



Research article

Raman spectroscopy integrated with machine learning techniques to improve industrial sorting of Waste Electric and Electronic Equipment (WEEE) plastics

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ABSTRACT

Current industrial separation and sorting technologies struggle to efficiently identify and classify a large part of Waste of Electric and Electronic Equipment (WEEE) plastics due to their high content of certain additives. In this study, Raman spectroscopy in combination with machine learning methods was assessed to develop classification models that could improve the identification and separation of Polystyrene (PS), Acrylonitrile Butadiene Styrene (ABS), Polycarbonate (PC) and the blend PC/ABS contained in WEEE streams, including black plastics, to increase their recycling rate, and to enhance plastics circularity. Raman spectral analysis was carried out with two lasers of different excitation wavelengths (785 nm and 1064 nm) and varying setting parameters (laser power, integration time, focus distance) with the aim at reducing the fluorescence. Raman spectral data were used to train and test Discriminant Analysis (DA) and Support Vector Machine (SVM) algorithms in an iterative procedure to assess their performance in identifying and classifying real WEEE plastics. Analysis settings were optimized considering industry requirements, such as process productivity (classification rate, short measuring time for fast identification) and product quality (purity of the sorted polymers). Classification models were trained, in a first approach, only on the target WEEE plastics; and in a second approach, on all polymers expected in the WEEE stream, leading to a realistic overview of the potential scalability of the advanced sorting methods and their limitations. The best classification models, based on DA of Raman spectral data obtained with the 1064 nm laser at 500 mW and 1.0 s, led to classify PS and ABS with a purity up to 80 %.

1. Introduction

Waste Electrical and Electronic Equipment (WEEE), commonly classified as e-waste, represents one of the most rapidly expanding categories of waste on a global scale, especially within Europe. It covers a large range of devices such as mobile phones, computers, televisions, fridges, household appliances, lamps, medical devices, and photovoltaic panels (European Commission, 2022). According to Eurostat, 4.9 Mt of WEEE were collected in Europe in 2021 (Waste statistics, 2022), being composed of 2.6 Mt of WEEE plastics. Only 54 % of WEEE plastics were collected, and only 0.4 Mt (15 % of total) reached specialized WEEE plastic recycling facilities in Europe. About 50 % of the plastic waste input is recycled (180 kt) and can be further used as secondary raw materials for manufacturing new products; however, the other half is considered non-recyclable and is usually sent for disposal to landfills or incinerated (Haarman et al., 2023).

In recycling facilities WEEE plastics are treated by mechanical separation, employing a series of sorting steps with technologies based on different physical principles: separation by density (sink-float method), electrostatic separation, and sensor-based sorting techniques like near infrared (NIR) spectroscopy. WEEE plastic recyclers face several technical challenges to recover efficiently some target plastics, due to the complexity of the plastic waste mixture. WEEE plastics usually present high content of additives, such as fillers, plasticizers, stabilizers, brominated flame retardants (BFR) or pigments, which difficult their identification with conventional spectroscopic sorting technologies. In many WEEE treatment facilities, plastics that are contaminated with these additives are typically not recovered and are instead combined within the same fraction. Given that this fraction contains BFR, it is classified as hazardous waste, leading to its common incineration or disposal in landfills.

To avoid downcycling of non-hazardous plastics, reliable and

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feasible advanced sorting processes must be identified to improve the efficiency of WEEE plastics sorting, to increase plastics circularity, and to reduce the release of emissions and hazardous chemicals to the environment (Sormunen et al., 2022a). In this sense, methods which rely on fundamental properties of the material at the atomic/molecular levels, can be much more accurate for plastics classification and sorting. Reflectance spectroscopy (in the near and mid-infrared, NIR-MIR), Raman scattering, and emission spectroscopy (Fluorescence, Laser Induced Breakdown Spectroscopy (LIBS)) are the main spectroscopic techniques used for plastics identification (Adarsh et al., 2022).

Black plastics are the most challenging WEEE stream for sorting, because most of them contain carbon black, which makes them show very low reflectance in the NIR region, hindering their classification with current industrial equipment (Chainé et al., 2022). X-ray fluorescence (XRF) is a sorting method applicable to black plastics, especially for detecting plastics that include specific high molecular weight elements, such as bromine found in BFR (Haarman et al., 2020). Nonetheless, it is crucial to recognize that this technique does not distinguish among the different types of polymers present. Some other approaches are currently being developed like Hyperspectral Imaging (HSI) in the mid-infrared spectral range (Rozenstein et al., 2017; EVK DI KER-SCHHAGGL GMBH), and Terahertz spectroscopy (Küter et al., 2018; Mikloweit). Both approaches allow sorting a few types of black plastics but have limitations to be implemented due to expensive instrumentation, low throughputs, and the large particle sizes required. MIR can be also applied to detect black plastic (Signoret et al., 2020), but spectra is strongly affected by the presence of water and spectra acquisition is slow.

Raman spectroscopy can be mainly applied to determine the molecular composition and structure of almost any organic substance. This technique shows some advantages for practical application in post-consumer plastics sorting compared to other spectroscopic techniques like NIR or LIBS. It overcomes the shortcomings of NIR, such as water absorption and poor spectral resolution (Tsuchida et al., 2009). LIBS is applicable to large polymer scope, but it struggles when distinguishing polymers with similar chemical formula (Neo et al., 2022).

Raman spectroscopy presents a promising tool for enhancing the extraction of plastics from WEEE. Nevertheless, its application in industrial settings remains limited (Gruber et al., 2019). This restriction is primarily due to the extended measurement durations, which generally vary from 10 to 60 s, necessary to obtain a Raman spectrum of sufficient quality during laboratory assessments (Ghosal et al., 2018; Ren et al., 2023; Jianpeng et al., 2023). Furthermore, the technique is fairly susceptible to interference from stray light. But advances in camera and spectrometer technologies in recent times have allowed high spatial and spectral resolution of the Raman signal. In fact, nowadays there are commercial Raman spectrometers with small laser sources for excitation and miniature charge-coupled devices (CCD), that can be used for in situ applications and for installation in industrial sorting units (Adarsh et al., 2022). A few Raman sorting prototypes based on conveyors have been developed to classify post-consumer plastics waste using a 785 nm laser (Patent WO1998019800; Tsuchida et al., 2009), or glass and minerals waste using a 532 nm laser (de Biasio et al., 2020). Saimu Corporation (Japan) also developed an industrial sorter based exclusively on Raman spectroscopy for sorting packaging plastic waste (Sormunen and Järvinen, 2021).

