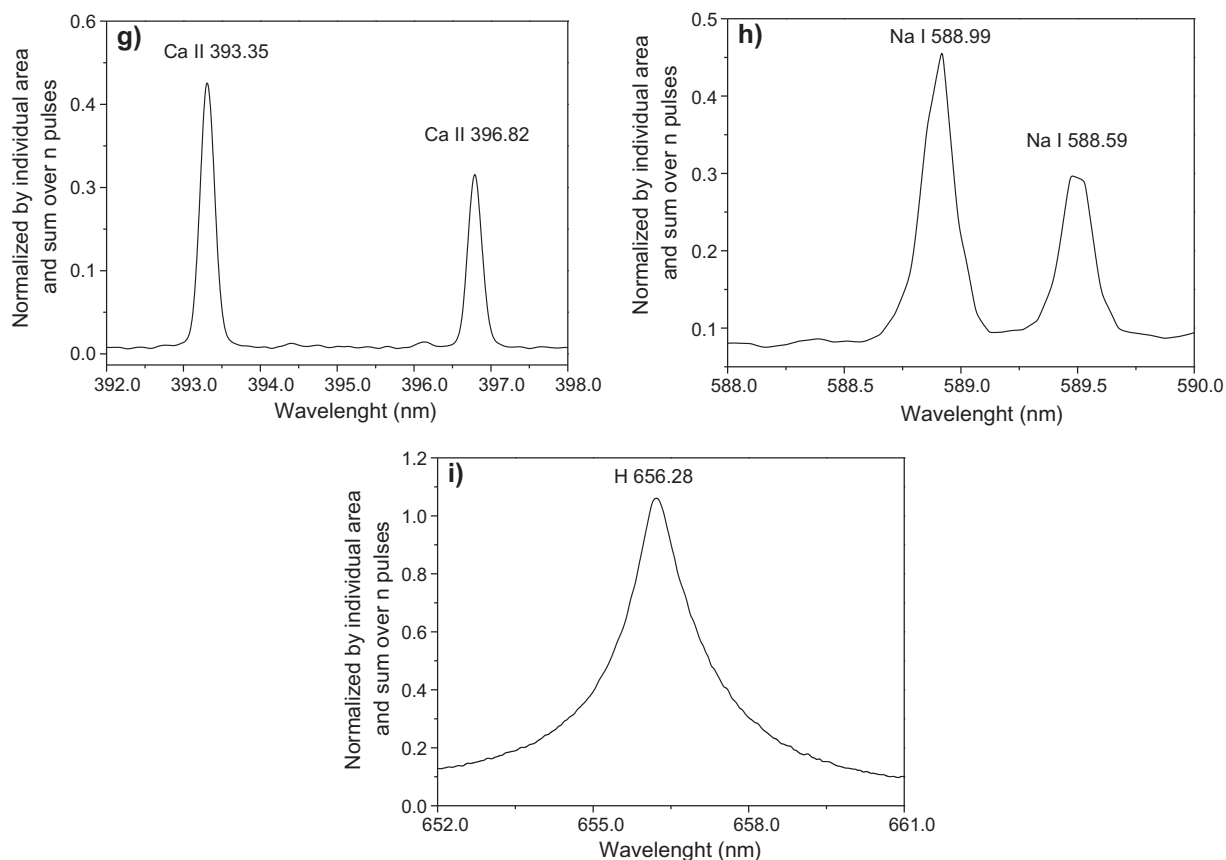


Fig. 3 (continued)

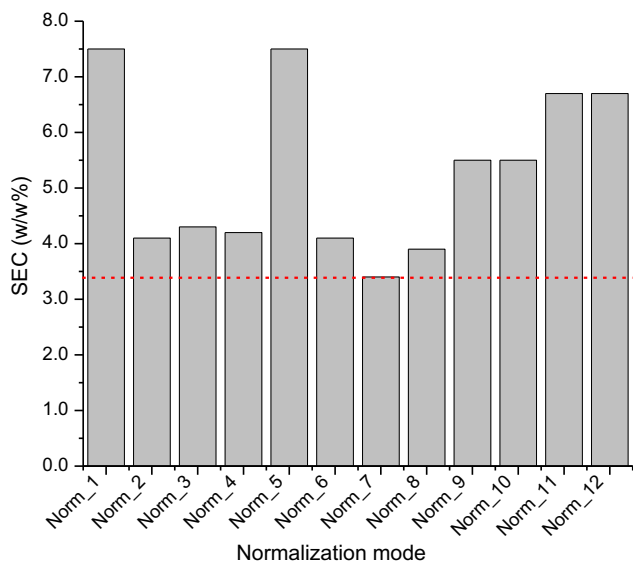


Fig. 4. Standard error of calibration (SEC) using the normalization modes (from Norm\_1 to Norm\_12) proposed to obtain calibrations models for PC and ABS.

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

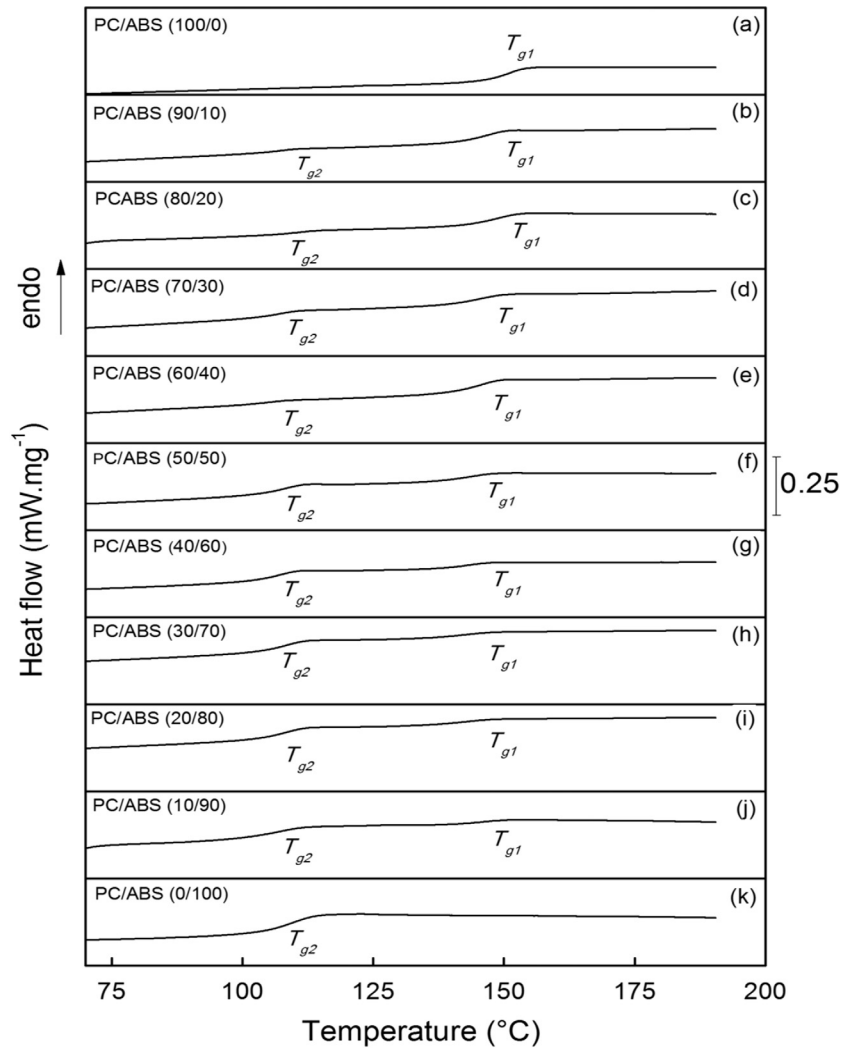
In addition, 33 samples (see Table 4), which had an unknown PC/ABS content, were analyzed as obtained (not spiked), and its predicted PC and ABS content was obtained using LIBS and the PLS model. The results were also compared through visual inspection of the thermogram obtained by DSC analysis.

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 <sup>2</sup>	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<sub>g</sub> 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) <sup>a</sup>
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

<sup>a</sup> 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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## Supplementary material

### **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**

Vinicius Câmara Costa<sup>a</sup>, Francisco Wendel Batista Aquino<sup>a</sup>, Caio Marcio Paranhos<sup>b</sup> and Edenir Rodrigues Pereira-Filho<sup>a\*</sup>

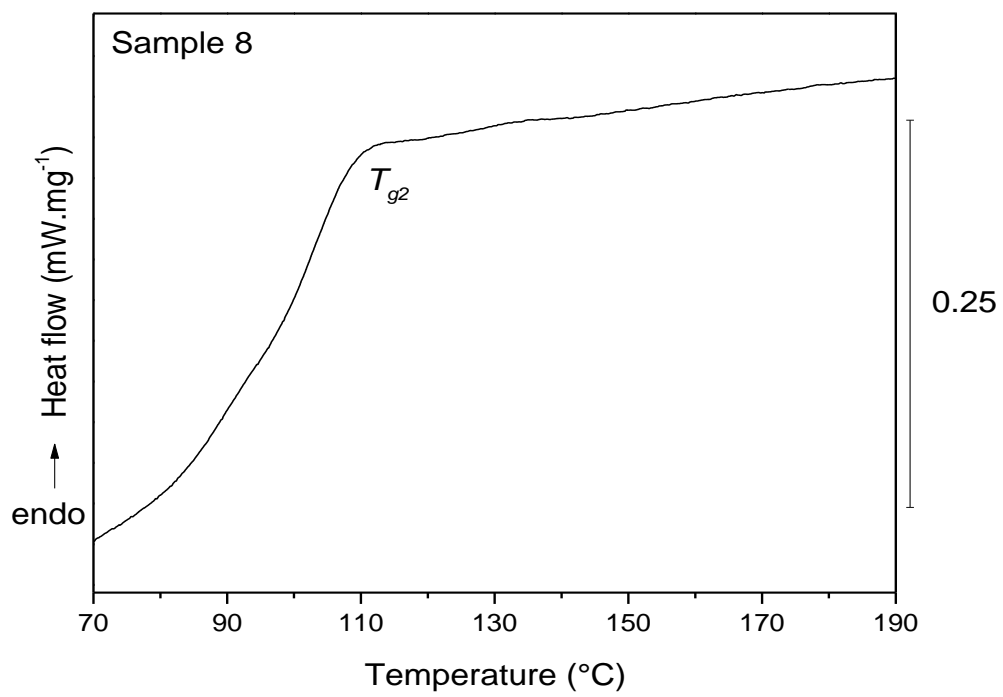
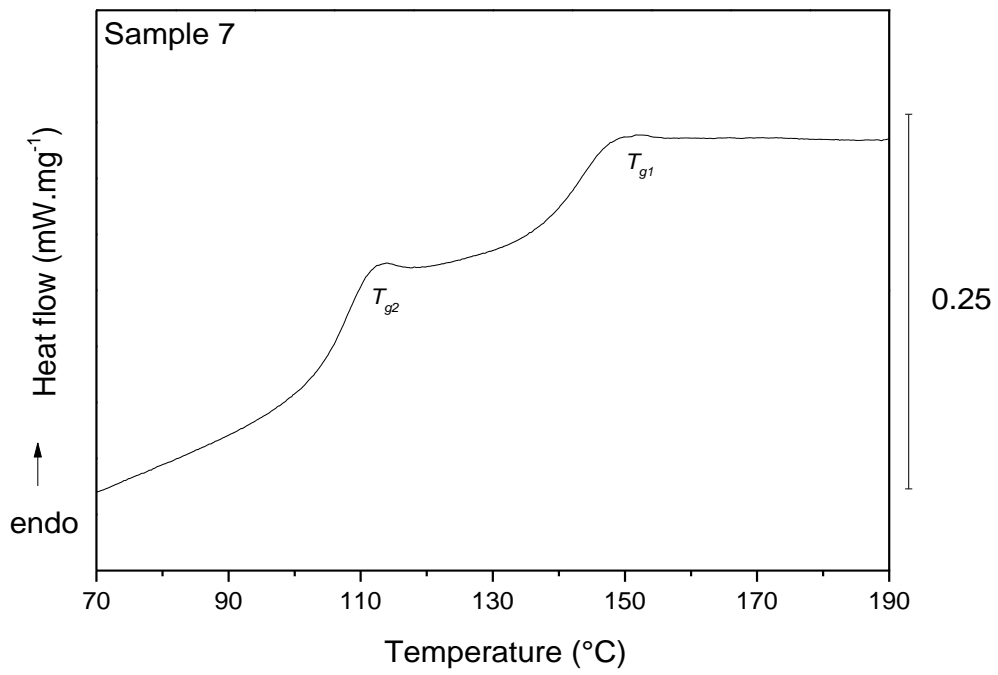
<sup>a</sup>Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip code 13565-905, São Carlos, SP, Brazil.

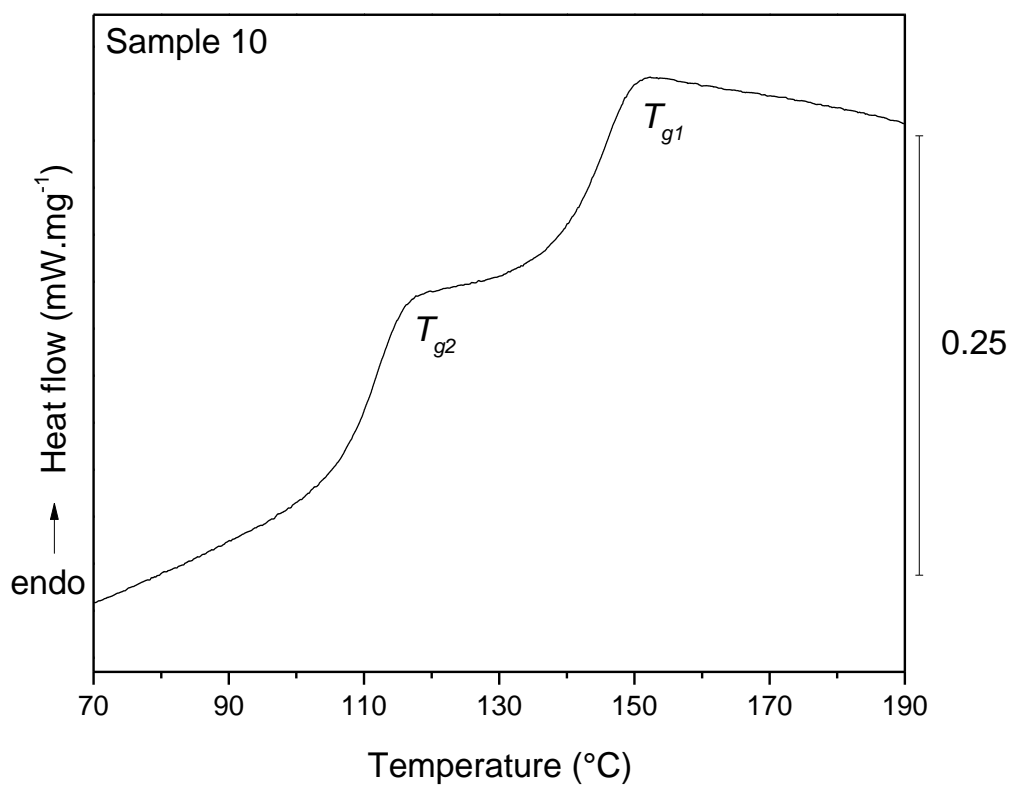
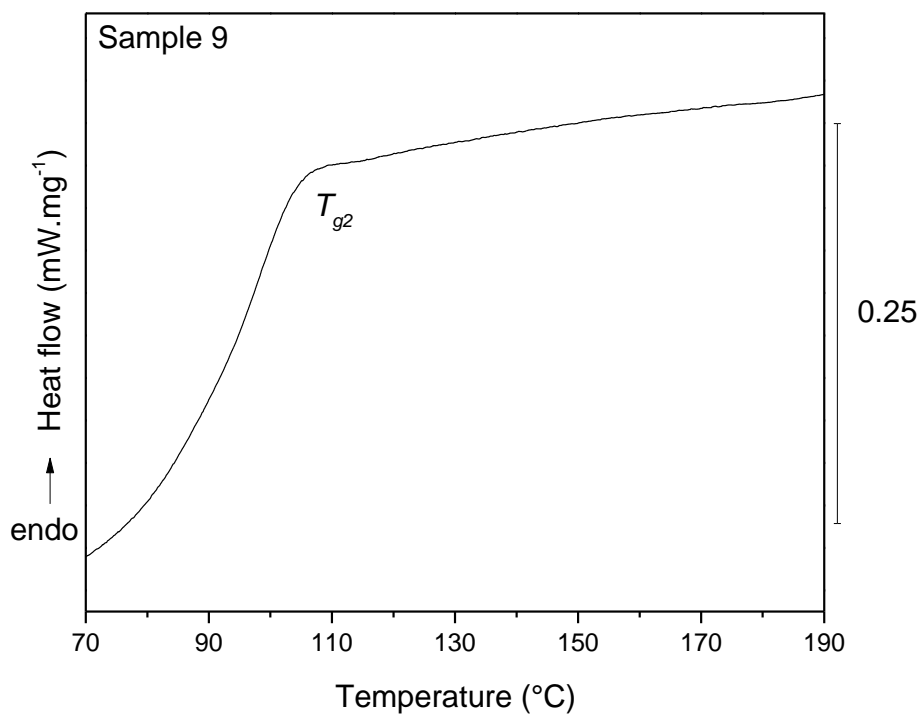
<sup>b</sup>Laboratório de Polímeros, Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip code 13565-905, São Carlos, SP, Brazil.

