Received: 25 May 2022 | Revised: 22 September 2022 | Accepted: 30 September 2022

DOI: 10.1002/jrs.6457

RESEARCH ARTICLE

Journal of RAMAN SPECTROSCOPY WILEY

Raman spectroscopic strategy for the discrimination of recycled polyethylene terephthalate in water bottles

Rosa Peñalver | **Félix Zapata** | **Natalia Arroyo-Manzanares** | **Ignacio López-García** | **Pilar Viñas**

Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, Murcia, Spain

Correspondence
Prof. Natalia Arroyo-Manzanares and Prof. Pilar Viñas, Department of Analytical Chemistry, Faculty of Chemistry, University of Murcia, E-30100 Murcia, Spain.
Email: natalia.arroyo@um.es and pilarvi@um.es

Funding information
Spanish MICINN, Grant/Award Number: PGC2018-098363-B-I00; Comunidad Autónoma de la Región de Murcia, Grant/Award Number: 19888/GERM/15; European Commission (FEDER/ERDF)

Abstract

A reliable and quick strategy for the discrimination between recycled and virgin polyethylene terephthalate water bottles was developed by applying Raman spectroscopy combined with chemometrics. Chemometric models were created by orthogonal partial least square discriminate analysis (OPLS-DA) using the Raman spectra dataset in the range of 600–1800 cm^{-1}. The Pareto scale model allowed the classification of virgin and recycled terephthalate of polyethylene (PET) samples with a percentage of success of about 95%. In addition, PLS regression was carried out to determine the level of recycled material in the PET water bottles with a good fit ($R^2 = 0.8920$). This analytical approach shows a quick, accurate, and robust way to detect and quantify the adulteration of plastic bottles with recycled plastic materials to avoid fraud in the recycling plastic area.

KEYWORDS

adulteration, Chemometric, polyethylene terephthalate (PET), Raman spectroscopy, recycled

1 | INTRODUCTION

Polyethylene terephthalate (PET) is a polyester with excellent physical and chemical properties, which allows its usage in many different applications. Since the 1980s, PET has been widely used in the manufacture of textile fibers, being recently mainly used in food and beverage packaging (69–97%).[1] PET bottles are single-use plastic materials that are quickly discarded into waste, with a significant volume ending up in the environment and, concretely, in the oceans. One of the most efficient ways to decrease the quantity of PET waste is to recycle those wastes, as is described in the circular economy priorities of the European Commission.[2] Continuous research across the world has allowed us to develop great advancements in the methods involved in PET recycling.[3] It is worth mentioning the importance of the cleaning process optimization during recycling, which is key to ensure the good quality of the recycled material.[4,5] On the other hand, since plastic waste is cheaper than virgin plastic, plastic packaging materials may be adulterated with low-quality recycled resins during the manufacturing process. Those recycled materials may have impurities from the recycling process and their previous life[6,7] which may affect the quality and/or safety of the final plastic product. In addition, plastic packages for certain applications, such as drug containers must be made of virgin materials rather than recycled plastics.[8]

There is not a specific authoritative method for the detection of the adulteration of plastic materials with less expensive recycled resins during manufacturing. Chromatographic approaches based on headspace-gas chromatography–mass spectrometry (HS-GC–MS),[6,9] microwave assisted extraction followed by GC–MS,[10] and ultra-performance-liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF-MS)[11] have been carried out with the purpose of discriminating between recycled and virgin plastics. In the same way, thermal analytical tools such as differential scanning calorimetry, thermal gravimetric, and melt flow index analyses have been applied to determine thermal polymer properties which vary between virgin and recycled polymers, being useful for authentication purposes.[1,12] These analytical approaches are time-consuming and labor-intensive existing a clear need to develop rapid, nondestructive, and straight-forward analytical methodologies to determine this potential adulteration. On the other hand, infrared spectroscopy has been used for the discrimination of different types of plastics.[13–15] The differentiation of several polymeric materials is possible due to the specific vibrational characteristics of each polymer. However, few studies focused on the discrimination between virgin and recycled plastics by infrared spectroscopy have been reported since the physical and chemical differences between virgin and recycled polymers are normally evidenced by very slight spectral differences.[8,16,17]

Similarly, Raman spectroscopy is a fast, low-cost, and nondestructive vibrational technique, little explored but potentially useful for the discrimination of recycled plastics. In addition, its coupling with chemometric models is expected to enhance the discrimination between virgin and recycled materials based on their slight spectral differences.

