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Analysis Method

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

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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 spectrometry (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

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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^{-1}. 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 μs and spot size of 50, 100, and 150 μm 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 μm 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 (PExPC, PExPS, PExPA, PCxPS, PCxPA, PSxPA) 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 μs and spot size of 100 μm.

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
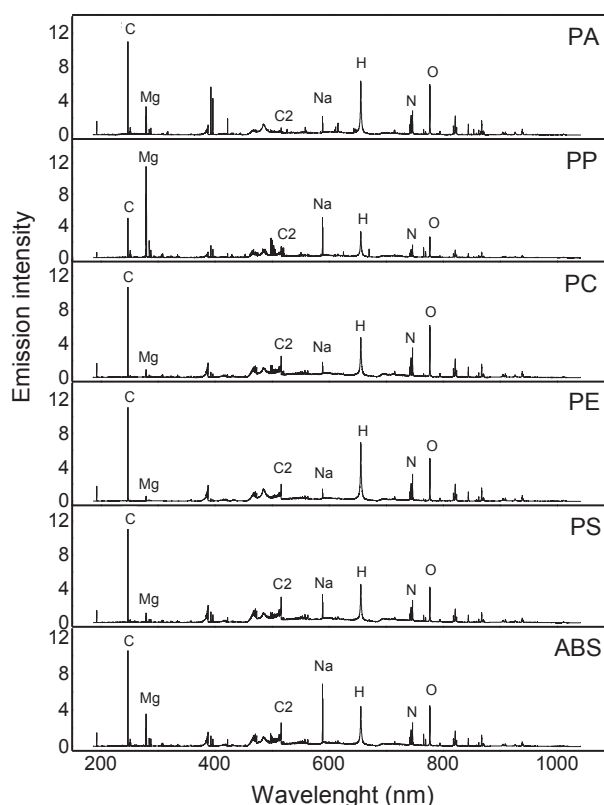

Fig. 1. Representative spectra of the analyzed polymers: ABS, PS, PE, PC, PP and PA.

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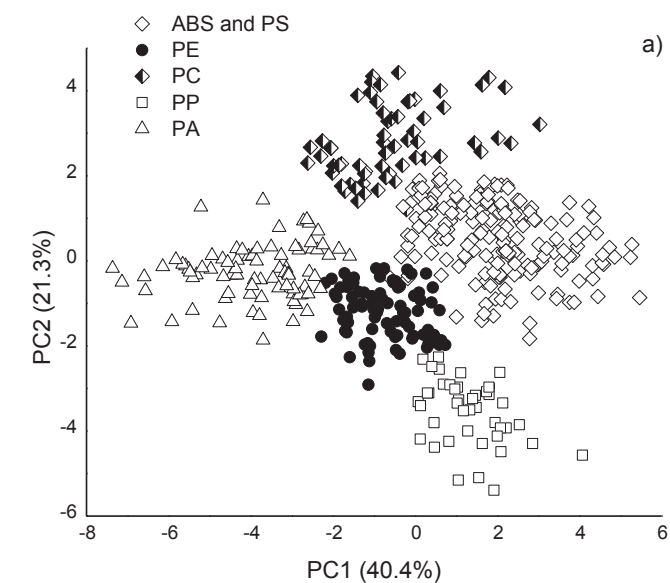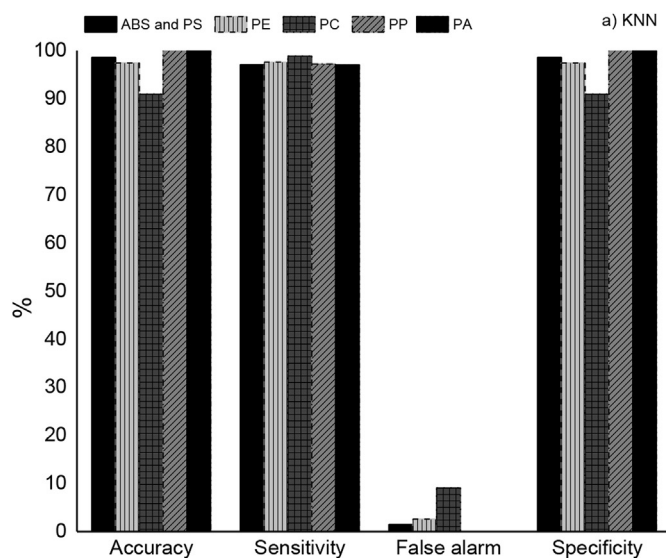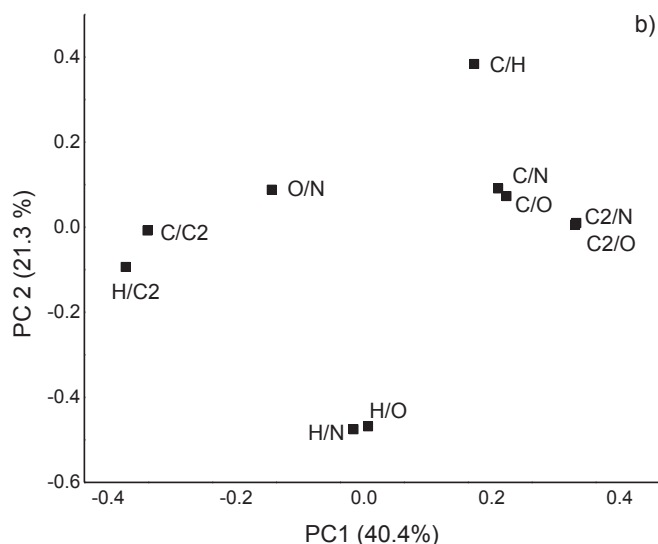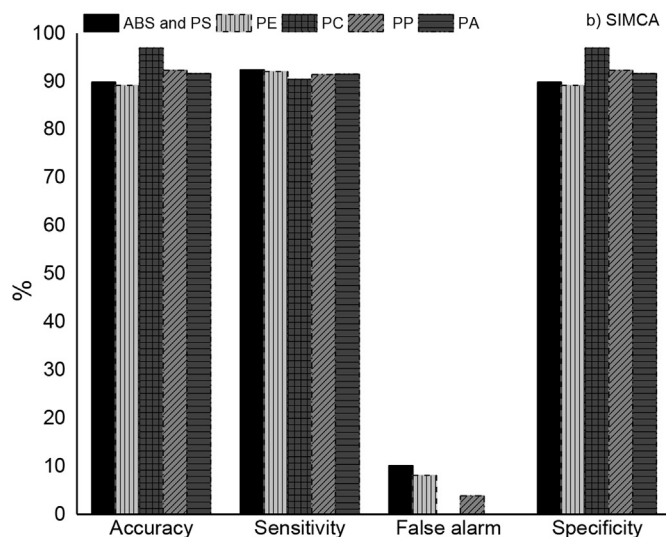
Fig. 2. (a) Score and (b) loading plots for PC1xPC2 of the analyzed polymers.

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[a]	PPO/PS[a]	ABS or PS	Not predicted
3	POM[b]	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

[a] Blend of poly(phenylene oxide)/polystyrene.
[b] 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 (Tg) 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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