Parallely, machine learning techniques have recently gained popularity in plastic waste treatment (da Silva et al., 2020) and plastics identification (Feng et al., 2023; Sunil et al., 2024). Machine learning methods based on supervised learning are used in spectroscopy to find patterns in the spectral data of the samples. They have demonstrated being a useful tool for increasing plastic recycling rates by automating plastics sorting and recycling processes, when they are combined with different spectroscopic techniques such as NIR, MIR, Raman spectroscopy (Chen et al., 2017; Musu et al., 2019), LIBS or HSI (Neo et al., 2022). In this sense, there are several studies, for instance, focused on

the use of a confocal Raman spectrometer with a 532 nm laser, combined with Partial Least Squares Regression (PLSR) (da Silva et al., 2020) and Support Vector Machine (SVM) (Chen et al., 2017; Yang et al., 2022); or a Raman apparatus with a 785 nm laser and a CCD detector, combined with Principal Component Analysis (PCA), Support Vector Machine (SVM) and Artificial Neural Networks (ANN), that achieved high accuracy (>95 %) when classifying polypropylene (PP), PS and ABS (Musu et al., 2019). A hybrid system based on LIBS and Raman spectroscopy has also been studied for the classification of different types of post-consumer plastics (Polyethylene Terephthalate (PET), Polyethylene (PE), PP and PS), using PCA for spectral data analysis (Shameem et al., 2017). To improve the industrial sorting, novel deep learning techniques have been developed for chemometric analysis using Raman spectral data to identify recyclable post-consumer plastics (PE, PP, PET) (Neo et al., 2023). However, this study did not include other types of WEEE plastics.

This study assessed the use of Raman spectroscopy to enhance the current industrial classification process for WEEE plastics, emphasizing its advantages compared to other spectroscopic techniques (Neo et al., 2022; Yang et al., 2022). The primary objective was to precisely recognize WEEE plastics regardless of their colour. The following advantages of Raman spectroscopy were considered in terms of its potential application in real-time classification systems for plastics sorting: Raman spectroscopy shows higher spectral resolution than NIR; the Raman scattering phenomenon is less sensitive to the direction of the detector and to the sample roughness; and non-contact measurement is possible, whereas tight contact measurement is required in other spectroscopic techniques like Fourier Transform Infrared Spectroscopy (FTIR) using the attenuated total reflection (ATR).

Classification models were developed using a combination of Raman spectroscopy and machine learning techniques for sorting three polymers' categories from the main common WEEE plastics (Haarman et al., 2020): (1) Polystyrene (PS), as a mixture of High Impact Polystyrene (HIPS) and General-Purpose Polystyrene (GPPS); (2) Acrylonitrile butadiene styrene (ABS); and (3) Polycarbonate/Acrylonitrile butadiene styrene (PC/ABS), as a mixture of PC and PC/ABS. These target polymers have a high-medium density and usually contain certain additives (BFR, fillers, pigments) that make them even heavier, hindering their proper sorting with current available technologies and are not recovered, as stated before. Improving PS, ABS and PC/ABS separation from the other WEEE plastics, regardless their additive content, would enhance not only the overall plastics recyclability, but also will make possible future brominated WEEE plastic recovery. Novel recycling approaches emerged in the last years for decontamination of this plastic waste (CreaSolv® Process; Reinhardt et al., 2021; Cacho et al., 2024), but these treatments do also require input plastic waste sorted by the base polymer to assure output quality.

In this study the excitation wavelengths of 785 and 1064 nm were evaluated to reduce the fluorescent effect that often overlaps certain Raman bands of interest of technical plastics. The 532 nm wavelength was excluded as a shorter wavelength since, although it provides more intense Raman signal, it is also affected by a higher fluorescent effect. Short measuring time was evaluated for fast identification and classification of WEEE plastics, with the aim at developing an advanced sorting process that could be further scaled-up in a real-time classification line. Machine learning methods were used to find patterns in the Raman spectra of WEEE plastics acquired at short measuring times, which showed noisy and weak Raman signal that is difficult to identify by using spectral library matching. The technical feasibility of the classification models was evaluated considering industry requirements such as the recovery, purity, and accuracy rates for the sorted WEEE plastics.

This research on the use of Raman spectroscopy for plastics sorting differs significantly from previous studies in several key aspects that emphasize both its originality and its advancement of the field. One of the most innovative elements is the use of the 1064 nm excitation wavelength at short integration time. While several previous studies

required longer integration times when using this laser, this study managed to reduce measurements time to only 1.0 s. This not only speeds up the analysis process, essential for on-line classification systems, but also optimizes process productivity and efficiency. This is precisely what the industry demands.

In addition, the nature of these samples represents a significant advance beyond the state-of-the-art. Unlike previous studies that focused on cleaner unprocessed materials or post-consumer plastics with less additives, the samples used in this study were taken from different fractions from the real WEEE treatment process. They were composed of more than 14 different polymers, covering almost all the possible variability found in this waste stream. Consequently, this approach is much closer to the reality of the recycling industry, but also makes their identification and classification even more difficult.

2. Materials and methods

2.1. WEEE plastics

WEEE plastic samples from a recycling plant were provided by the company COOLREC B.V. (The Netherlands), an authorized WEEE manager. These samples were shredded plastic wastes from refrigerators (light-coloured plastics), Small Domestic Appliances (SDA) and Information and Communication Technologies (ICT) equipment (light-coloured and dark plastics); and heavy plastics obtained after the density separation process ($\rho > 1.1$ kg/L, dark and black plastics). A representative sample of each WEEE stream was characterized employing different identification techniques, such as NIR and FTIR-ATR spectroscopy, XRF and/or the burn test to identify certain black plastics.

Known WEEE plastic samples were selected to develop the classification models, including 14 polymer groups: Polystyrene (PS), Acrylonitrile butadiene styrene (ABS), Polycarbonate (PC), PC/ABS, Polyethylene (PE), Polypropylene (PP), Polyamide (PA), Polyvinylchloride (PVC), Polymethylmethacrylate (PMMA), Polyoxymethylene (POM), Polyethylene Terephthalate (PET), Polyurethane (PUR), Polyphenylene Ether and Styrene Butadiene (PPE + SB) and Polybutylene terephthalate (PBT). A matrix of Raman spectral data was built considering the actual composition of waste fractions, with 471 WEEE plastic samples composed of different polymers (see Table 1), with the following distribution: 44 plastics from refrigerators (9 %), 207 plastics from SDA/ICT (44 %) and 220 heavy plastics (47 %), containing in total 45 % black and 55 % non-black plastics.

2.2. Raman measurements

Raman spectroscopy is a non-destructive analytical technique based

Table 1
WEEE plastics per type and colour.

Polymer	Black (No. Samples)	Non-Black (No. Samples)	Total (No. Samples)
PS	47	57	104
ABS	39	78	117
PC + ABS	37	25	62
PC	38	13	51
PE	18	7	25
PP	11	23	34
PA	17	13	30
PVC	4	11	15
PMMA	0	12	12
POM	0	8	8
PET	0	4	4
PUR	0	5	5
PPE + SB	0	2	2
PBT	0	2	2
Total (No.)	211	260	471

on inelastic light scattering that uses a laser as a source of high intense monochromatic light. Raman spectroscopy provides information about vibrational, rotational, and other low frequency transitions in molecules (HORIBA Scientific, 2023), which allows a better understanding of its chemical structure, phase and polymorph, crystallinity, and molecular interactions, which makes this technique useful for chemical identification.