In this study, Raman spectroscopy was used to get the spectral analytical fingerprint of the virgin and diverse composition of recycled PET mineral water bottles. For the first time, a strategy based on the application of a statistical model based on partial least squares (PLS) to the Raman spectra dataset enabled the measurement of the amount of recycled plastic in the PET bottle composition. This tool could be applied to detect adulteration of virgin plastics and/or deliberate counterfeit in the percentage of recycled PET declared by manufacturers of mineral water bottles, mitigating possible frauds in the recycling plastic area.

2 | MATERIALS AND METHODS

2.1 | Samples

A total of 400 samples from 80 different mineral water bottles from 25 different brands were analyzed (five different pieces were cut and analyzed per bottle). The samples were cut into small pieces of approximately 0.3 cm × 0.4 cm and placed over aluminum foil to be measured by Raman spectroscopy. If similar spectra (undistinguishable to the naked eye) were obtained for the five pieces of the same bottle, then the material was assumed to be homogeneous. Thus, the dataset consisted of 400 spectra (125 samples of 100% wt. recycled PET, 55 samples of 50% wt. recycled PET, 45 samples of 25% wt. recycled PET, 15 samples of 15% wt. recycled PET, and 160 samples of 0% wt. recycled PET). PET mineral water bottle samples were purchased on the market from different suppliers. The provided recycled PET content in the samples was the one declared by the supplier in the bottle label. In the absence of additional information, we took this value as the real one.

2.2 | Instruments and software

Raman spectra analyses were carried out using an i-Raman BWS41 portable spectrometer system acquired from B&W Tek Europe GmbH (Lübeck, Germany) equipped with a laser working at a 785 nm wavelength. 354 mW ± 15% was the maximum laser output power at the system's excitation port and 285 mW in the probe.

Spectra were obtained from 500 to 3250 cm^{-1} with a resolution of 4 cm^{-1} (i.e., data spacing of 1.12 cm^{-1}). For the measurements, the laser power at the probe was set to 10% of the maximum, which was 28.5 mW, in order to avoid fluorescence, excessive scattering, and sample heating. Spectra were recorded by collecting 10 scans and using 5 s of exposure time per scan. BWSpec 3.27 software was used for data acquisition and instrument control. The Unscrambler X 10.1 software (CAMO, Oslo, Norway), and SIMCA-P v14.1 (Umetrics, Malmö, Sweden) were used for data processing and multivariate chemometric analysis.

2.3 | Data processing and chemometric analysis

After subtracting the dark and background spectrums, the obtained spectral data were exported to a.csv file. The csv files were imported to the Unscrambler X and SIMCA-P software, generating a raw data matrix containing the 400 spectra and all Raman shift wavelengths (dimension 400 × 2470). First of all, Raman spectra were cropped to 600–1800 cm^{-1} (new matrix dimension 400 × 1072), after checking that most of the characteristic Raman signals of PET water bottles were located within this range (known as the IR/Raman fingerprint).

Afterward, spectral data were linear baseline corrected, mean normalized, and smoothed (Savitzky–Golay, polynomial order 2, five points) using the Unscrambler X software. Finally, (i) a principal component analysis (PCA) was calculated for preliminary exploratory discrimination using the Unscrambler X, (ii) an orthogonal partial least squares discriminant analysis (OPLS-DA) was calculated for classification purposes using SIMCA-P, and (iii) a partial least squares regression analysis (PLS-regression) was developed for quantifying/determining the PET-recycled content in water bottles using the Unscrambler X.