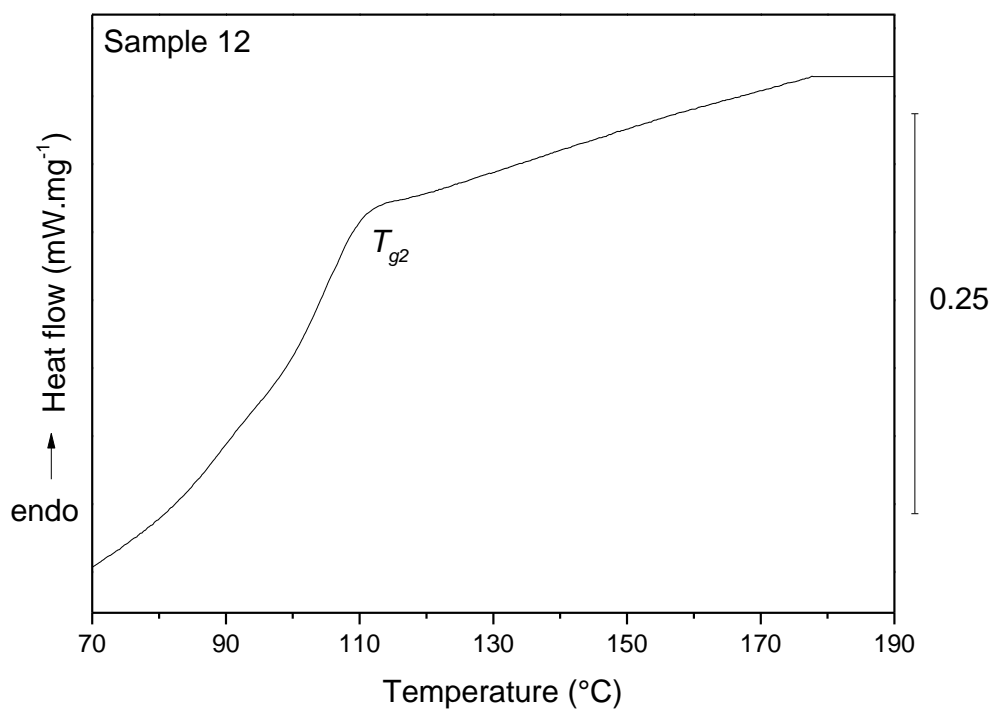
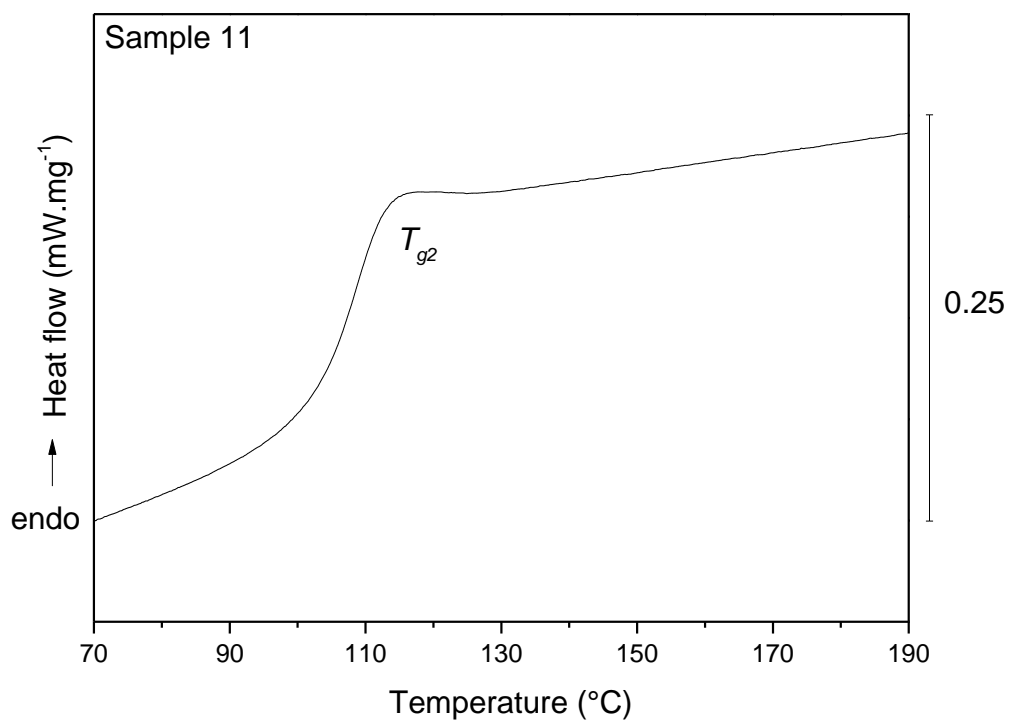
\*Corresponding author: Grupo de Análise Instrumental Aplicada (GAIA), Departamento de Química (DQ), Universidade Federal de São Carlos (UFSCar), PO Box 676, Zip code 13565-905, São Carlos, SP, Brazil.

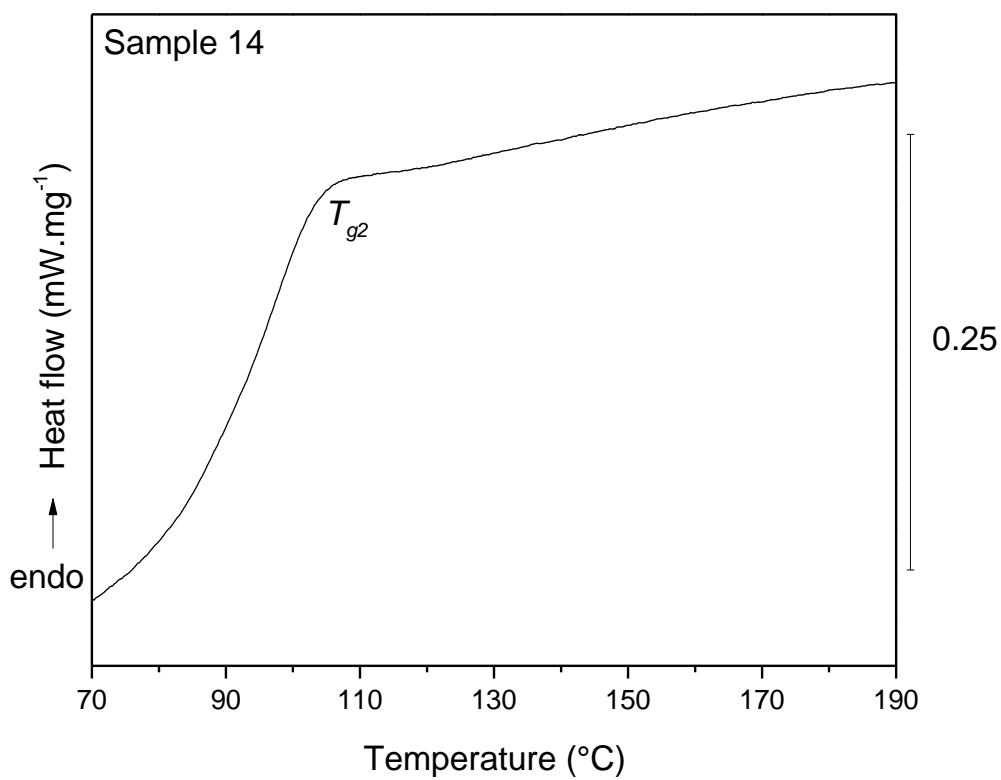
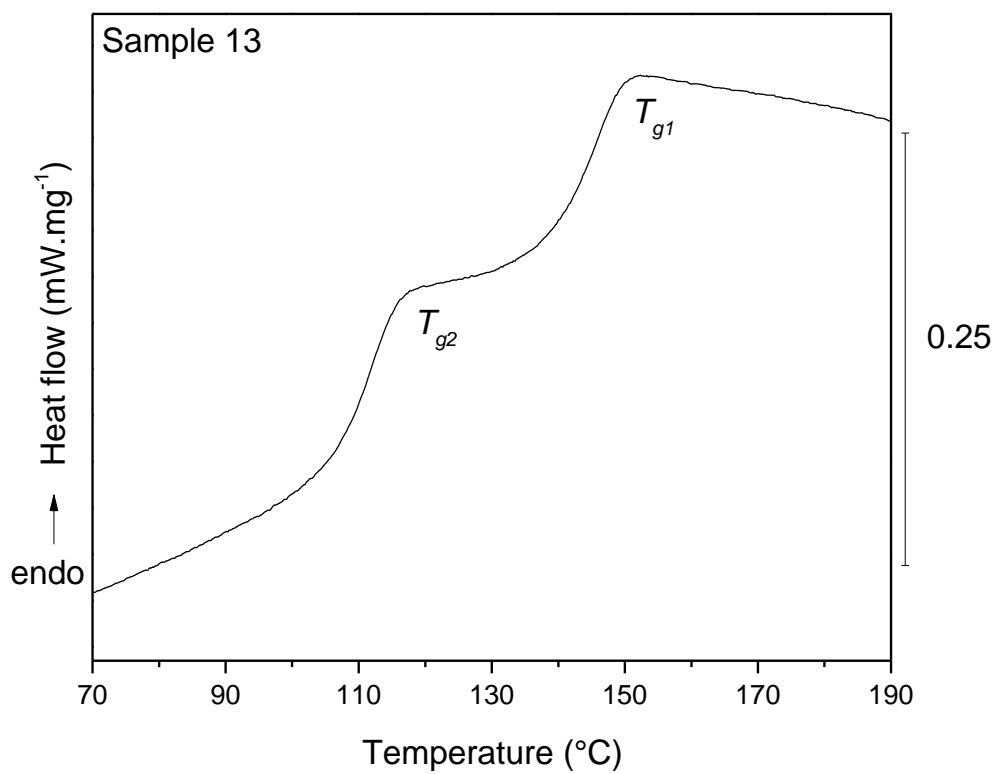
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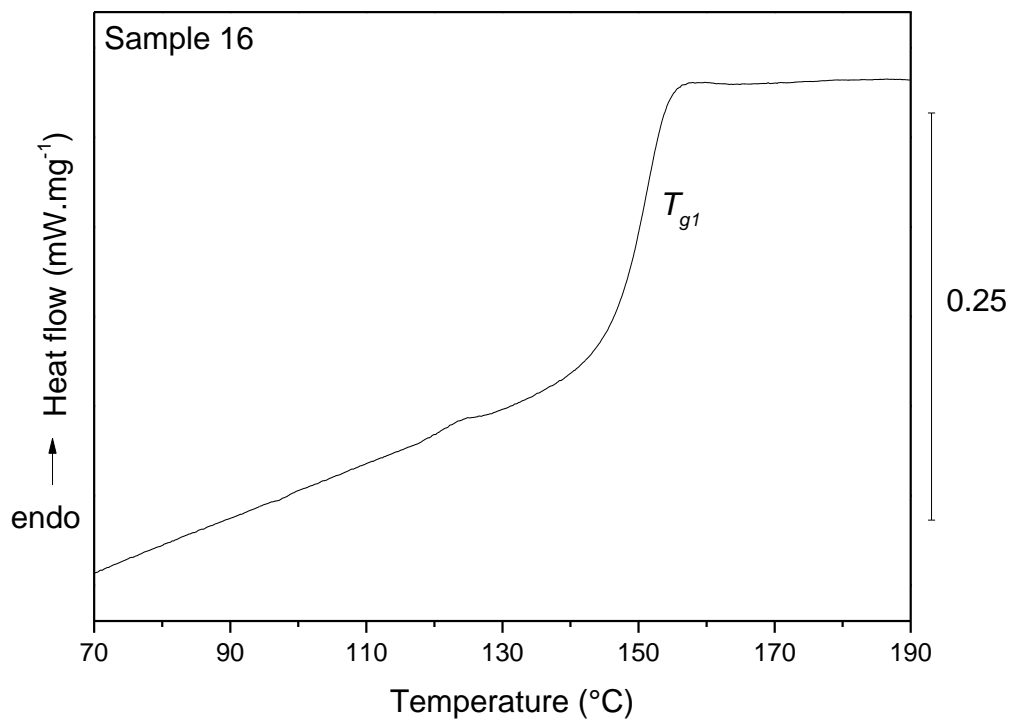
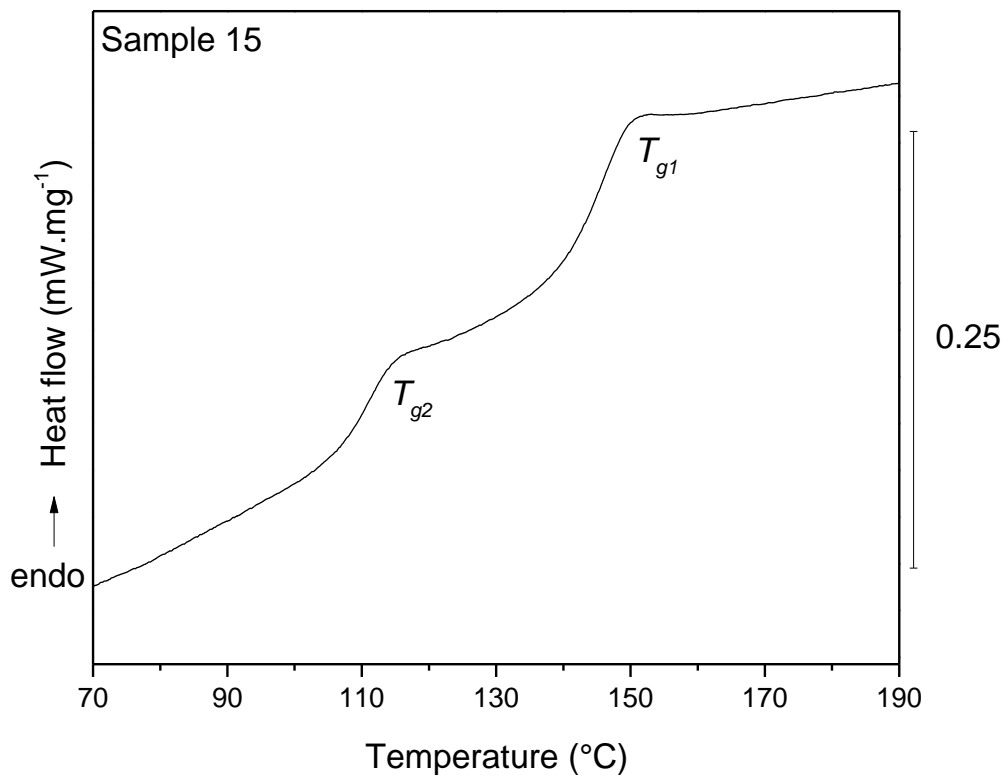
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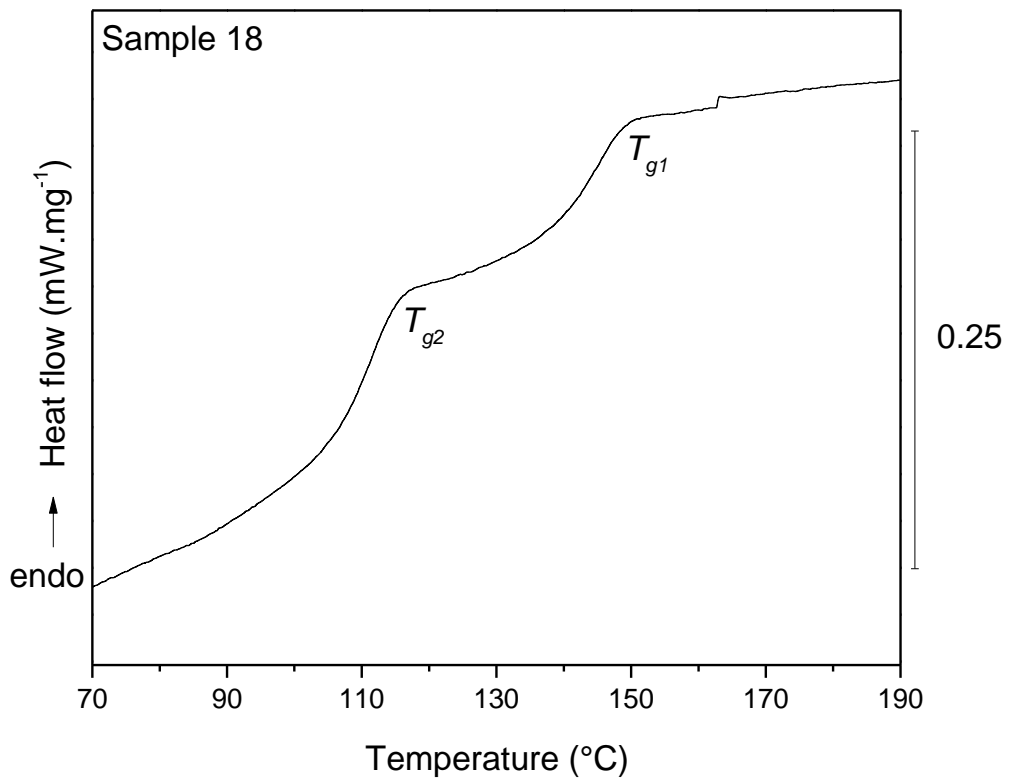
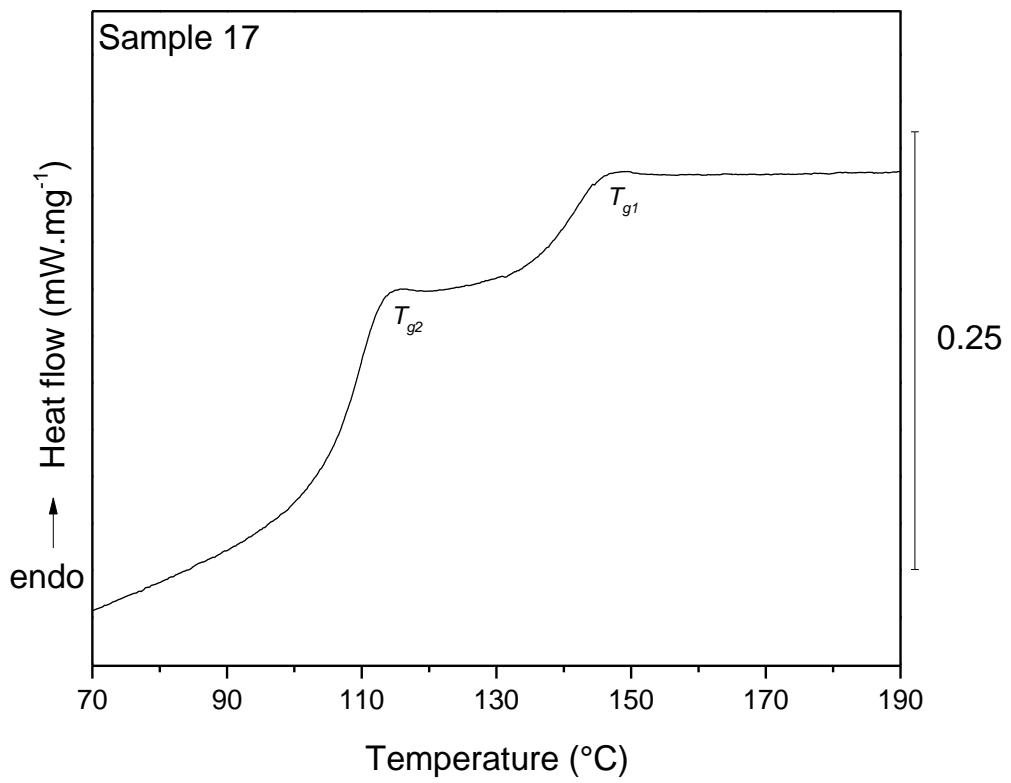