For each Raman measurement the plastic sample was placed on a sample holder and irradiated with the selected excitation wavelength for a certain time, using a laser probe coupled to the spectrometer. The scattered light was collected by the laser probe and reached the detector of the spectrometer. The spectrometer transformed the signal into a Raman spectrum with the characteristic bands and/or fluorescence of the analyzed material. As a reference, Table 2 shows the wave number (cm^{-1}) where the more intense Raman signal is typically obtained for target plastics (PS, ABS, PC) (Lobo and Bonilla, 2003). The polymer blend PC/ABS has the characteristic Raman bands for both PC and ABS. Raman set-up is displayed in Fig. 1.

Fluorescence can mask most of the weak Raman effect, leading to a Raman spectrum of low quality. Consequently, the selection of the laser wavelength is critical (Edinburgh Instruments, 2021). Different excitation wavelengths ranging from the UV to the NIR can be employed, depending on samples features, as the wavelength of the laser influences the intensity of the Raman signal. The longer wavelength, the lower intensity of the Raman signal, but also the lower fluorescence. In this study two portable Raman spectrometers with different excitation wavelengths were employed to analyze WEEE plastics.

- A Raman spectrometer with a 785 nm excitation laser (Optosky, ATR3110-785), with a coupled laser probe (Length: 1.5 m; Outer Diameter (OD) ≥ 8), Maximum power: 500 mW) and an ultra-high sensitivity CCD detector (Effective pixels: 521). Raman shift in the range of 200–3500 cm^{-1} , with a spectral resolution of 8 cm^{-1} . Integration time can be fixed within the range of 4 ms–15 min.
- A Raman spectrometer with a 1064 nm excitation laser (Optosky, ATR3110-1064) and a coupled laser probe (Length: 1.5 m; OD ≥ 8 , Maximum power: 500 mW) and a high sensitivity 512 pixels InGaAs array detector. Raman shift is in the range of 200–2700 cm^{-1} , with a spectral resolution of 13 cm^{-1} . Integration time can be fixed within the range of 10 ms–20 min.

250 known WEEE samples were analyzed with both excitation wavelengths. Measurement settings were tuned in both Raman spectrometers to reduce the fluorescent effect and to optimize the quality of the Raman spectra. Several combinations of laser powers ($P = 0$ –500 mW) and integration times ($t = 0.1$ –60 s) were tested to obtain the highest intensity in the Raman bands. The focus distance (4–6 mm) was adjusted for each wavelength to get the better spectral resolution. All Raman measurements were conducted at room temperature (25 °C).

Table 2
Characteristic bands for target polymers (Lobo and Bonilla, 2003).

Polymer	Chemical bond	Wave number (cm^{-1})
PS	Substituted benzene ring	622
	Ring-mode vibration	1002/1033
	Ring-mode vibration	1584/1603
ABS	Aromatic ring	1003, 1584, 1603
	C=C	1641, 1653, 1667
	C \equiv N	2238
PC	1,4-disubstituted aromatic ring	638, 709, 1114, 1181
	Aryl ester	1236
	Methyl	1366/1386
	Aromatic ring	1510, 1594/1600

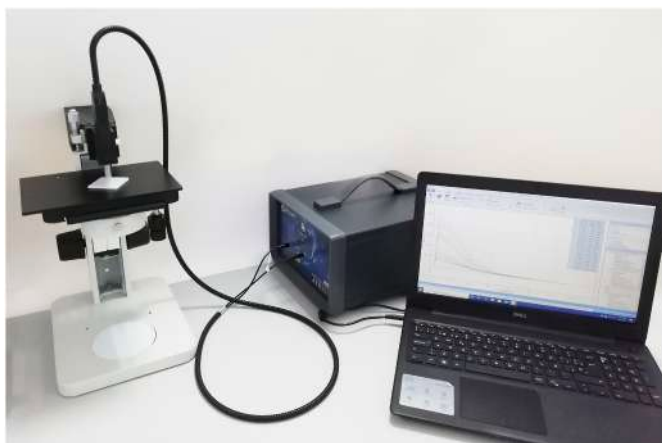


Fig. 1. Set-up for Raman spectroscopy analysis.

2.3. Spectral data analysis with machine learning

Firstly, spectral data were pre-processed to reduce the amount of unwanted information introduced to the classification model, i.e., background signal and fluorescence in the Raman spectrum, mainly due to uncontrollable fluctuation in the laser-matter interaction and signal from non-target molecules in the sample. Commonly used pre-processing methods based on mathematical transformations of the spectral data were tested (Ren et al., 2017; Yi et al., 2020; Luna et al., 2019): normalization methods (area, mean and unit vector normalization), scattering effect correction methods (Standard Normal Variate (SNV), Multiplicative Scatter Correction (MSC), detrending (DT)), deresolve, baseline correction, smoothing (Savitzky-Golay and Gaussian filtering), derivatives (1st and 2nd derivative), and outlier segregation.

Next, two supervised machine learning algorithms, Discriminant Analysis (DA) and Support Vector Machine (SVM), were applied to develop and optimize a classification model for efficiently sorting WEEE plastics into more than two classes. Full cross-validation was applied to assess and compare the different models generated and their classification ability.

DA is commonly used for dimensionality reduction and classification in spectroscopy applications (Zeng et al., 2021; Yaping et al., 2023). It provides class separability by drawing a decision region between the different classes, trying to maximize the ratio of the between-class variance and the within-class variance. Different approaches were tested to better categorize the data points by varying the shape of that boundary. The simplest form is a straight line, referred then as Linear Discriminant Analysis (LDA), based on equal covariance matrixes for the classes. This classifier showed good predictive results even when normal distribution and covariance homogeneity were not met (Xue and Titterton, 2008). Quadratic boundaries were also used, assuming different covariance matrices for each class, in the so-called Quadratic Discriminant Analysis (QDA). A third classifier based on Mahalanobis method, which uses ellipses to define the distance from the centre of the classes, was also tested. Additionally, PCA was applied before DA to reduce data dimensionality by feature extraction. In this way, principal components (PC), which are linear combinations of the original variables, were used as input to DA models, reducing data variability while retaining the most significant features of the original data. The corresponding algorithms are described elsewhere (Dixon and Breerton, 2009; Stefan et al., 2019). Compared to other models, DA eases data interpretation and can achieve more accurate class separation (Hayati et al., 2024). This model has been successfully used to classify different kinds of plastics (Xiaoyu et al., 2020; Qinyuan and Jia, 2021).