3 | RESULTS AND DISCUSSION

3.1 | Raman spectra of recycled-PET water bottles

Although degradation products may be formed during the recycling process of PET, the Raman spectra of both virgin and recycled-PET samples displayed the characteristic bands of PET material (see Figure 1).

As extensively reported in literature,[18–21] these bands correspond to the fundamental vibrational modes of PET material. They have been summarized in Table 1. In summary, the intense band located at 1730 cm^{-1} is due to the C=O (ester) stretching; the most intense band located at 1614 cm^{-1} is due to the C=C aromatic stretching; the bands between 1450 and 1400 cm^{-1} belong to CH_2 and CH bending vibrations; the bands within the range 1300–1000 cm^{-1} are due to C(O)-O stretching and O-C-O stretching, whereas the bands below 900 cm^{-1} are associated to C-C benzene ring modes and C-H out-of-plane bending vibrations. It should be noted that no additional Raman bands were visually perceptible in the recycled PET bottles. However, the raw Raman spectra of recycled PET bottles displayed a worse baseline than virgin PET bottles (Figure 1), which implies that the former were more affected by fluorescence than the latter due to different matrix composition.

As evidenced in Figure 2, the baseline slope, diffuse background, and spectral noise observed in raw Raman spectra, mainly due to fluorescence, scattering, and heating effects, were minimized after data processing (i.e., cropping to 600–1800 cm^{-1}, baseline correction, normalization, and smoothing).

3.2 | Chemometric estimation of the recycled-PET content in water bottles

PCA analysis was carried out to extract the main information from the spectral data to explore the potential

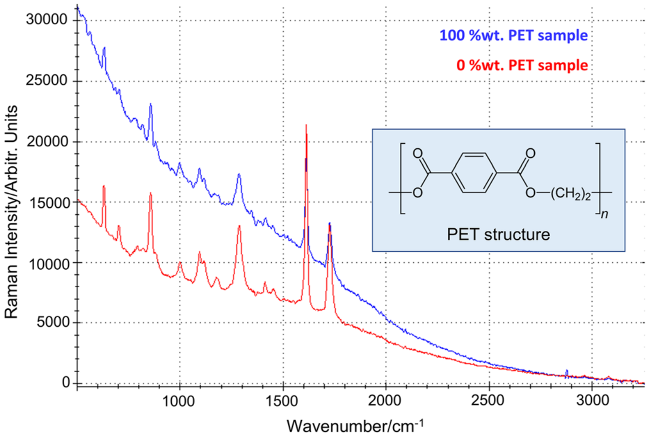

FIGURE 1 Two selected raw Raman spectra, one from a 100% wt. PET recycled sample (blue line) and the other from a 0% wt. recycled PET sample (red line). [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Assignment of the major PET Raman bands according to the literature[18–21]

Raman shift (cm^{-1})	Vibrational mode
1725	C=O stretching (ester)
1614	C=C aromatic stretching
1415	CH_2 & C–H bending
1292	C(O)-O (ester) stretching
1180	C–O–C stretching
1119	C(O)-O (ester) stretching
1096	C–O–C stretching
1001	C–O stretching (O-CH_2)
858	C–H out-of-plane bending, C–C stretching
704, 633	Ring modes of benzene ring, C–H out-of-plane bending

discrimination among the different PET samples. In brief, this preliminary PCA analysis was mainly explained by the PC1 and PC2 components (which explained 95% and 4% of the variance, respectively). In such a preliminary PCA (whose scores are displayed in Supplementary Material Figure S1), it was observed that the virgin and recycled-PET samples were mostly separated from each other, except for some samples with low recycled-PET content (15–25%) that partially overlapped with virgin samples. The key spectral differences that explain this separation among virgin and recycled samples for each principal component are summarized in the loadings plot displayed in Figure S2. In brief, major differences in these loadings were located around the characteristic Raman