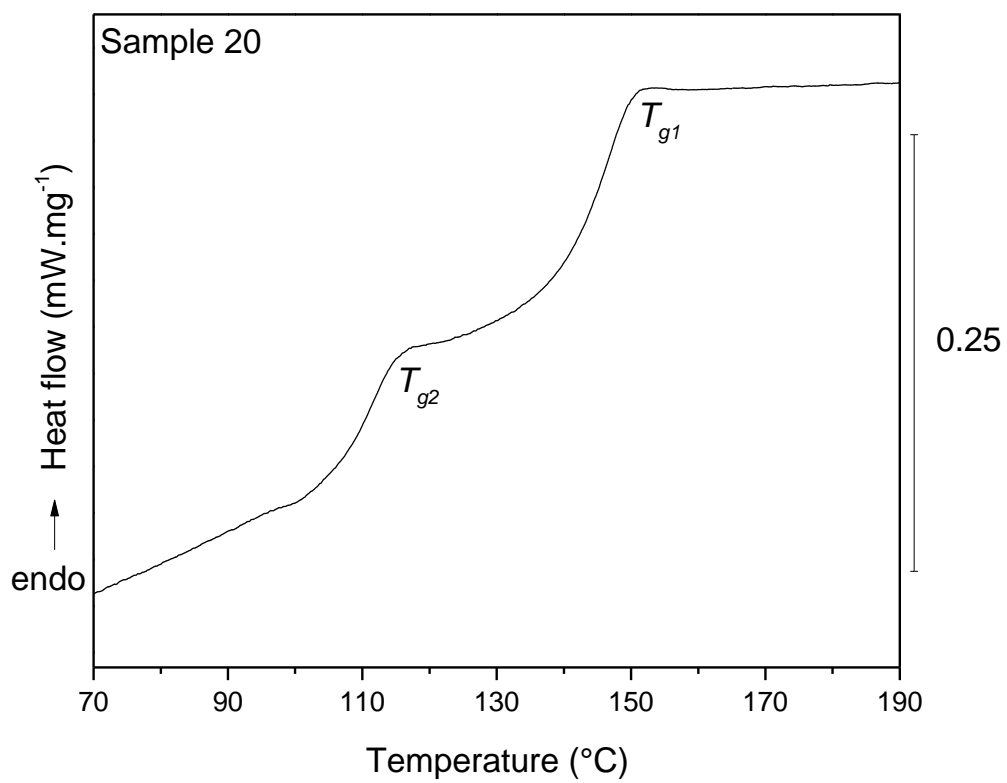
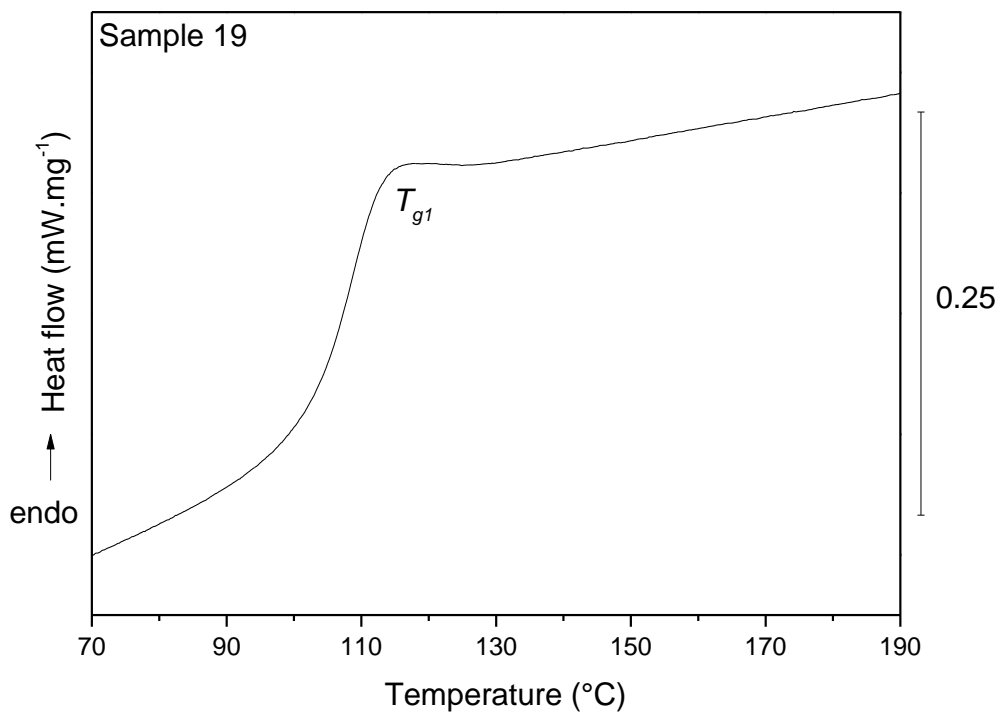




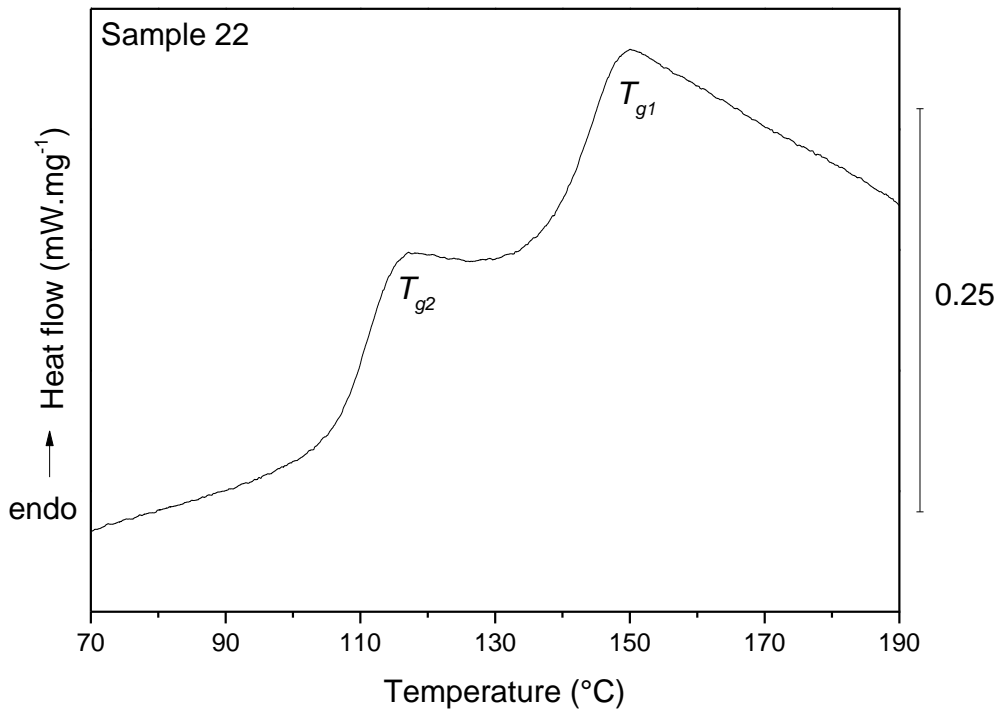
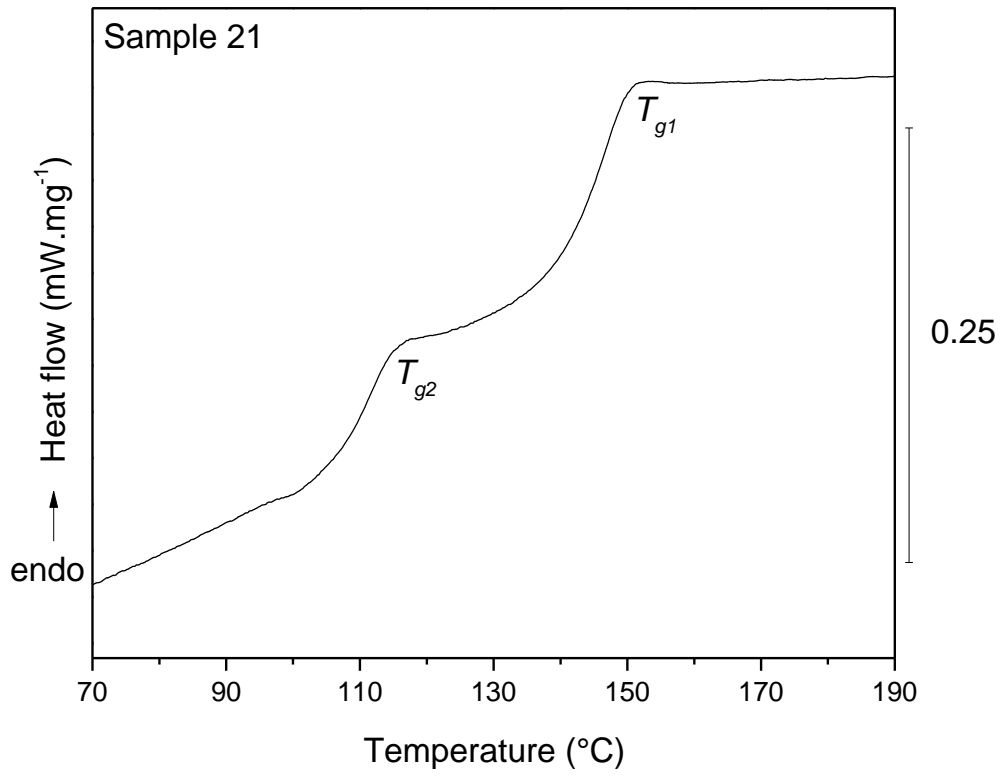