On the other hand, SVM constructs a decision boundary to maximize the distance between the different classes. Unknown samples are classified based on the side of the decision boundary that they fall on in a

non-probabilistic manner (Wang, 2005). For the implementation of the Support Vector Classification (SVC) LIBSVM code was used (Chang and Lin, 2011). Specifically, C-SVC method has been applied based on a one-vs-one multiclass scheme. Several kernel functions were used to transform the parameter space: Linear, Polynomial, Radial basis function (RBF) and Sigmoid. Overall, this technique stands out for its ability to attain more generalized results compared to other methods, such as Neural Networks, by avoiding local minima and effectively modelling non-linear data (Lahmiri et al., 2018). As a result, it is quite commonly used to solve multi-class prediction problems (Lee et al., 2004), including plastic classification (Junjuri et al., 2019). Equal probabilities for class membership were assumed.

A sensitivity analysis was conducted with those algorithms to study the effect that short integration time had in the performance of the classification method. In Raman analysis a longer integration time leads to a higher signal-to-noise ratio (S/N); however, a too long integration time can saturate the detector when analysing WEEE complex plastics. On the other hand, the identification of WEEE plastics must be performed as fastest as possible to achieve a sorting process with higher efficiency that could be potentially scaled-up. With that aim, data sets were constructed with Raman spectra of 178 non-black WEEE plastics (61 PS, 80 ABS, 13 PC, 24 PC/ABS) acquired with the 1064 nm laser at 500 mW at two short integration times (1.0 s and 2.0 s). DA and SVM models were trained and tested by dividing the sample set into the calibration (CAL) and validation (VAL) sets in a ratio of 2:1. In this screening, black plastics were excluded to avoid background and fluorescence interference in the model.

Then, the remaining WEEE plastics (Table 1) were analyzed to acquire Raman spectral data with the optimum settings (Integration time: 1.0 s, laser power: 500 mW, and wavelength of 1064 nm) for training the classification algorithms. In a first approach, a 3-category classification model was developed, only focused on the target plastics to sort from the WEEE stream: (1) PS, (2) ABS, and (3) PC/ABS. In a second approach, an additional category was added to the classification model, named as OTHER, to separate the other polymers that could be found in the WEEE stream (PE, PP, PA, PVC, PMMA, POM, PET, PUR, PPE + SB, PBT), and to study its influence in the recovery of target plastics. Accordingly, a 4-category model was obtained: (1) PS, (2) ABS, (3) PC/ABS, (4) OTHER.

To develop the classification models, two new datasets were built with the Raman spectral data of analyzed WEEE plastics. The dataset used for training the 3-category model was composed of 333 samples (Table 3), divided into 52 % of non-black samples and 48 % of black samples, with the following polymers distribution: PS (29 %), ABS (35 %), PC/ABS (36 %). While the dataset used for training the 4-category model was composed of 471 samples (Table 4), 55 % non-black and 45 % of black plastics; with a balanced distribution between the 4 categories: PS (22 %), ABS (25 %), PC/ABS (24 %) and OTHER (29 %). In the OTHER category, plastics distribution was representative of the heavy plastics stream. Additionally, each dataset was divided into a ratio CAL:VAL = 2:1. Based on either DA and SVM algorithms, 12 models were built for sorting the 3 categories of the target WEEE plastics (PS, ABS and PC/ABS) and more than 50 models for sorting 4 categories (PS, ABS, PC/ABS, OTHER).

To assess the technical feasibility of applying Raman spectroscopy in

Table 3

Calibration/validation sets for the 3-category model: No. samples per dataset, polymer, and colour.

3-Category model	CAL				VAL			
	PS	ABS	PC/ABS	Total	PS	ABS	PC/ABS	Total
WEEE Samples								
Blacks	27	25	53	105	13	14	27	54
Non-Blacks	40	51	24	115	17	28	14	59
Total	67	76	77	220	30	42	41	113

Table 4

Calibration/validation sets for the 4-category model: No. samples per dataset, polymer, and colour.

4-Category model WEEE Samples	CAL					VAL				
	PS	ABS	PC/ABS	OTHER	Total	PS	ABS	PC/ABS	OTHER	Total
Blacks	27	25	54	34	140	20	14	21	16	51
Non-Blacks	40	51	24	59	174	37	27	14	28	106
Total	67	76	78	93	314	57	41	35	44	157

WEEE plastic recycling, the following requirements were considered to evaluate the performance of trained classification models from an industrial perspective.

- Recovery rate (% Recovery): the ratio between the number of correctly classified samples of a polymer out of the total number of samples of that polymer in the dataset, expressed in percentage (%). The recovery rate of a group is directly related to the accuracy of the classification model.
- Purity rate (% Purity): the ratio between the number of correctly classified samples (correct predictions) out of the total number of samples classified by the model in that category (total predictions), expressed in percentage (%). Purity is directly related to the precision of the classification model and allows understanding the level of contamination of the sorted polymers.
- Accuracy rate (% Accuracy): the total percentage of samples correctly classified by the model out of the total number of samples in the dataset, expressed in percentage (%). Unlike recovery and purity rates, which evaluate model performance in individual categories, the accuracy reflects the overall performance of the model where all categories are considered. This indicator is especially useful when comparing different output models.

The criteria followed to define the best performing models were, in order of preference: (1) models that achieved the highest accuracy; (2) models that achieved high recovery and purity rates; (3) in case high rates for those requirements were not fulfilled at the same time, purity was prioritized to sort high-quality recycled plastics avoiding down-cycling and to get the highest market value from WEEE streams. In the end, the best performing model was selected trying to maintain an adequate balance in terms of accuracy, purity, and recovery.

3. Results and discussion

3.1. Optimization of measuring settings

First, Raman analysis of 471 WEEE plastic samples was carried out to study the influence of using different wavelengths in the quality of the Raman spectra. Representative raw spectra of WEEE plastics were

acquired with both excitation wavelengths (785 nm/1064 nm).

With the 785 nm laser, intense fluorescent effect was broadly observed in the shift range of 100–1000 cm^{-1} . Non-black PS and ABS samples showed the common characteristic band at 1000 cm^{-1} (Figs. 2 and 3); however, the characteristic band of nitrile ($\text{C}\equiv\text{N}$, 2238 cm^{-1}) was hardly observed in ABS samples (Fig. 3). Consequently, PS and ABS could hardly be differentiated. A few samples of non-black PC and PC/ABS showed defined peaks in the spectrum (Figs. 4 and 5). Black plastics showed fluorescence or overheated under the laser beam at low integration times ($t \leq 1.0$ s), even saturating the detector (e.g., black PC/ABS measured with 785 nm in Fig. 4). Thus, Raman spectra of poor quality was obtained for dark/black WEEE plastics.