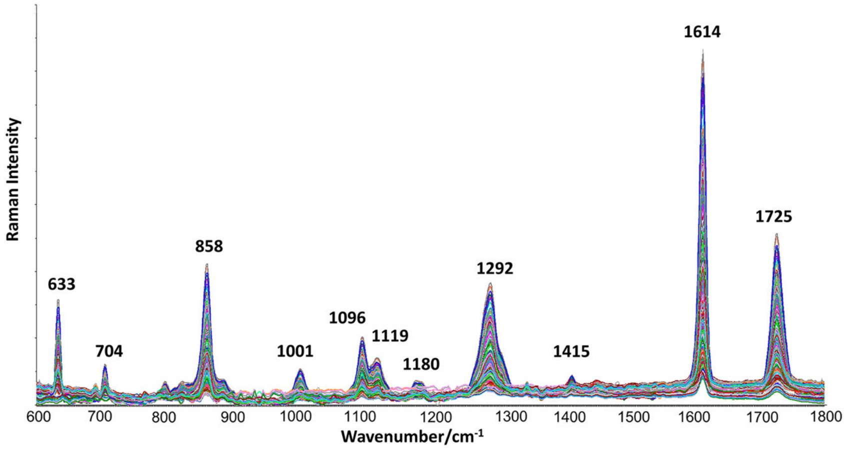

FIGURE 2 Raman spectra of all samples after data processing (i.e., cropped, baseline corrected, normalized, and smoothed). [Colour figure can be viewed at wileyonlinelibrary.com]

bands of PET (i.e., slightly higher or lower wavenumber with respect to the PET Raman bands: 1727 vs 1725 cm^{-1}, 1615 vs 1614 cm^{-1}, or 1291 vs 1292 cm^{-1}). In particular, negative bands in the loading plot of PC1 corresponded to negative scores values in the PC1 axis (where virgin PET samples were located). This result might indicate that the characteristic Raman bands of virgin PET bottles are slightly shifted with respect to PET-recycled bottles.

This result was further corroborated, improved, and statistically validated by orthogonal partial least square discriminative analysis (OPLS-DA). To calculate the OPLS-DA model, the preprocessed Raman spectra dataset was split into two groups; 80% of the data was for training and the remaining 20% for validation of the model. In order to obtain the best model that would allow the classification of the samples, six scaling (unit variance none (UVN), unit variance (UV), Freeze, Pareto none (ParN), Pareto (Par), and centering (Crt)) and logarithmic transformation or raw data were tested.[22] It should be noted that even though the recycled PET samples included different declared percentages of recycled material (15, 25, 50, and 100% wt.), all of them were grouped into the same category defined as recycled.

The outcome of the diverse chemometric models used (number of components, R2X(cum), R2Y(cum), R2X (cum), and Q2(cum) parameters), the classification rate obtained for each category in the validation and calibration set, along with the percentage of success for each category in the validation set, are displayed in Table S1. The analytical parameters such as specificity, sensitivity, accuracy, and precision of the OPLS-DA method were calculated by the following equations (1, 2, 3, and 4) FN (false negative rate) is the percentage of virgin samples wrongly identified as recycled; FP (false positive rate) is the percentage of PET-recycled samples wrongly identified as virgin; TP (true positive rate) is the percentage of samples correctly identified as virgin; and TN (true negative rate) is the percentage of samples correctly identified as recycled[23]; all these for the determination of virgin samples. On the contrary, if the point of view regards the determination of recycled bottles, the rates mean the opposite. Those analytical parameters were calculated for both classes (the virgin and the recycled samples) in the validation set.