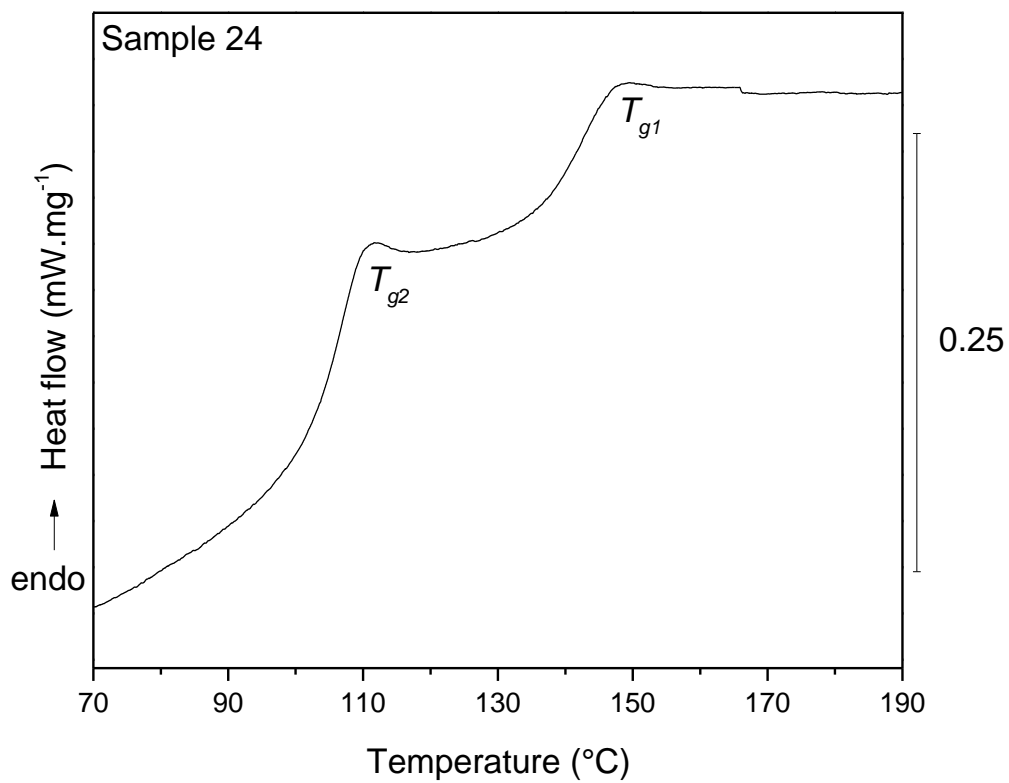
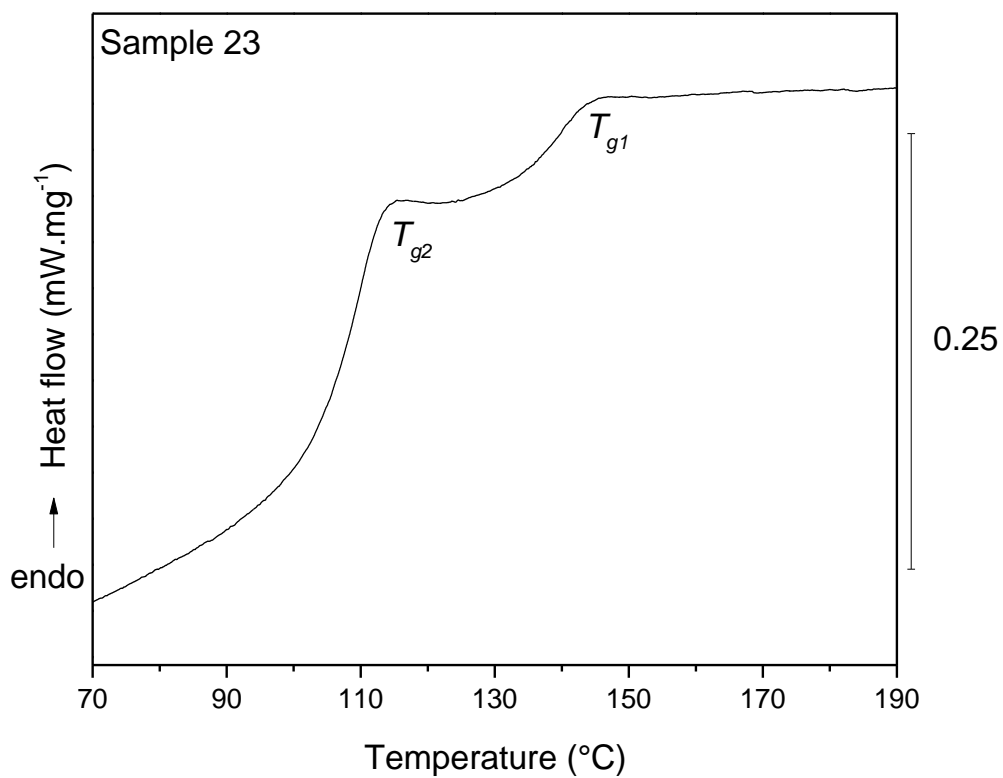


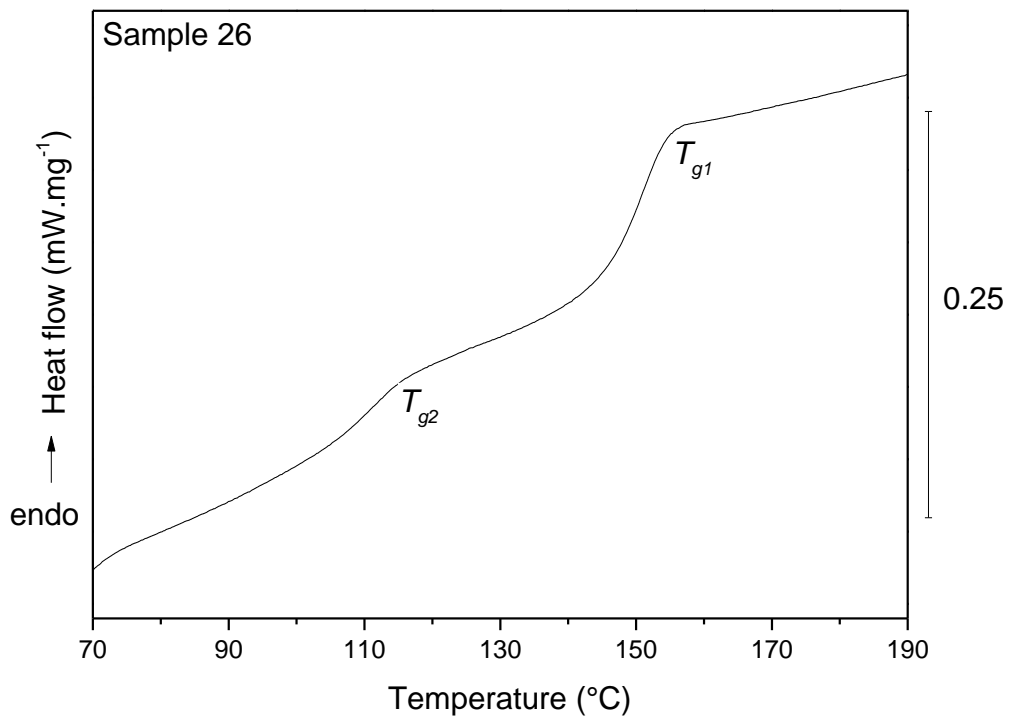
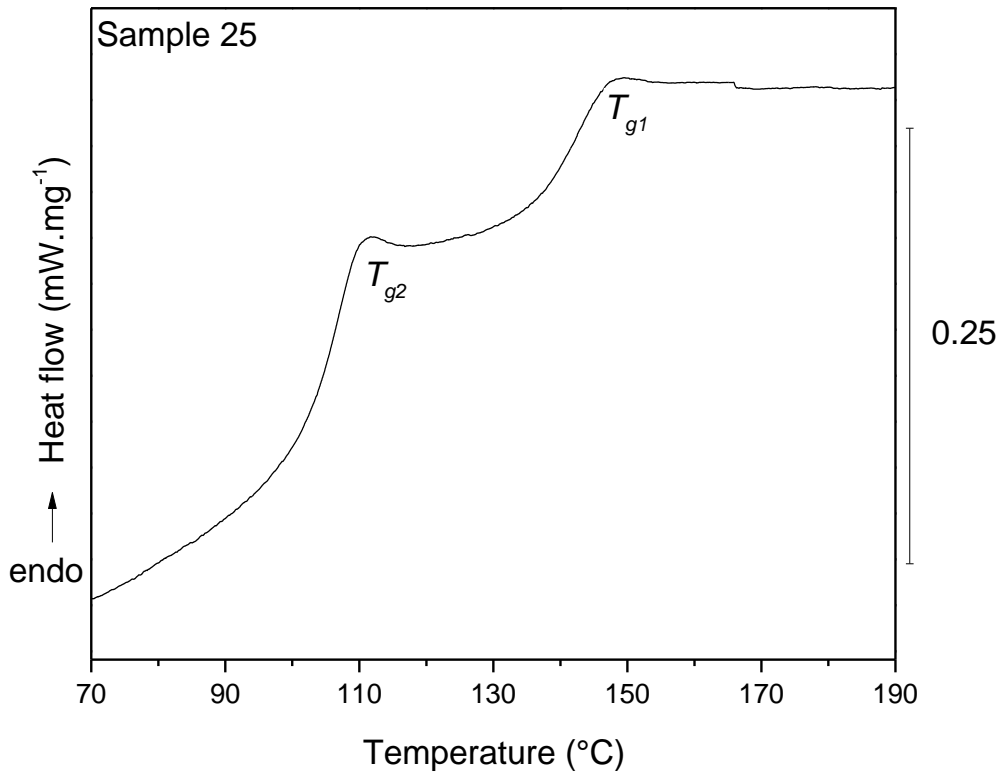


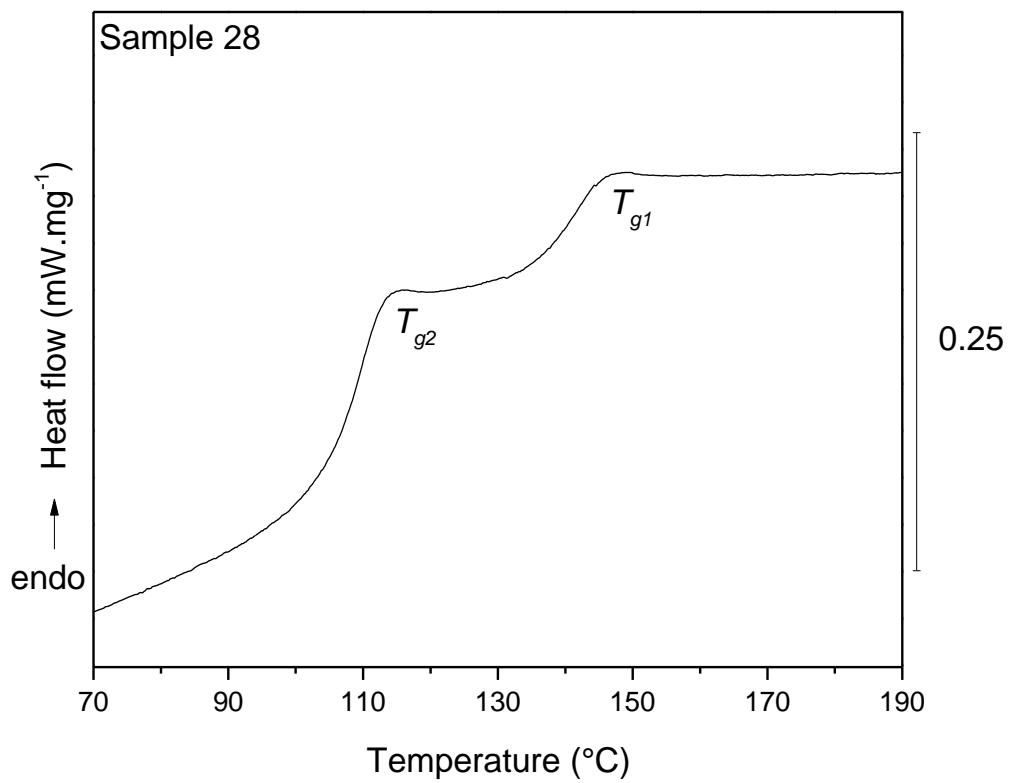
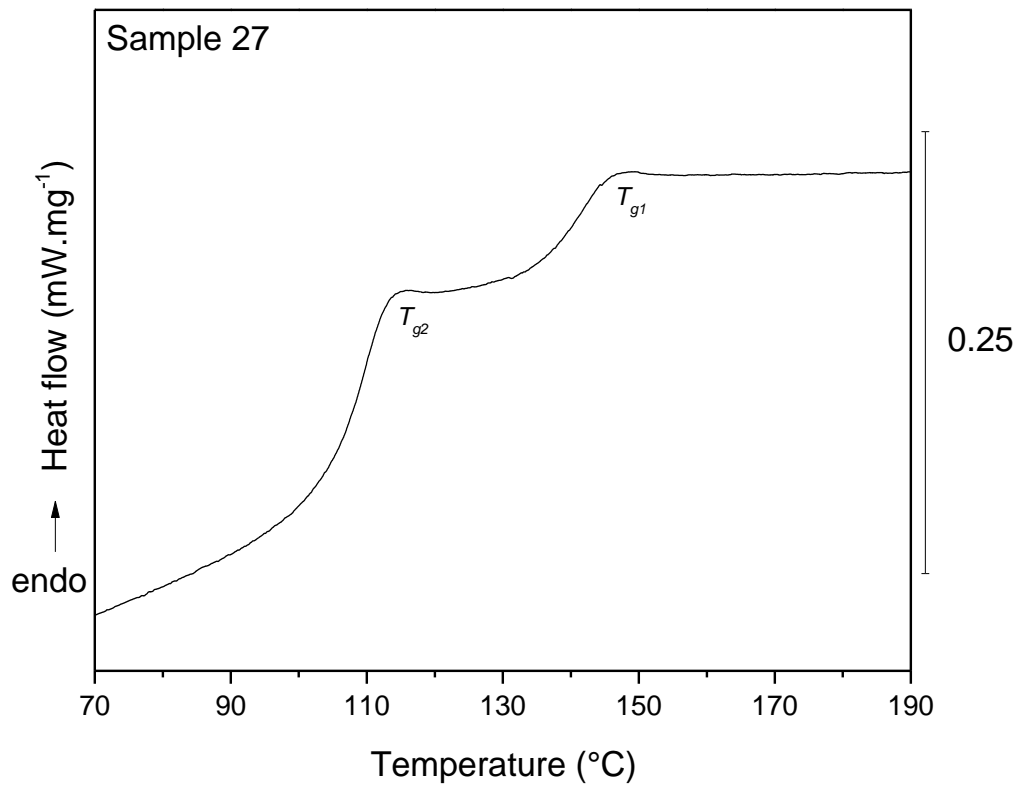


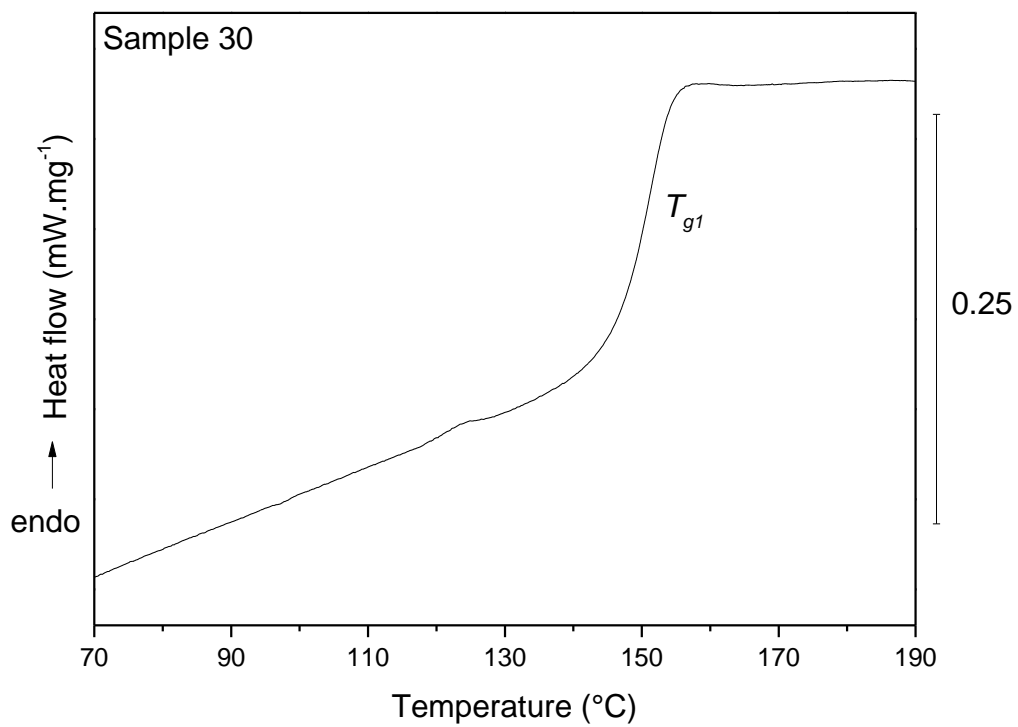
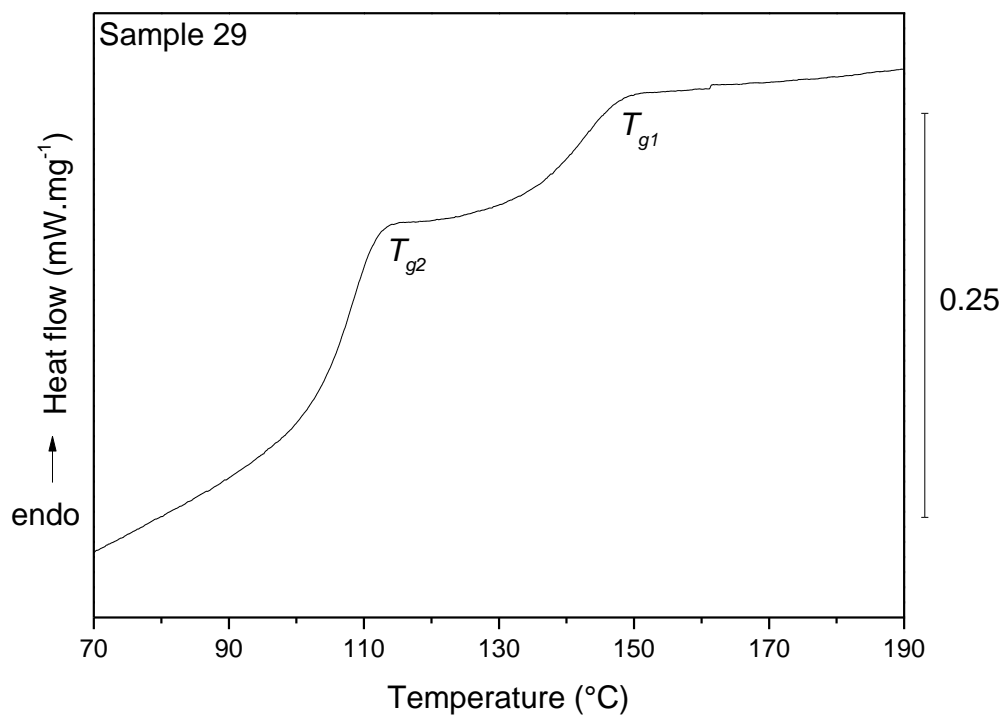