With the 1064 nm laser, the fluorescence intensity of non-black samples was reduced in the Raman shift range <1000 cm^{-1} but observed within 1500–2600 cm^{-1} shift range. Compared to spectra obtained with the 785 nm laser, Raman signal was weaker, thus, longer integration time was needed to obtain Raman bands of higher intensity. The characteristic band of PS (1000 cm^{-1}) was observed in several samples, which were mainly non-black plastics. In some light-coloured ABS samples, the characteristic band of $\text{C}\equiv\text{N}$ was also observed (Fig. 3). Under the 1064 nm laser beam, dark and black plastics overheated to a lesser extent than under the 785 nm laser but resulting in noisy Raman spectra.

It was concluded that discriminating target plastics using traditional identification patterns was difficult with both wavelengths (785 nm or 1064 nm) did not lead to successful discrimination between target WEEE plastics, due to the fluorescence interference and the low signal-to-noise ratio (S/N). This was particularly noticeable in dark plastics. Nevertheless, the 1064 nm excitation wavelength was selected to develop the classification models, because it provided the most interpretable Raman spectral data for WEEE plastics.

Regarding the sensitivity analysis on short integration times, Fig. 6 showed that good recovery rates were achieved with both integration times (Table 5). But, at 1.0 s the fluorescence signal decreased and better recovery rates were obtained for all polymers categories (>80 %). 1.0 s was selected as the preferred integration time to develop the classification models, considering the further scale-up of the sorting process in a real-time classification line. Finally, as the intensity of the Raman signal was not so high with the 1064 nm excitation laser at 1.0 s, Raman

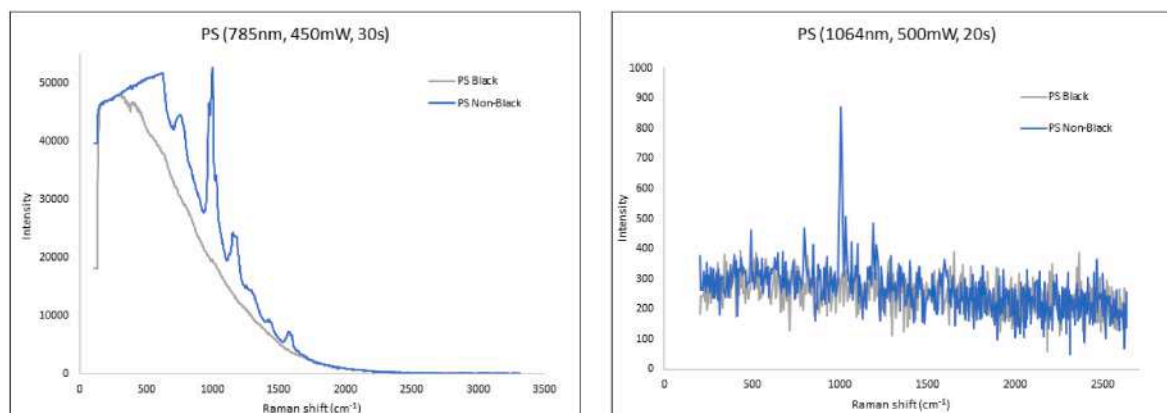


Fig. 2. Raman spectrum of PS obtained with different wavelengths: 785 nm vs. 1064 nm.

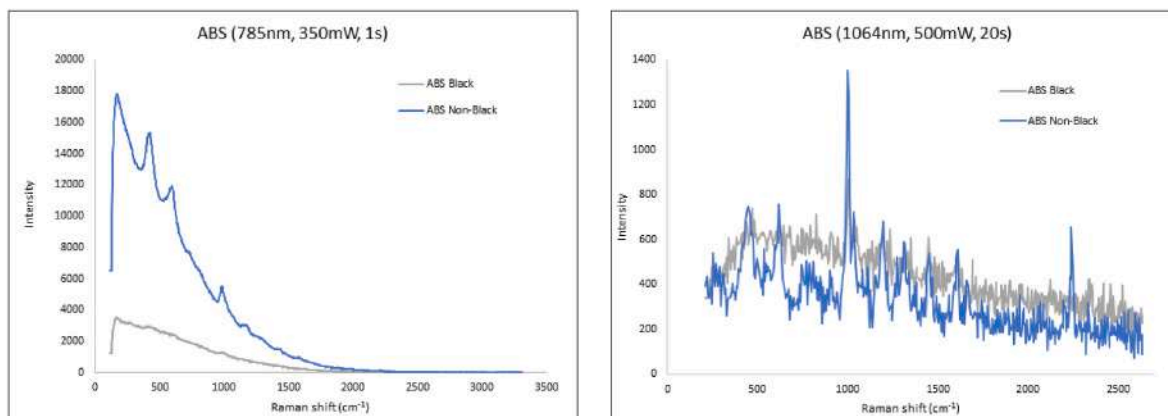


Fig. 3. Raman spectrum of ABS obtained with different wavelengths: 785 nm vs.1064 nm.

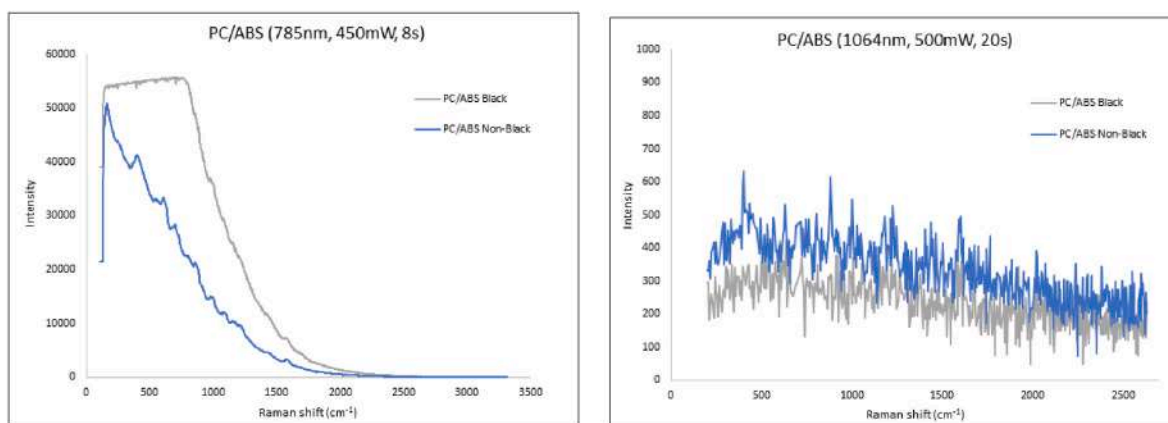


Fig. 4. Raman spectrum of PC/ABS obtained with different wavelengths: 785 nm vs. 1064 nm.