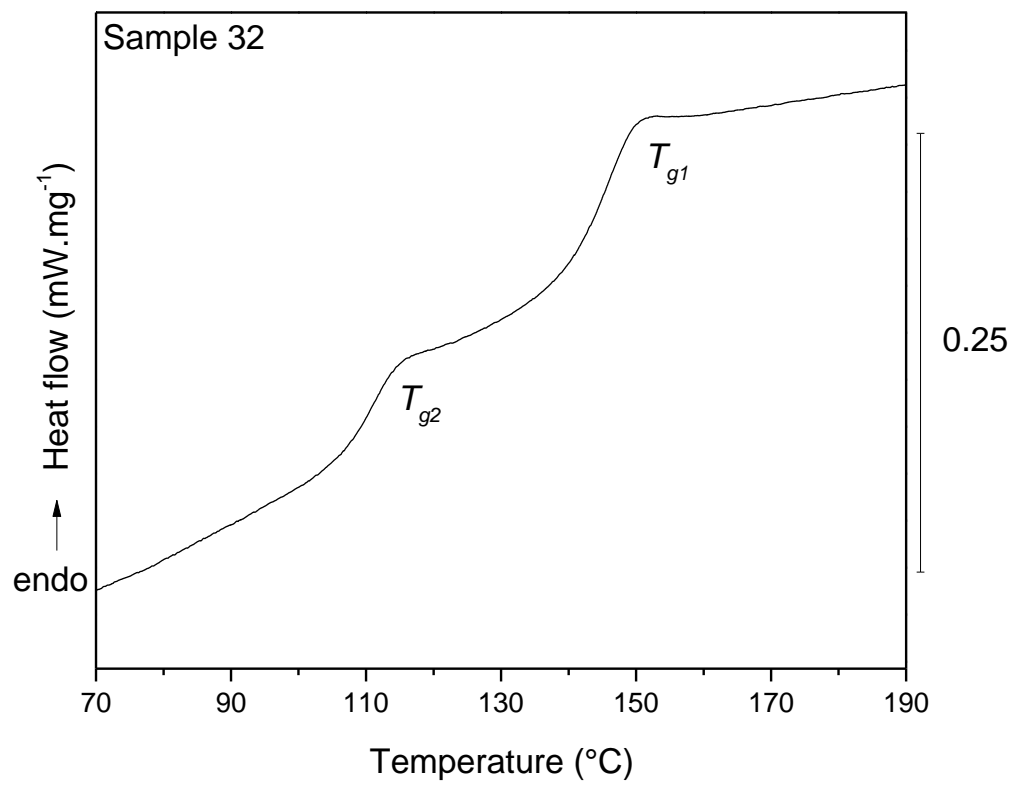
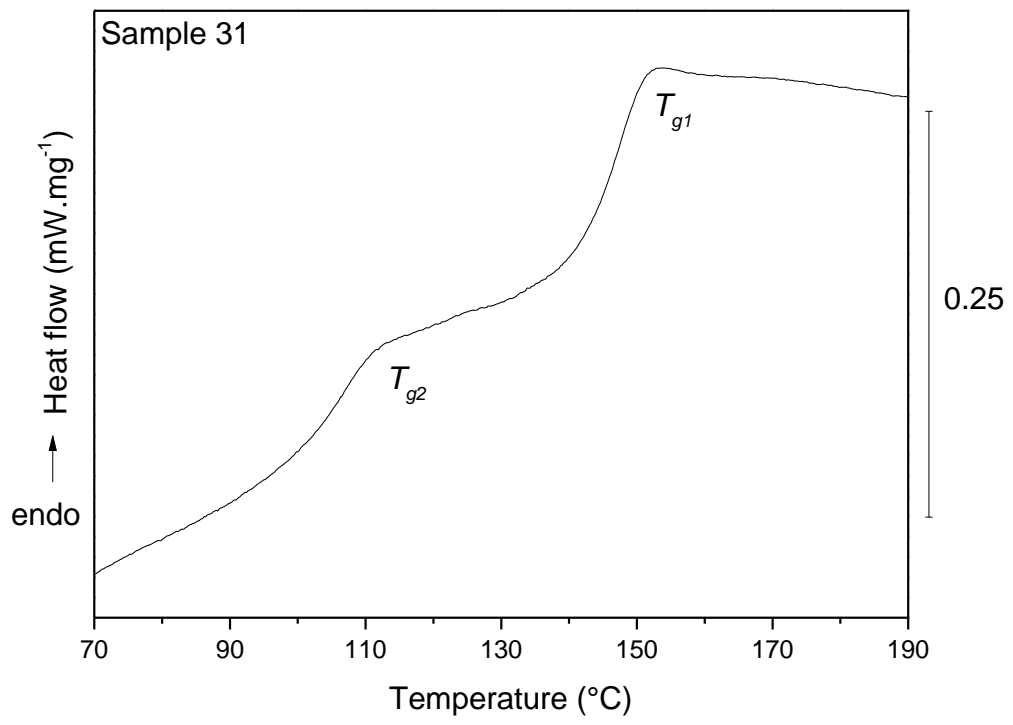


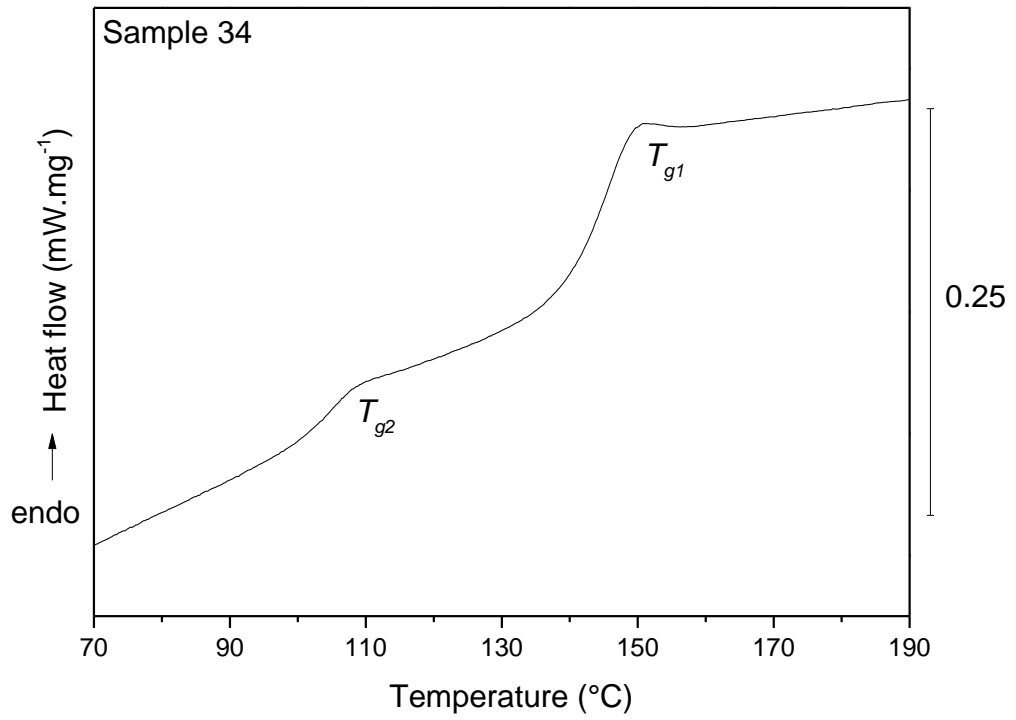
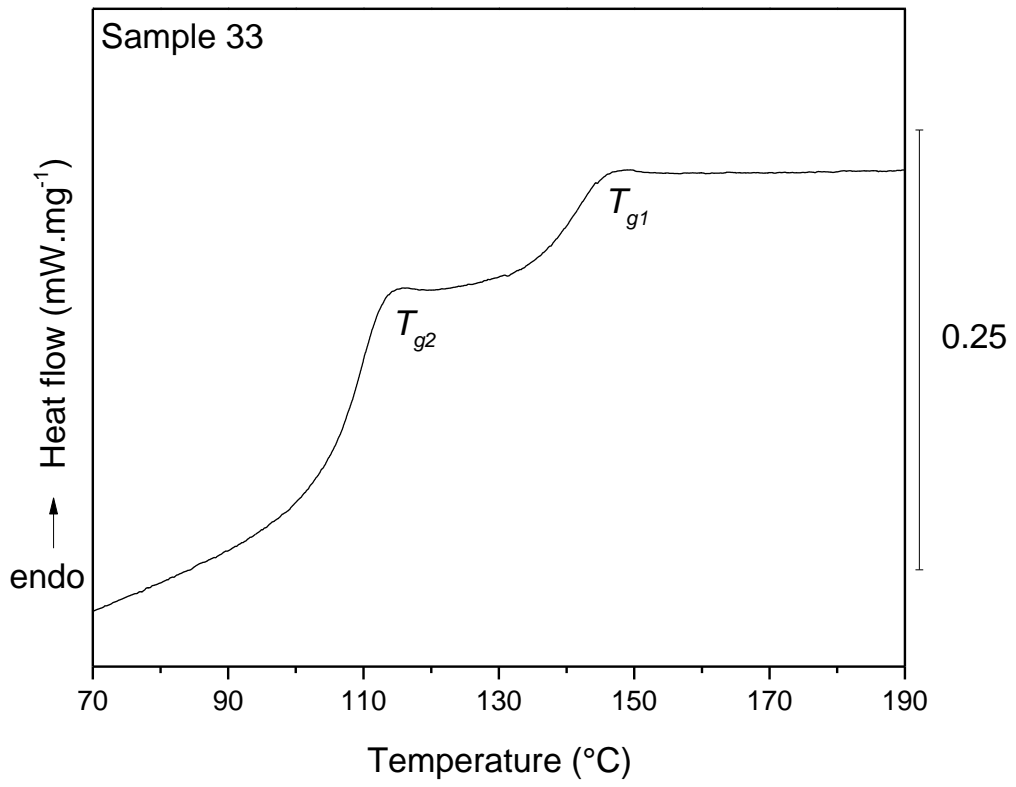


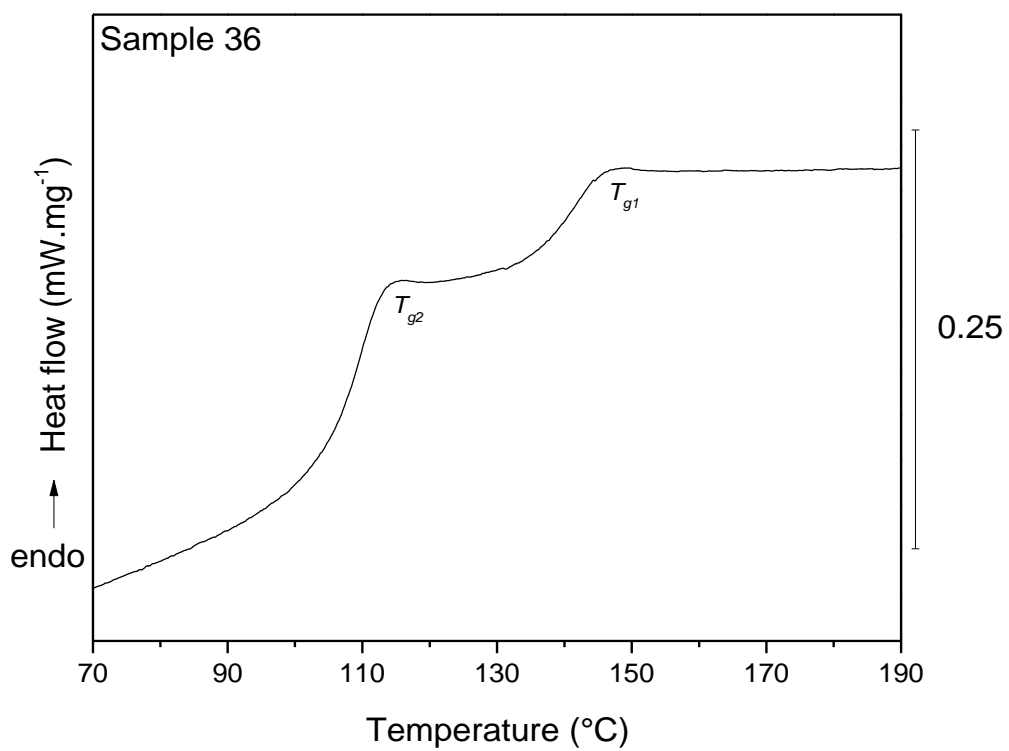
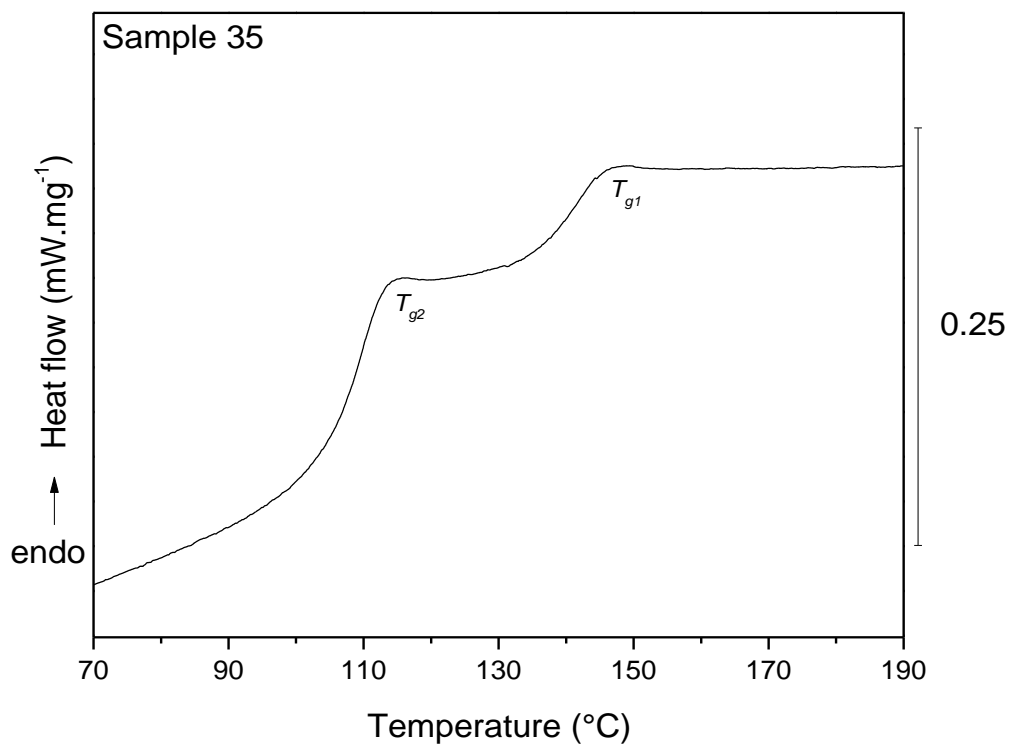