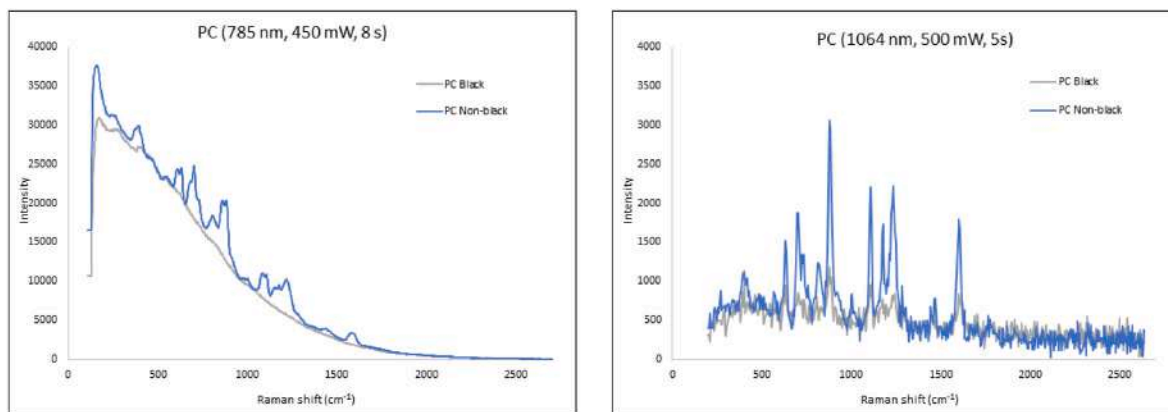


Fig. 5. Raman spectrum of PC obtained with different wavelengths: 785 nm vs. 1064 nm.

spectra were acquired with the maximum power (500 mW).

3.2. Classification models

Raman spectral data of WEEE plastics acquired with optimized settings as defined in section 3.1 (laser: 1064 nm, laser power: 500 mW, integration time: 1.0 s), were processed combining the pre-treatments and machine learning algorithms described in section 2.3, to develop a classification model that could sort mixed target polymers from a WEEE stream in one step. Next, the 3 and 4 categories models that best classify target WEEE plastics according to the technical feasibility

criteria are presented.

3.2.1. 3-Category classification model

Table 6 shows the best 5 models evaluated for 3 categories. As can be observed, accuracy ranged from 58 % to 66 %, clearly depending on the pretreatments applied to the spectral data and on the machine learning models used. The best performing pretreatments were normalization, baseline correction, Gaussian smoothing, deresolve and detrending, each with a different impact on the results. Regarding machine learning algorithms, QDA and SVC with Linear kernel showed better performance. Among them, QDA provided the best results, with an accuracy of

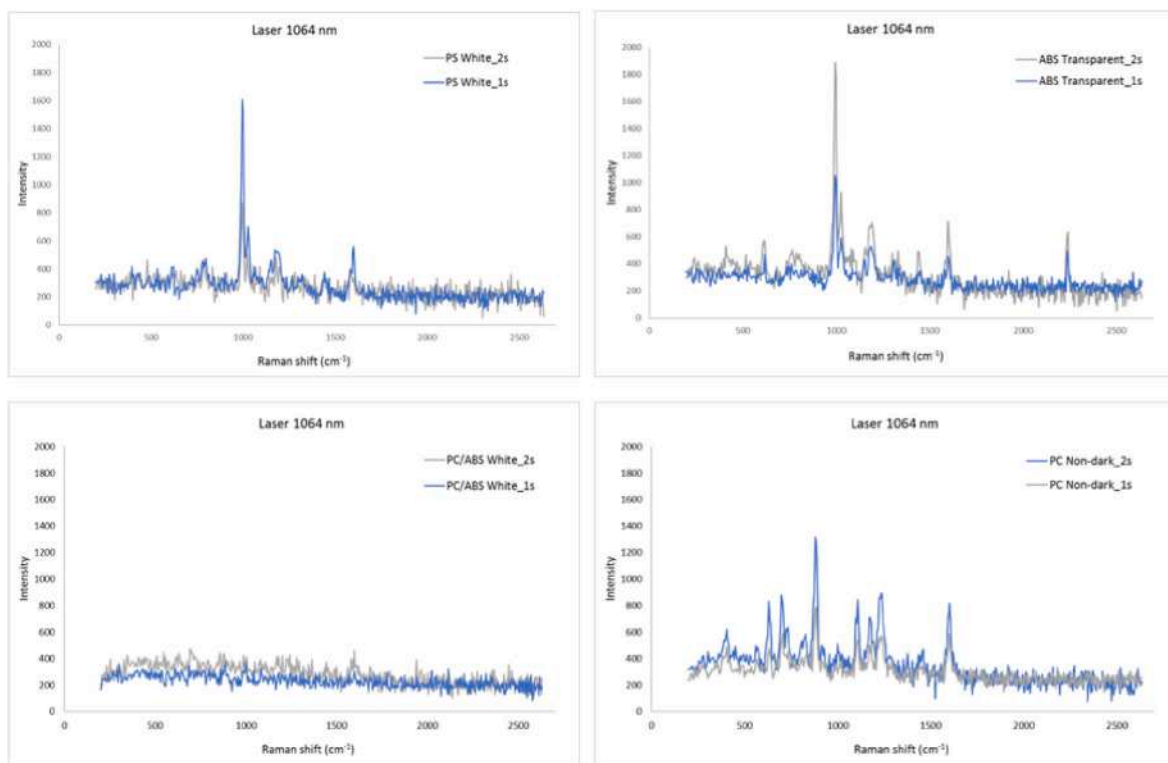


Fig. 6. Raman spectrum of WEED plastics (Laser 1064 nm, 500 mW) at different integration times: 1.0 s vs. 2.0 s.

Table 5
Sensitivity analysis results: Influence of integration time in the recovery rate.

Integration time (Laser 1064 nm, 500 mW)	% Recovery		
	PS	ABS	PC/ABS
1.0 s	80 %	93 %	93 %
2.0 s	77 %	81 %	77 %

Table 6
Adjustments and results of the best performing models for 3-category classification.

Pre-treatment	Model	% Accuracy	Polymer	% Purity	% Recovery
Normalization, smoothing, detrend	PC = 5 QDA	66.3	PS	81	61
			ABS	79	48
			PC/ABS	59	90
Normalization, smoothing, detrending	PC = 5 QDA	65.7	PS	93	46
			ABS	75	53
			PC/ABS	60	98
Baseline, smoothing, deresolve	PC = 5 QDA	65.7	PS	63	61
			ABS	83	48
			PC/ABS	61	88
Baseline, smoothing, deresolve	SVC	58.7	PS	50	57
			ABS	66	63
			PC/ABS	61	56
Smoothing, deresolve	SVC	58.3	PS	52	61
			ABS	67	65
			PC/ABS	59	49

up to 66 %, indicating that this approach is more suitable for this type of spectral data. On the other hand, SVM models provided slightly lower results in terms of accuracy, although they were still effective for certain groups. In contrast, Linear and Mahalanobis DA and SVC combined with other kernels did not achieve to effectively model the polymer class based on Raman spectra.

Together with the accuracy, the recovery and purity were also

assessed to define the performance of each model for each classification group. Imbalances in individual groups were observed. The models with higher accuracy showed the following trend: they led to a high recovery of PC/ABS with low purity, and to a lower recovery of PS and ABS with high purities.

Next, the best performing 3-category model will be analyzed in more depth. It was achieved with 3 pre-treatments (normalization, Gaussian smoothing and detrending), applying a QDA method, and considering all the Raman spectral range ($197\text{--}2633\text{ cm}^{-1}$). Area normalization was applied to reduce the scale effects arising from varying analysis conditions and changes in spectra intensity. Gaussian smoothing filter was used to reduce the noise. By applying Polynomial fitting the trend component in the signal was subtracted. All these transformations enhanced the visibility of analyte-specific information. Regarding the model, even though different kernels were used to transform the parameter space, SVC methods showed lower prediction ability due to overlapping between the groups. The heterogeneity of covariance matrices is probably the reason why Quadratic boundary performed better than Linear and Mahalanobis.

For a more detailed analysis of the classification performance the confusion matrix for the best 3-category model was evaluated (Table 7). In the matrix, each row shows the number of samples of a certain polymer found in the different category groups and the recovery rate; whereas each column contains the number of samples classified in a category and the purity. Significant trends were observed in these results. First, an excellent recovery of 90 % for PC/ABS stood out, indicating a high accuracy in the identification of samples belonging to this

Table 7
Confusion matrix for the 3-category classification model.

Category	PS	ABS	PC/ABS	% Recovery
PS	17	2	9	61 %
ABS	3	19	18	48 %
PC/ABS	1	3	37	90 %
% Purity	81 %	79 %	58 %	–

group. Purities of sorted PS and ABS were good, hovering around 80 %, indicating accurate and reliable recovery for most of the samples classified in these groups.

However, some limitations were identified for this 3-category classification model. In particular, medium recovery was obtained for PS (61 %) and for ABS (48 %), which was attributed to the misclassification of several PS and ABS samples as PC/ABS class. Spectra of PC/ABS showed in general a very noisy signal and weak characteristic peaks. As a result, most PS and ABS samples with low intensity spectra, even after pre-processing the spectral data, were erroneously classified as PC/ABS. Sample misclassifications between the 3 categories were most likely because PS, ABS and PC/ABS show common Raman bands (Table 2). For instance, the styrene peak at 1000 cm^{-1} and the C=C double bond in the aromatic ring (1603 cm^{-1}) are characteristic peaks of the three polymers and the nitrile peak is observed at 2238 cm^{-1} both in ABS and PC/ABS.

Regarding classification results per type of colour (black and non-black plastics), 78 % non-black plastics and 56 % black plastics were correctly identified, and distinctive patterns were observed per polymer type. This strong correlation between samples colour and identification accuracy was highlighted particularly for PS and ABS. It was observed that recovery rate for black PS and ABS barely reached the 10 %. By contrast, higher recovery rate was achieved for non-black samples, reaching almost 90 % for PS and around 70 % for ABS. On the other hand, a very different behaviour was observed for the PC/ABS group. The classification of PC/ABS samples was not dependent on their colour, and recovery rates over 80 % were achieved for non-black and black samples. Both black coloured and PC/ABS samples showed highly noisy spectra. Furthermore, it was noted that a large proportion of the samples classified in the PC/ABS group showed high fluorescence in the Raman spectrum, as black PS and ABS samples did. These similarities in the spectra were most likely the reason for these erroneous model predictions.

3.2.2. 4-Category classification model

Table 8 shows the results of the 5 best performing models obtained to classify 4 categories. They showed similar patterns to the 3-category models, although with certain differences. In this case, the accuracy of the models ranged between 55 % and 57 %, which represents a reduction compared to the range observed for the 3-category models. This decrease in accuracy was expected due to the inclusion of a fourth group containing 10 different polymers, which introduced more noise and greater variability in the spectral data, complicating the classification process.

Table 8
Adjustments and results of best performing models for 4-category classification.

Pre-treatment	Model	% Accuracy	Polymer	% Purity	% Recovery
Smoothing, normalization, baseline, deresolve	PC = 5	57.3	PS	75	42
	LDA		ABS	78	33
			PC/ABS	48	66
			OTHER	54	86
Baseline, smoothing, deresolve	PC = 5	54.8	PS	60	33
	LDA		ABS	77	48
			PC/ABS	68	43
			OTHER	43	86
Smoothing, baseline, deresolve	PC = 5	54.8	PS	65	36
	LDA		ABS	77	48
			PC/ABS	68	43
			OTHER	43	86
Smoothing, baseline	PC = 5	54.8	PS	78	39
	LDA		ABS	81	50
			PC/ABS	67	40
			OTHER	41	84
Normalization, smoothing, detrend	PC = 5	54.0	PS	78	39
	Mahalanobis		ABS	69	52
	DA		PC/ABS	56	43
			OTHER	43	77

Among the applied pretreatments, the ones that showed the best performance, regarding the overall accuracy and the recovery and purity of the individual groups, were baseline correction, Gaussian smoothing, and deresolve. Some of these pretreatments were already identified for the 3-category model, what confirmed that they were robust and effective methods for improving spectral data quality and for optimizing the overall classification results. Once again, the DA-based models showed the best results, specifically the LDA. On the other hand, the Mahalanobis DA and SVC models again showed lower results in this classification, confirming that they are not so suitable for this type of data with high spectral variability and low intensity. Finally, all the best performing models classified PS and ABS with the highest purity. The OTHER category showed an opposite behaviour, with high recovery and low purity. While PC/ABS class achieved more balanced results for both indicators.

The best performing model to sort 4 categories (PS, ABS, PC/ABS, OTHER) was obtained with 4 pre-treatments (Gaussian smoothing, normalization, baseline correction and deresolve), applying a LDA model, and considering only the spectral range within $564\text{--}2275\text{ cm}^{-1}$. In this case, linear interpolation and triangle kernel filter were additionally applied to correct the slope in the baseline and reduce the effect that very noisy spectra had in the results, respectively. Signal detrending was not considered in this case as it did not result in a better classification. Finally, the additional reduction of the Raman shift range aid in lowering the dimensionality of the problem and the variability in the input data by removing noisy and low-relevance spectral bands. The overall accuracy of this LDA model was 57 %, over other alternative solutions. Again, SVC methods showed lower prediction ability due to overlapping between the groups. Here, although normal distribution and covariance homogeneity assumptions did not hold, the linear decision boundary achieved the best performance. This could be explained by the fact that, by increasing the number of groups, the greater simplicity of the Linear DA helped to manage the greater variability between groups more effectively, avoiding overfitting that could occur with the QDA.