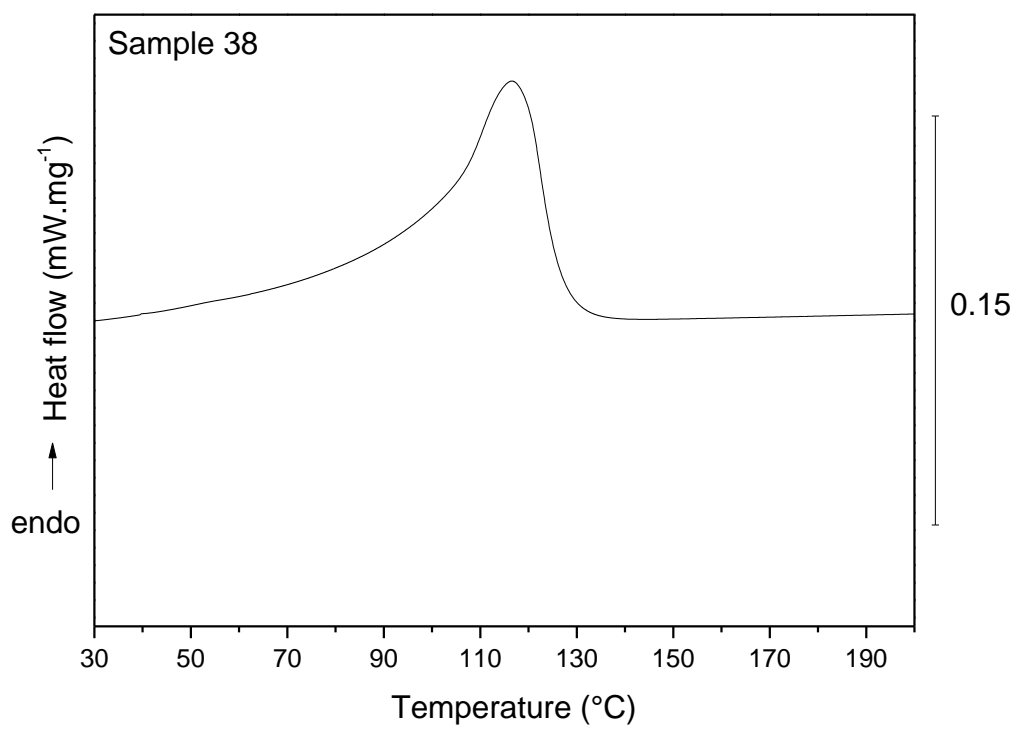
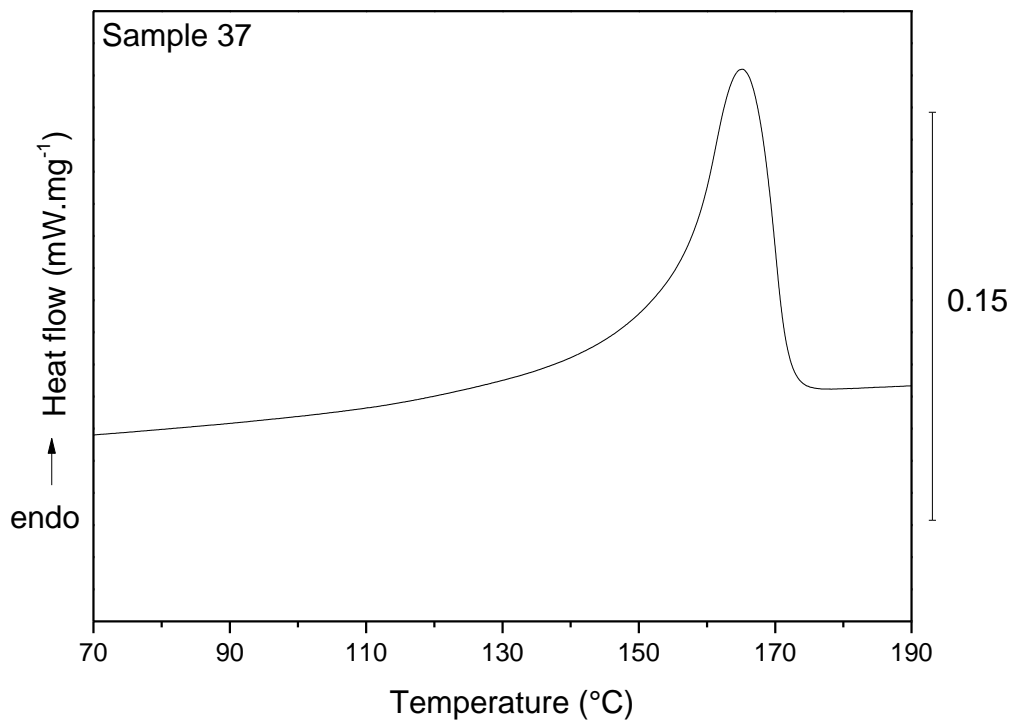


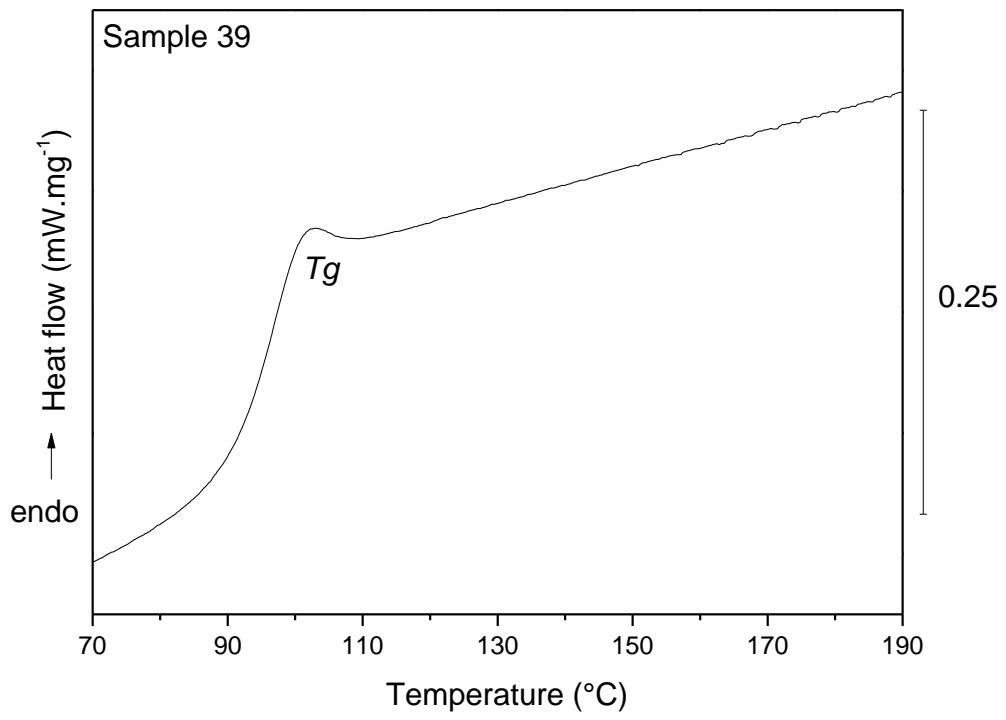








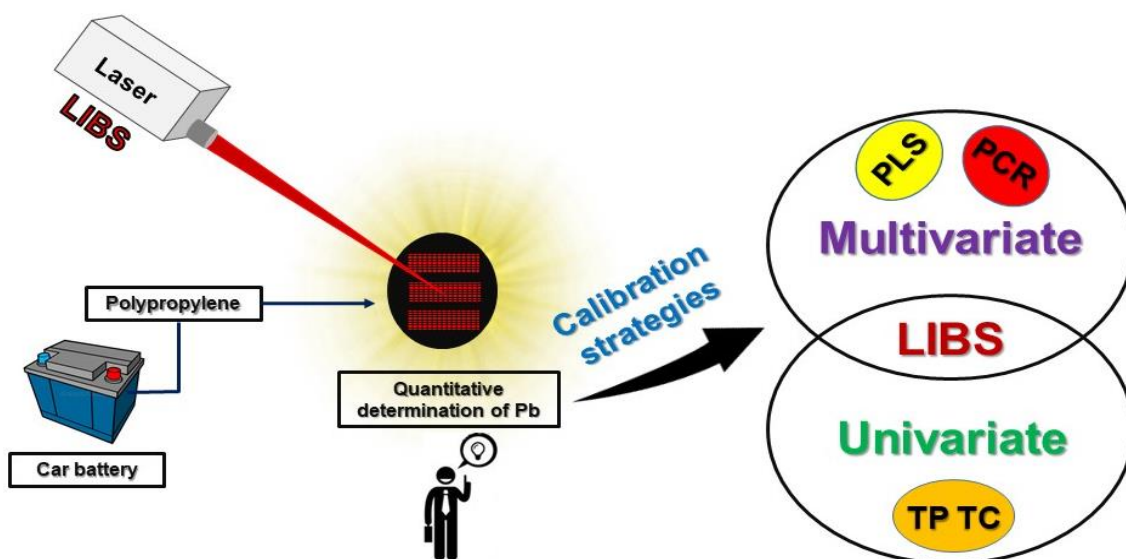




## **Chapter 4 – Unpublished Results**

#### 4.1 Calibration strategies for determination of Pb content in recycled polypropylene from car batteries using laser-induced breakdown spectroscopy (LIBS)

Vinicius Câmara Costa, Matheus Lima de Mello, Diego Victor Babos, Jeyne Pricylla Castro and Edenir Rodrigues Pereira-Filho



## **Abstract**

In this study, a new univariate calibration strategy named two-point calibration transfer (TP CT) was applied to solid sample analysis by laser-induced breakdown spectroscopy (LIBS). In addition, the strategies of multivariate calibration, known as partial least squares (PLS) and principal component regression also were evaluated. The proposed calibration strategies were used for direct determination of Pb in recycled polypropylene from car batteries. The %trueness values calculated by comparing the predicted concentrations for PLS, PCR and TP CT calibrations strategies were evaluated from reference concentrations obtained by inductively coupled plasma emission spectrometry (ICP OES). For PLS the trueness value ranged of 74 to 139%, for PCR ranged of 74 to 123% and for TP CT ranged of 100 to 127%, showing in general the good predictive capacity of the proposed strategies. In addition, the relative standard deviation (%RSD) values for PLS ranged of 3 to 37%, for PCR ranged of 5 to 30% and TP CT ranged of 6 to 21%. In general, the values of the % trueness and %RSD for TP CT strategy were best. The calibration strategies proposed in this study is highly compatible with LIBS, and it may contribute to minimizing matrix effects in direct solid analyses in complex samples as polymers

**Keywords:** LIBS; matrix effects; polymers; multivariate calibration; two-point calibration transfer.

## 1. Introduction

Polypropylene (PP) is a polymer produced from polymerization of the propylene or propene gas. It is a type of plastic that can be molded when subjected to high temperature, so being classified as a thermoplastic, which can be recycled. The PP is widely used in various applications, due to its characteristics as low cost, good chemical, mechanical and thermal resistance [1,2]. The automotive industry is one of the main segments where the PP is employed, as casing material in car batteries. However, other plastics of greater resistance as acrylonitrile-butadiene-styrene (ABS) has been becoming more widespread. Thus, tons of PP have been generated after the end of the useful life of batteries, and as a form of reuse are used in the manufacture of other materials such as, chairs, cups and plates [3].

Recycling is a viable alternative to minimize the generation of PP solid waste from car batteries. However, these materials may have high concentrations of lead (Pb) due to the battery constituents [4]. Thus, the monitoring of the Pb level must be carried out before the materials are sent for recycling. Generally, the determination of Pb in polymers is performed by spectroanalytical techniques as, atomic absorption spectrometry (AAS) [5], inductively coupled plasma optical emission spectrometry (ICP OES) [6] or inductively coupled plasma-mass spectrometry (ICP-MS) [7]. These techniques require the introduction of the sample in solution form, and for this, acid digestions procedures using open or closed system are employed. In general, this step of the analytical sequence is laborious, and systematic errors can also be introduced from due to contamination, sample manipulation or analytes losses by volatilization, which affect the accuracy of the final results [8,9].

In contrast to conventional sample preparation methods involving acid digestion, the direct analysis of solid samples shows up as a less laborious and attractive

alternative. In this scenario laser-induced breakdown spectroscopy (LIBS) has been gaining prominence due its attractive features such as: (i) high analytical frequency; (ii) multi elementary capability; (iii) nondestructive analysis; (iv) minimum sample preparation; (v) allows analysis under atmospheric conditions; and (vi) real-time and on-situ analysis [10,11]. LIBS is a powerful tool for qualitative analysis, however, it requires considerable effort in quantitative analysis, mainly due to matrix effects [12]. Commonly the matrix effects are more pronounced in complex samples, such as polymers, which contain in their composition different amounts of flame retardants (Al, Br, Mg, P and Sb), pigments (Ti) and loading agents (Ca) [13,14].

In order to minimize these matrix effects and allow direct analysis of the sample by LIBS, some univariate and multivariate calibration strategies have been used. Among the univariate calibration strategies more employed, stand out, matrix-matching calibration (MMC) [15], standard addition (SA) [16], internal standardization (IS) [17] and calibration-free (CF) [18]. Recently new univariate calibration alternatives have proposed, such as multi-energy calibration (MEC) [19], one-point gravimetric standard addition (OP GSA) [20] and slope ratio calibration [21]. These strategies are presenting satisfactory results for the quantitative determination by LIBS, because employ an efficient matrix-matching method between samples and standards, which minimizes the matrix effects related to the direct analysis of solids [22-24].

Multivariate calibration strategies also provide measurements with satisfactory precision and accuracy in LIBS. One of the main advantages of these methods is the possibility of proposing a calibration model in the presence of interferents. In addition, some intrinsic limitations of each multivariate method must be known, so that erroneous conclusions are not obtained in the calibration of the method. The main multivariate calibration tools applied in LIBS are partial least squares (PLS) [25],

multiple linear regression (MLR) [26], principal component regression (PCR) [27] and artificial neural networks (ANN) [28].

Given the above, this study aims to evaluate different calibration strategies for the direct determination of Pb in PP samples recycled. A new univariate calibration strategy named two-point calibration transfer (TP CT) [29] is evaluated, in addition the multivariate calibration strategies as PLS and PCR are used for comparison. This study is the first application of TP CT for polymers.

## **2. Experimental Section**

### **2.1. Instrumentation**

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 spectrometer recording spectral information from 186 to 1,042 nm. Channel spectral range (1) 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 instrument. These parameters were the laser pulse energy, ranging from 0 to 100 mJ, the gate delay, that is the time interval between the incidence of the laser pulse and the start of signal recording by the spectrometer, ranging from 0 to 2  $\mu$ s, and the spot size (diameter of laser beam), ranging from 50 to 250  $\mu$ m. The Axiom 2.5 software also manages the movement of the sample, assisted by an automated XYZ stage and a 1280 x 1024 complementary metal-oxide semiconductor (CMOS) color camera imaging system. At 1.05 ms, the software establishes the gate width, which is the time the spectrometer registers the emission signals.

An ICP OES (iCAP 7000, Thermo Scientific, Waltham, MA, USA) was used as a comparative technique for the Pb determination. Argon gas (99.996%, White Martins-Praxair,



Sertãozinho, SP, Brazil) was used to generate the plasma in all ICP OES measurements. The instrumental conditions were established as the manufacturer recommendations, as being: power (1.2 kW), plasma gas flow (15.0 L min<sup>-1</sup>), auxiliary gas flow (1.5 L min<sup>-1</sup>), nebulizer gas flow (0.7 L min<sup>-1</sup>) and sample introduction flow rate (2.1 ml min<sup>-1</sup>). The emission lines monitored were Pb 216.9 and 220.3 nm.

## **2.2 Reagents and solutions**

Ultrapure water (18.2 MΩ cm resistivity) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) was used to prepare all the solutions. Nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) were previously purified using a sub-boiling distillation system Distillacid™ BSB-939-IR (Berghof, Eningen, Germany), for digestion of the samples. All glassware and polypropylene flasks were washed with soap, soaked in 10% v/v HNO<sub>3</sub> for 24 h, and rinsed with deionized water prior to use.

### **2.2. Strategy of the sample preparation to analyze samples by LIBS and ICP OES**

The crushed PP samples were provided by a recycling company, and they had different sizes and shapes with masses ranging from 50 to 200 mg. This mass is sufficient for analysis by LIBS, however it is not enough to perform an acid digestion in triplicate (n=3) for further analysis by ICP OES. As, LIBS exhibits severe problems with calibration, the use of the information acquired in combination with reference techniques as ICP OES is mandatory. In this sense, the samples were submitted to a single step of preparation aiming at sequential analysis by LIBS and ICP OES. The samples were prepared according to the following procedure, and Figure 1 shows a pictorial description of steps. A total of 10 samples encoded between S1 to S10 were obtained from this procedure.

a) Several fragments of polymers were confined in an aluminum holder (central diameter 2.4 cm, 3.0 mm thick) up to complete a final mass of 1.5 g;

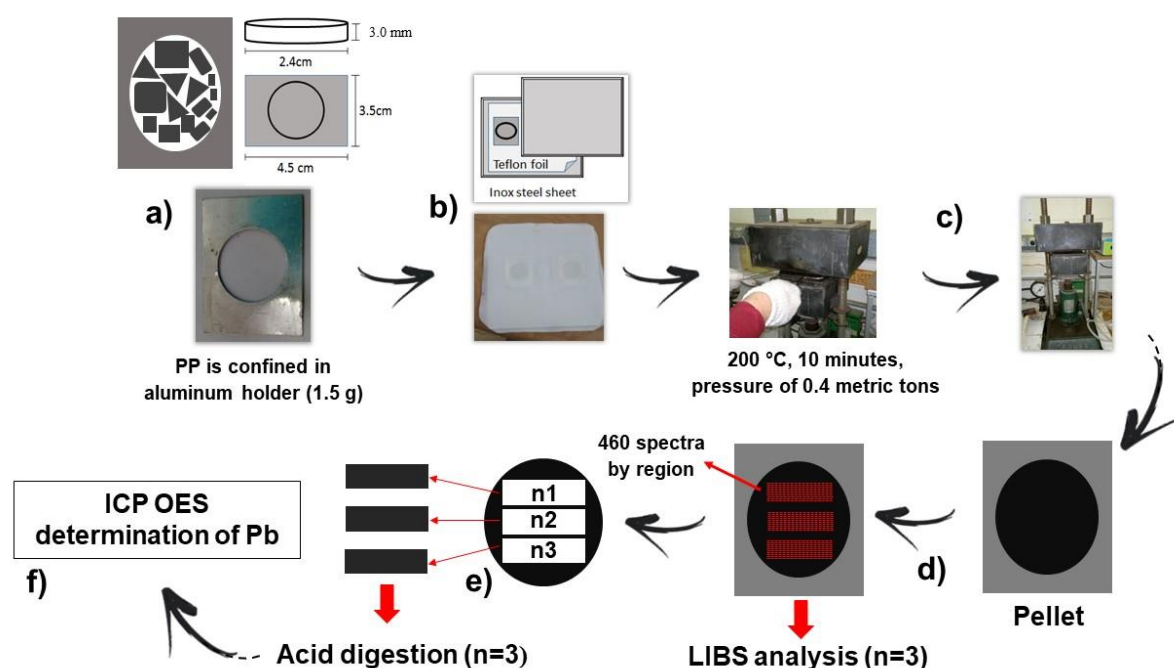
(b) The aluminum holder was placed between two pieces of Teflon foil and the full set-up was packed between two stainless steel plates;

(c) After this, the material was placed in a thermopress (Caver Inc. model C Wabash, IN, USA) and it was heated at 200°C over 10 minutes, with a pressure of 0.4 metric tons (to avoid molten polymer losses);

(d) After cooling, the pellets were ready for analysis by LIBS. Three different regions (n=3) were analyzed and a total of 460 spectra were obtained from each region, totalizing 1360 spectra per samples;

(e) Afterwards, the regions (n=3) analyzed by LIBS were carefully cut with the aid of a ceramic knife. A portion of each region (n=3) was removed and an acidic digest was performed;

(f) Finally, the digested samples were analyzed by ICP OES for the Pb determination. These values were used as references for proposition of the calibration strategies by LIBS.



**Figure 1.** Pictorial description of the experimental procedure used for sample preparation and data collection.

### 2.3. Sample preparation for ICP OES analysis

ICP OES was used as a comparative technique to evaluate the accuracy of the LIBS proposed method. Approximately 100 mg of sample was directly weighted in Teflon-PFA digestion vessels followed by the addition of 8 mL of acid mixture of HNO<sub>3</sub>/HCl (3:1 v/v). The

samples were digested in an assisted microwave oven (Speedwave xpert, Berghof, Germany) with 60 mL volume-closure bottles (DAP 60). The heating program was composed of the following steps: (1) temperature ramp up to 200°C in 5 minutes, (2) kept at 200°C for 10 minutes and (3) 5 min to reach 230°C and (4) 20 min hold at 230°C. After the digested, the solutions were transferred to falcon tubes, and high-purity water was added to achieve a total volume of 50 mL. In order to evaluate the accuracy of the digestion procedure, a certified reference materials (CRM) ERM-EC681k of polyethylene was submitted to the same procedure.

#### **2.4. Multivariate optimization of LIBS instrumental parameters**

In the LIBS system used, it was possible to adjust two parameters: laser fluence (FL) and delay time (DT). These variables play an important role in the quality of the spectral information acquired. In this case, a central composite design (CCD) was used to optimize these variables. The laser pulse fluence was tested at five levels (1448, 1811, 2699, 3514 and 3820 J·cm<sup>-2</sup>) and delay time was also tested at five levels (0.5, 0.7, 1.2, 1.7 and 1.9 μs). A total of 11 experiments were carried including triplicate in the central point, that was used to estimate the *pure error* (PE) of the models proposed. A single sample was used to optimize instrumental conditions used in LIBS analyses, and a total of 112 spectra per experiment were obtained at different parts of the sample surface. The analyzes were made in raster mode.

The area, height and signal-to-background ratio (SBR) was used as response to CCD. A mathematical approach proposed by Derringer and Suich [30], which is based on desirability functions applied to optimize multi-response experiments, was used in this study. This approach first converts each response into an individual desirability value ( $d_i$ ), which ranges between  $0 \leq d_i \leq 1$ . In this case,  $d_i = 1$  corresponds to a desired response (the highest area, height and SBR), while  $d_i = 0$  represents a undesired response (the lowest area, height and SBR). Later, the  $d_i$  was combined into one single response call overall desirability (OD) [31]. Moreover, twelve normalization modes [32] were employed for data processing, and each

normalization mode was tested from the adjustment of the best regression model using the analysis of variance (ANOVA).

## **2.5. Calibration strategies**

Three calibration strategies were evaluated, including two multivariate strategies using PLS and PCR and one new univariate strategy named two-point calibration transfer (TP CT). For the proposition of the PLS and PCR models, several emission lines of Pb were selected, and the area and height of the signal were calculated for each one. For each pellet, around 460 spectra were acquired to obtain a representative analysis, and 12 normalization modes were calculated. In function of each normalization type, 12 models PLS and PCR were evaluated. The best normalization was selected through lowest standard error of cross validation (SECV).

For calibration strategy using TP CT, is necessary the use of a standard, that can be a certified reference material or even a sample. In this case, it was used the sample S10 that present 0.20% w/w Pb. This sample was chosen as the standard because, it has an intermediary concentration between the all samples investigated. First, the 460 spectra obtained for each pellet (n=3) are divided in two sets (two points): one with 100 spectra and other one with 360 spectra. These sets were separately summed (raw data), where the intensity of point 2 is higher than point 1. After this, the area and height of emission lines of Pb were selected. So, is made a calibration curve with two points for each emission line evaluated, where in the axis x is the number of spectra (100 and 360) and in the axis y is the intensity of both points. This is made for an interrogated sample and for the sample chosen as standard, combining the slopes of both curves ( $slope_{sample}$  and  $slope_{std}$ ) and the Pb standard concentration (known) ( $C_{std}$ ) to calculate the unknown sample concentration ( $C_{sample}$ ), as showed in Eq. (1).

$$C_{sample} = C_{std} \times \frac{Slope_{sample}}{Slope_{std}} \quad \text{Equation 1}$$

## 2.6 LIBS data handling

Aurora (Applied Spectra) and National Institute of Standards and Technology (NIST) were used for emission lines identification of Pb. All spectra obtained by LIBS were first normalized/standardized using two homemade routines calculated using MATLAB® 2018a (The Mathworks Inc., Natick, MA, USA).

i) The first routine, *libs\_treat*, was applied to calculated 12 different modes of normalization: (norm\_1) average of all spectra; (norm\_2) signal normalization by the norm, then, average over all spectra; (norm\_3) signal normalization by the area, then, average over all spectra; (norm\_4) signal normalization by the highest signal, then, average over all spectra; (norm\_5) sum of all spectra; (norm\_6) signal normalization by the norm, then, sum over all spectra; (norm\_7) signal normalization by the area, then, sum over all spectra; (norm\_8) signal normalization by the highest signal, then, sum over all spectra; (norm\_9) signal normalization by C I 193.09 nm emission line, then, average over all spectra; (norm\_10) signal normalization by C I 193.09 nm emission line, then, sum over all spectra; (norm\_11) signal normalization by C I 247.85 nm emission line, then, average over all spectra; (norm\_12) signal normalization by C I 247.85 nm emission line, then, sum over all spectra [32].

ii) The second routine, *libs\_par2*, was used to calculate the peak area (sum of signals) and peak maximum (height of signal) of a selected region of the spectra for Pb emission lines. With these values of area and height of this selected region, the models can be calculated.

## 3. Results and discussion

### 3.1 Reference method by ICP OES

After acid digestion of the samples, the determinations of Pb were obtained by ICP OES. The certified reference material of polyethylene ERM-EC681k which have a certified value of  $98 \pm 6 \text{ mg kg}^{-1}$  of Pb, was employed for evaluation of the accuracy of the digestion

procedure. Using the proposed procedure of digestion, the concentration of Pb found was  $94 \pm 9 \text{ mg kg}^{-1}$  ( $n=3$ ). Statistical evaluation, using Student t-test, showed there is no significant difference between values obtained and the certified value at 95% confidence level, confirming the accuracy of this procedure. In this way the values of references by ICP OES can be used with reliability for the proposition of the strategies of calibration by LIBS. According to the values obtained by ICP OES the samples concentrations (%w/w  $\pm$  standard deviation) were: S1 ( $0.213 \pm 0.016$ ); S2 ( $0.368 \pm 0.015$ ); S3 ( $0.172 \pm 0.012$ ); S4 ( $0.214 \pm 0.009$ ); S5 ( $0.146 \pm 0.014$ ); S6 ( $0.184 \pm 0.005$ ); S7 ( $0.178 \pm 0.013$ ); S8 ( $0.167 \pm 0.013$ ); S9 ( $0.125 \pm 0.033$ ); and S10 ( $0.205 \pm 0.008$ ).

### **3.2. Multivariate optimization of LIBS instrumental parameters**

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 [33]. In this context, the instrumental parameters of the LIBS must be optimized in order to minimize undesired effects during the analyzes. Thus, the instrumental conditions of the LIBS were studied in detail, and one representative sample was used to optimize the variables laser pulse fluence and delay time, using a CCD.

As response to CCD, the  $di$  value was obtained from signal area, height and SBR using the most intense emission line of Pb I 405.78 nm. Subsequently, the  $di$  values were combined into a single response. This process was repeated for each normalization and 12 regression models were calculated. The best normalization mode was selected through the regression model with the best adjustment. Table 1 presents the operating conditions for all the experiments performed, i.e., the eleven experiments that correspond to the selected experimental design, including triplicate at the central point, and the responses in function of the OD using the best normalization mode.

The ANOVA evaluation showed that normalization 3 presented the best regression model. In normalization 3 the signal is normalized by the individual area and averaged over  $n$  pulses. The model was generated in function of OD to obtain the best description of the

experimental region and six coefficients  $b_0$  *constant*,  $b_1$  (FL) and  $b_2$  (DT) *linear coefficient*,  $b_1^2$  (FL)<sup>2</sup> and  $b_2^2$  (DT)<sup>2</sup> *quadratic coefficients*, and  $b_{12}$  (DT x FL) *interaction coefficients*, were calculated. The coefficients  $b_2$  (DT) and  $b_{12}$  (DT x FL) were not significant at the 95% confidence level, thus, the non-significant coefficients were removed, and the model was calculated again.

The new model calculated was statistically significant, by comparing *the mean square of regression* (MSR) and *mean square of residue* (MSr), the  $F_{\text{calculated}}$  (188.85) being 37-fold higher than the  $F_{\text{tabulated}}$  (5.12) at the 95 % confidence level. In addition, the proposed model do not presented lack of fit because the  $F_{\text{calculated}}$  (0.513) for ratio between *mean square of lack of fit* (MSlof) and *mean square of pure error* (MSpe) was lower than the value of  $F_{\text{tabulated}}$  (19.37) at the 95 % confidence level. Table 2 shows the final ANOVA results for the optimization of instrumental parameters.

**Table 1.** Matrix of central composite design (CCD) with the variables evaluated for LIBS and results obtained from overall desirability (OD) for normalization 3.

Experiment	Laser pulse fluence		Delay time		OD
	Coded	Real (Jcm <sup>-2</sup> )	Coded	Real/ (μs)	
1	-1	1811	-1	0.7	0.09
2	1	3514	-1	0.7	0
3	-1	1811	1	1.7	0.54
4	1	3514	1	1.7	0.54
5 (CP)	0	2699	0	1.2	0.44
6 (CP)	0	2699	0	1.2	0.47
7 (CP)	0	2699	0	1.2	0.50
8	-1.42	1448	0	1.2	0.31
9	1.36	3820	0	1.2	0.26
10	0	2699	-1.41	0.5	0
11	0	2699	1.41	1.9	0.71

CP, central point.

These parameters demonstrate good predictive capability of the model. Eq. (2) presents the final regression model with the significant coefficients and their confidence intervals at a confidence level of 95%, calculated in function of OD.

$$\text{Eq. (2) } OD = 0.473 \pm 0.040 (b_0) + 0.249 \pm 0.023 (DT) - 0.102 \pm 0.029 (FL)^2 - 0.065 \pm 0.028(DT)^2$$

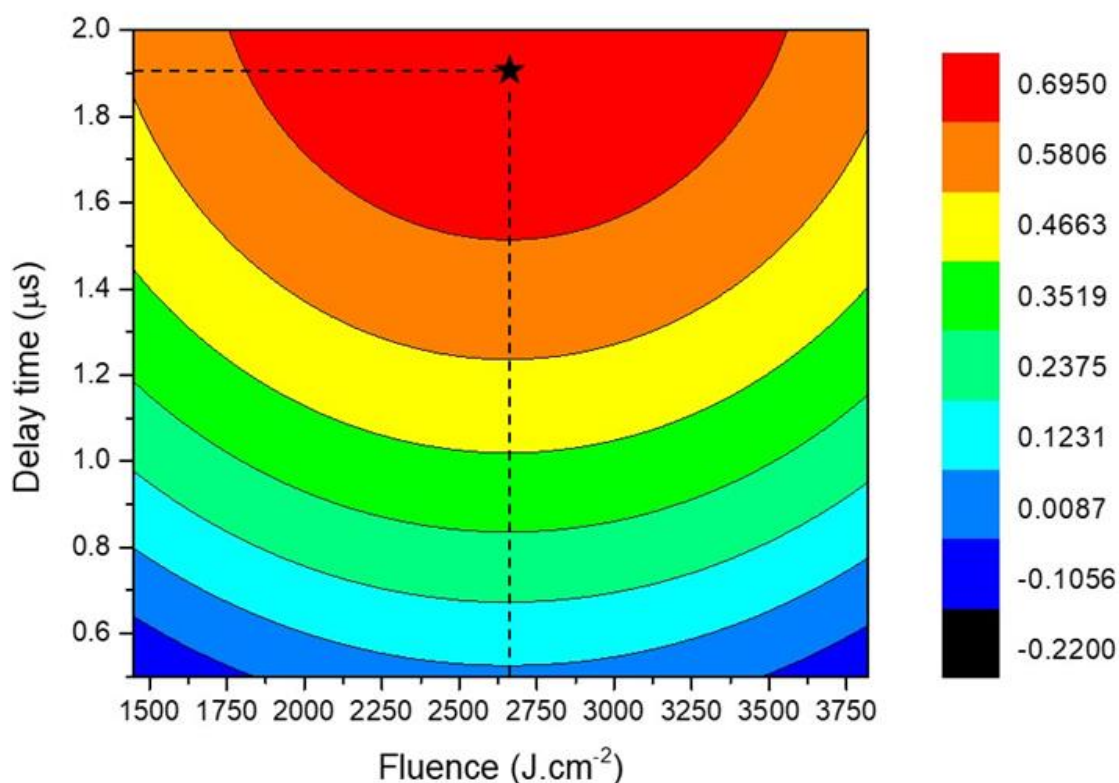
After obtaining the appropriate model, it is possible to choose the conditions of commitment to the variables studied. The analysis of Figure 2 (contour plot) shows that the appropriate conditions corresponds to a delay time of 1.9  $\mu\text{s}$  and laser pulse fluence of 2699  $\text{J.cm}^{-2}$ . These conditions are in agreement with the high OD values presented at Table 1 in the experiment 11.