Table 9 shows the confusion matrix for the best 4-category model. When looking at the individual category results, whereas a low-medium recovery rate was obtained for the target polymers (41 % PS, 34 % ABS, 66 % PC/ABS), other polymers in the WEEE fraction achieved high recall (86 % OTHER). Regarding purity, sorted PS and ABS achieved almost 80 %; nevertheless, the purity of sorted PC/ABS and OTHER streams was only around 50 %. In the 4-category model, around 30 % of PC/ABS samples were misclassified as OTHER, being the incorrect prediction more pronounced for PS and ABS, where more than 50 % of the samples were misclassified as PC/ABS or OTHER indistinctively. This was the reason for the opposite behaviour of purity and recovery metrics in PS, ABS and OTHER categories, and mid results of PC/ABS for both metrics. Also in this case, although the pre-processing reduced noise signal and highlighted useful information in the spectra, still the similarity in Raman signal patterns may have caused the prediction errors. On the one hand, it was not possible to totally remove the fluorescence signal. It appeared especially in samples containing more fillers and/or additives, which was the case of the samples in the OTHER category. On the other hand, even if the input bandwidth was reduced, the 4 categories showed common characteristic peaks, as it was observed in the 3-category model. For example, aromatic ring (1603 cm^{-1}) appears in several of

Table 9
Confusion matrix for the best performing 4-category classification model.

Category	PS	ABS	PC/ABS	OTHER	% Recovery
PS	15	1	10	11	41 %
ABS	5	14	11	11	34 %
PC/ABS	0	1	23	11	66 %
OTHER	0	2	4	38	86 %
% Purity	75 %	78 %	48 %	54 %	—

the polymers in the 4 categories (PS, ABS, PC, PC/ABS, PUR, PET, PPE + SB and PBT).

Regarding classification results per type of colour (black and non-black plastics), 73 % non-black plastics and 38 % black plastics were correctly identified. For the target plastics, better classification was observed again for non-black plastics (76 % non-black PS, 52 % non-black ABS and above 90 % for non-black PC/ABS), rather than for black samples. In fact, barely 10 % of black PS and 50 % of black PC/ABS were correctly identified, and black ABS was not identified at all. On the other hand, it was observed that the classification of OTHER polymers was not dependent on their colour, and recovery rates over 80 % were achieved for both non-black and black samples. In this case, the Raman signal of the samples in the OTHER group was most frequently very weak and noisy and was affected by fluorescence. As happened previously with the PC/ABS class in the 3-category model, samples from other categories bearing these characteristics were wrongly identify as OTHER.

The extension of the number of categories in the model, from 3 categories and 4 types of polymers (the most abundant in WEEE) to 4 categories, and the fact that the OTHER category included virtually all types of polymers expected in WEEE streams, led to a huge increase in the variability of the input data to the model. This, together with the modest quality of the Raman signal and the fluorescence effect obtained at low measurement times, made the overall classification results worse. In fact, the overall accuracy of the prediction model decreased when the OTHER category was included the classification model. However, in both cases the final model optimization achieved high purity for the two most relevant polymers, PS and ABS, which was between 75 % and 81 %, to the detriment of recovery results and purity for the other groups. The 4-category solution also covered most of the polymers found in WEEE streams and the variability in additive and filler content. This increases the capacity of the proposed system to address safely the separation of WEEE plastic waste in the early stages of the treatment process.

4. Conclusions

This study outlines the classification models developed by combining Raman spectroscopy with machine learning techniques to detect the most prominent plastics (PS, ABS, and PC/ABS) within the WEEE plastics stream that recyclers are currently failing to recover, irrespective of their colour. To accomplish this goal, a 1064 nm excitation wavelength was utilized along with a short measurement time.

The selection of real WEEE plastics samples was crucial to obtain representative results and to evaluate the feasibility of the classification models. In fact, plastic samples from different fractions of an industrial WEEE recycling process were used, gathering more than 14 different polymers. Machine learning models were trained with Raman spectral data of a variety of polymers. Thus, this study faced the current identification and classification problems of the WEEE recycling industry.

Two approaches were considered to develop the models. On the first approach, the classification model was focused only on the target WEEE polymers, thus, containing 3 categories (PS, ABS and PC/ABS). On a second approach, a fourth category was added to the model to consider a more realistic picture of the WEEE plastics stream (PS, ABS, PC/ABS and OTHER). Several multivariate classification models were trained and tested based on DA and SVM algorithms, using Raman spectral data acquired at optimized measuring settings (Power: 500 mW, 1.0 s). The technical feasibility of the classification models was assessed considering the accuracy, and the recovery and purity rates achieved per classified polymer.

The following conclusions were derived for the models that exhibited the highest performance.

- They succeeded in sorting PS and ABS with 80% of purity, and correctly classified 75% of non-black WEEE plastics charged with additives and 40% of black WEEE plastics.
- They were based on QDA (3-category model) and LDA (4-category model). Indeed, DA-based algorithms showed better results than SVM when analyzing Raman spectral data with high variability, weak signal, and high interferences.
- Pre-treatments improved the performance of the classification models and partially reduced the interferences.
- The classification of target plastics (PS, ABS, PC/ABS) varied significantly when other WEEE polymers were considered in the model. Consequently, to assess the technical feasibility of a novel sorting method, it is important that classification models consider the variety of polymers of the real waste streams, as also suggested by some authors (Sunil et al., 2024).

The results of this study are a valuable contribution for researchers to establish further steps on combining spectroscopic techniques and machine learning to come up with solutions to enhance WEEE plastics sorting. These results highlighted that further research is needed to face the challenges of complex plastics identification, mainly to reduce the fluorescence to achieve high recovery and purity rates for target WEEE plastics. In this sense, technological advances in Raman instrumentation could help to reduce the fluorescence background and to achieve spectra of better quality at short integration time. For instance, time gating (TG) techniques have been proposed for this aim (Kotula et al., 2022; Kögler and Heilala, 2021).

It is important to note that all spectroscopic methods possess inherent limitations, as highlighted in a recent review discussing the integration of spectroscopy and machine learning for the swift identification of plastic waste (Yang et al., 2023). The authors propose that a multispectral approach could create a synergistic effect among various spectroscopic methods, thereby enhancing classification and facilitating their industrial use in plastic identification. Several studies have already explored this avenue by combining LIBS and Raman spectroscopy (Shameem et al., 2017; Sormunen et al., 2022b). Additionally, the application of deep learning techniques to analyze multispectral data related to plastic waste presents a promising direction for future research in this area.

CRedit authorship contribution statement

Ainara Pocheville: Writing – original draft, Visualization, Supervision, Investigation. **Iratxe Uribe:** Writing – original draft, Validation, Methodology, Investigation. **Paule España:** Writing – original draft, Validation, Methodology, Investigation. **Sixto Arnaiz:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that has been used is confidential.

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