**Table 2.** ANOVA in function of the OD with a 95% confidence level.

<b>Parameter</b>	<b>SS</b>	<b>Df</b>	<b>MS</b>	<b>F<sub>calculated</sub></b>	<b>F<sub>tabulated</sub></b>
<b>Regression</b>	0.5682	5	0.1136	189.85	5.12
<b>Residual</b>	0.0030	5	0.0006		
<b>Lack of fit</b>	0.0013	3	0.0004	0.513	19.37
<b>Pure error</b>	0.0017	2	0.0009		
<b>Total</b>	0.5712	10	0.0571		

**SS**, sum of square; **df**, degree of freedom; **MS**, media of square.





**Figure 2.** Contour plot for variables laser pulse fluency and delay time.

### **3.2 Evaluation of the calibration strategies**

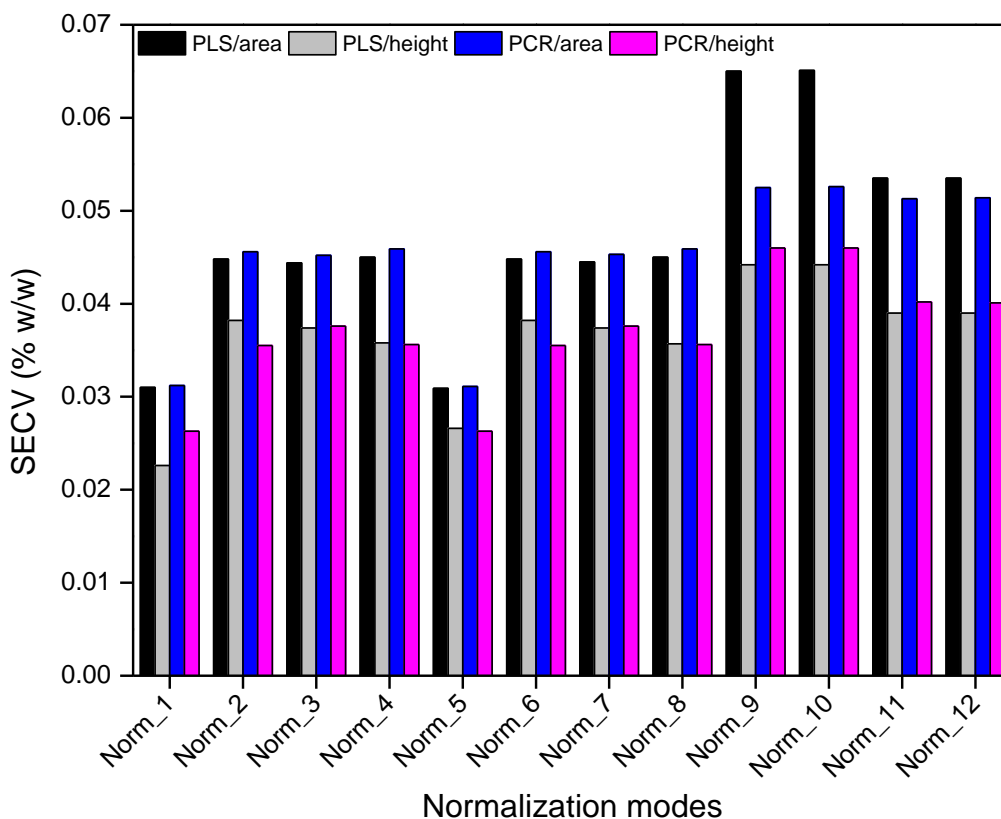
In this study, we evaluated three calibration strategies: two multivariate and one univariate strategy. The predictive capacity of these strategies were evaluated comparing the reference concentrations obtained by ICP OES. The multivariate calibration tools used in this study were PLS and PCR, and they are useful for analysis of complex samples, because allow to develop calibration models in the presence of interferences. This is very interesting for analysis by LIBS, mainly because the technique is susceptible to matrix effects. These tools are widely used, mainly PLS, and have the capability to use entire spectrum to perform calibrations (multivariate). However, in this study we do not use all the LIBS emission lines, since correlation errors between the emission line of the analyte and other emission lines can occur, generating erroneous results.

Thus, for the proposition of the PLS and PCR models, were selected only Pb emission lines free from interference. The selected emission lines (nm), in decreasing order of relative

intensity were: (I) 405.78; (I) 368.34; (I) 363.95; (I) 266.31 and (I) 287.33. Afterwards, the 12 normalization modes were assessed for these emission lines, and after normalizations, values of area and height were calculated. Thus, 24 models PLS and PCR were obtained, and the best normalization mode in combination with the area and the height of the several emission lines were selected in function of the lowest SECV. These normalizations are important to compensate the signal fluctuations (area or height) and sample matrix differences during data acquisition. Figure 3 shows the 24 models PLS and PCR using values of area and height, and as can be observed the SECV values for PLS and PCR models using the height were the lowest for normalization 1, that is only the average of the spectra.

For PLS and PCR models it was not possible to perform an external validation, since the number of samples is very small. In this sense, the models were validated in function of the cross-validation. The parameters obtained for proposed models were: to (i) PLS, 2 latent variables; standard error of calibration of 0.021% w/w;  $R^2$  of 0.9203; SECV of 0.023 %w/w; explained variance of 98%; to (ii) PCR, 2 principal components; standard error of calibration of 0.024% w/w;  $R^2$  of 0.9196; SECV of 0.026 %w/w; explained variance of 97%.

In relation to the univariate strategy called of TP CT it was not necessary to apply the normalizations mode because this strategy uses only the sum of the spectra. This strategy is a type of matrix-matching, and while on the matrix-matching conventional, a set of samples with concentrations determined by a reference technique, or certified reference materials are used as calibration standards, in the TP CT only one standard is required (certified reference material or a sample with intermediate concentration) [29].

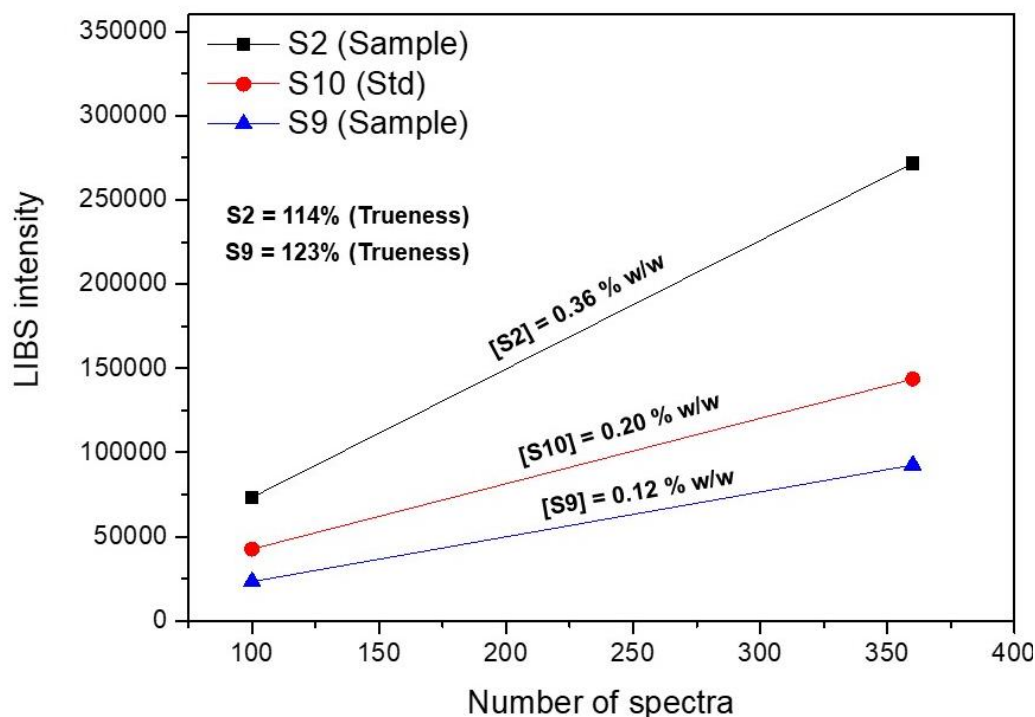


**Figure 3.** Standard error of cross validation (SECV) for all normalizations in function of the PLS and PCR models.

For the evaluation of this strategy the same emission lines (area and height) employed for PCR and PLS models were used. The criterion used to select the best emission line consisted of the evaluation of the % trueness in function of the reference values of ICP OES. The emission line more appropriate was (I) 363.95 using the height of the signal. Figure 4 shows an example of the S10 sample (0.20% w/w Pb), used as standard, and the samples S2 (0.36% w/w Pb) with highest and S9 (0.12% w/w Pb) with the lowest concentration, and their respective trueness. As in this case the reference matrix (standard) is similar to the sample, the results tend to be consistent, because the atomic emission phenomenon of the analyte is similar in the presence of the sample matrix and the calibration standard.

The calibration by TP CT were built using the Eq. (1), where in the axis  $x$  is the number of spectra (100 or 360) and in the axis  $y$  is the intensity of both points. Some studies have demonstrated that if the instrumental method is linear, the extrapolation using two point can

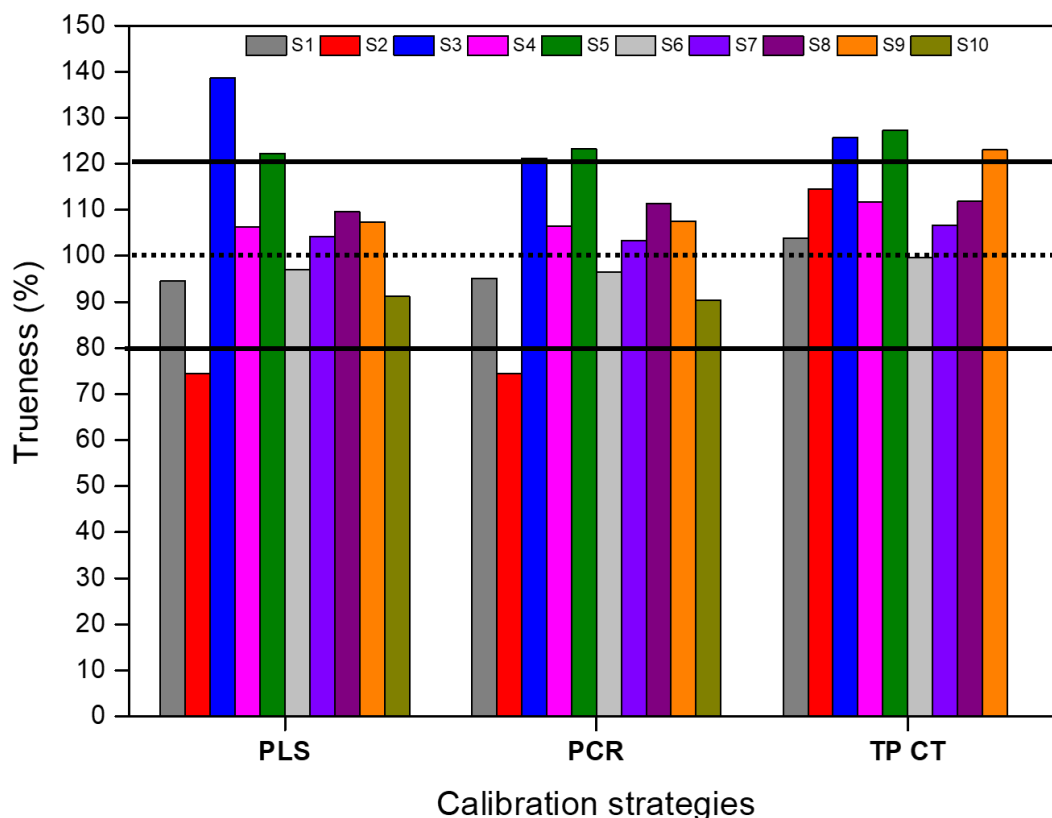
be obtained with the same precision than using multipoint [20,34-36]. The linearity was tested applying the test F, and in this case the ratio  $F_{\text{experimental}}/F_{\text{tabulated}}$  was calculated. This ratio  $\geq 10$  demonstrated that the variances are statistically different (the mean of square the regression is statistically different when compared with the mean of square the residues), thus the model can be considered linear, and the TP CT can be used.



**Figure 4.** TP CT applied for sample S2 and S9 using sample S10 as standard.

Figure. 5 shows the trueness values calculated by comparing the predicted concentrations for PLS, PCR and TP CT calibration strategies that were evaluated to the reference concentrations obtained by ICP OES. As can be observed for PLS the trueness values ranged from 74 to 139%, for PCR ranged from 74 to 123% and for TP CT ranged from 100 to 127%, showing in general the best predictive capacity of the proposed strategies. The sample S2 showed trueness values of 74% for the PLS and PCR models, and this was due to the limitation of cross-validation, which removes one sample for prediction while the other samples are used to calibrate. In the case of sample S4 that has the highest concentration (0.36 %w/w) cross-validation is not very efficient because the model is predicting a

concentration that is outside the domain of the calibration samples. The samples S3 and S5 showed a trueness above 120% for the three calibration strategies. Probably this is a reflection of the lack of homogeneity of the sample during the preparation step.



**Figure 5.** Trueness (%) values according to reference values for the three calibration strategies.

In addition, the relative standard deviation (%RSD) values for PLS ranged from 3 to 37%, for PCR ranged from 5 to 30% and TP CT ranged from 6 to 21%, demonstrating a better precision with the TP CT strategy. The lowest values %RSD for measurements using TP CT, when compared to the other strategies, may be related to the fact that in the TP CT only one emission line for Pb is used in the proposition of the linear calibration model, different from the models obtained for PLS and PCR where 5 emission lines were used, for both. Although using spectrum normalizations, which greatly contribute to the minimization of spectrum fluctuations obtained, the use of different lines in different spectral regions may contribute to the proposition of calibration model that increase the %RSD of the measurements. In general, the range of

trueness and %RSD value using all calibration strategies are in agreement with the values normally reported for determinations using LIBS.

The main advantage of the TP CT approach in relation to PLS and PCR is its simplicity because only two points are used in the calibration curve for each sample and only one emission line is used for the analyte. Besides that, it is important to mention that none normalization is required. In this case, for multivariate analysis just the average was enough, but on the other hand, in many studies is almost always necessary to do some normalization approach. In addition, choosing the best calibration method will depend of the problem in question and its complexity. Furthermore, it is important to highlight that there is no report in the literature using TP CT for LIBS for polymers analysis. The results presented demonstrate the considerable potential of the strategies proposed for determination of Pb in PP recycled using LIBS.

#### **4. Conclusion**

The calibration strategies proposed in this study is highly compatible with LIBS, and it may contribute to minimizing matrix effects in direct solid analyses in complex samples as polymers. The PLS and PCR model calibrations obtained presented good results with robustness and precision. In relation the new proposed univariate calibration strategy TP CT, we can highlight that it presented some advantages over PLS and PCR, as lower %RSD values, better values of %trueness and simplicity. Additional studies are required to evaluate the performance of this method for other solid samples, TP CT may represent an effective strategy in LIBS analyses, especially considering the accuracies observed for such complex matrix as the one evaluated in the present study. Each calibration approach has its advantages and limitations and can be observed according to its necessity and the intrinsic characteristics of the sample and the analyte. In addition, it is important to highlight that Pb concentrations in PP samples are alarming considering, that this material can be reused to the manufacture new objects such as mugs, plates and others.

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## **Chapter 5 – Conclusions**

## 5. Conclusions

In this thesis, it was possible to demonstrate several approaches for the qualitative and quantitative analysis of polymers samples by LIBS. In second chapter the LIBS together with several chemometrics tools were used for identification and classification of five groups of the most commonly used polymers in the electronics industry. Classification models (KNN and SIMCA) were developed using the theoretical ratios of the emission lines and molecular bands obtained from LIBS. In third chapter, showed that LIBS combined with PLS is a fast and quasi-nondestructive 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 about the metallic composition in these samples with analytical frequency of 20 samples per hour. In the fourth chapter, several calibration strategies were proposed in this study is combining solid sample and LIBS, and it may contribute to minimizing matrix effects in direct solid analyses in complex samples as polymers the new proposed univariate calibration strategy TP CT presented some advantages over PLS and PCR, as lower %RSD values, better values %trueness and simplicity.