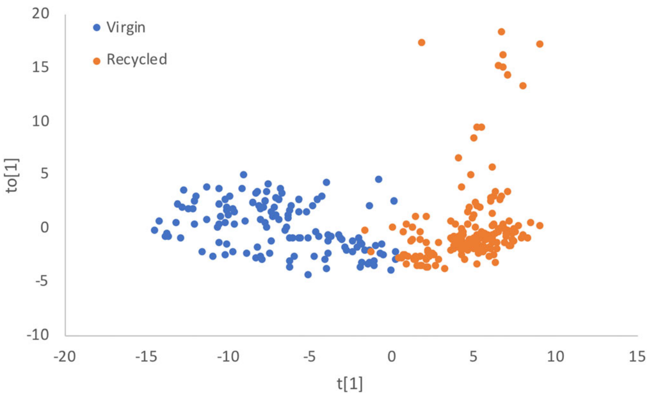

FIGURE 3 2-D OPLS-DA scores plot of Raman spectra of PET bottles, representing the blue dots virgin samples and the red dots PET-recycled samples. [Colour figure can be viewed at wileyonlinelibrary.com]

1. Accuracy $= (TP + TN)/\ (TP + TN + FP + FN) \times 100$
2. Sensitivity $= TP/(TP + FN) \times 100$
3. Specificity $= TN/\ (TN + FP) \times 100$
4. Precision $= TP/\ (TP + FP) \times 100$

As summarized in Table S1, the best results were obtained by means of the Pareto scale. The classification rates for calibration and validation were 95.61% and 95%, respectively, thus correctly classifying the measured samples. The two defined classes/categories (recycled-PET bottles and virgin PET samples) had statistically significant differences in their Raman fingerprint, by which

TABLE 2 Validation parameters of the Pareto model for the validation set (%)

Class/category	Sensitivity	Precision	Specificity	Accuracy
Virgin	88	100	100	95
Recycled	100	92	88	95

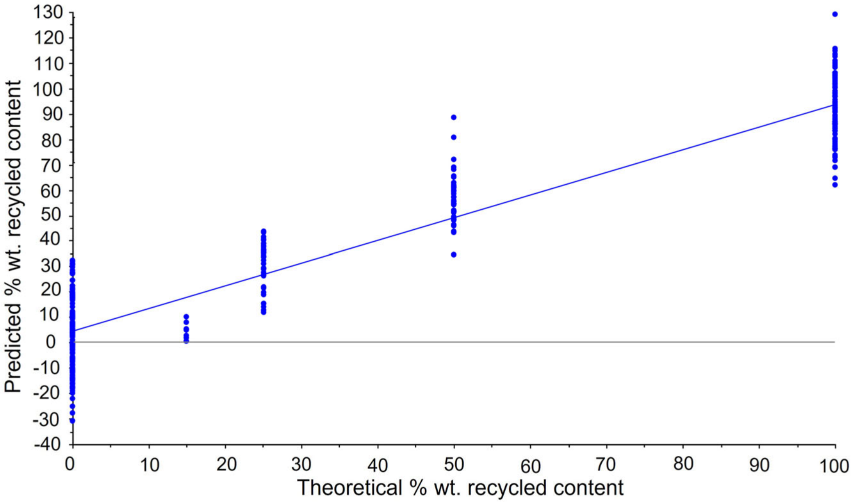

FIGURE 4 PLS regression calibration curve. [Colour figure can be viewed at wileyonlinelibrary.com]

they are located separately along two different regions in the OPLS-DA score plot displayed in Figure 3, as preliminary observed by PCA.

The discrimination among the two defined classes (virgin and recycled-PET bottles) using the OPLS-DA model (calculated within the Raman range of 600–1800 cm^{-1}) is statistically precise and accurate, as summarized in Table 2.

Finally, while OPLS-DA was carried out with a qualitative classification objective, PLS regression was further studied from a quantitative approach to estimate the level of recycled PET plastic in the water bottles. In this respect, the weight percentage of PET applied in the calibration and validation sets employed in the PLS model were separately considered: 0, 15, 25, 50, and 100% wt. The high values of the correlation for calibration (Figure 4) and validation (0.9445 and 0.9112, respectively) and the low values of root-mean-square error of calibration (RMSEC = 14.041) and prediction (RMSEP = 17.953), showed the good predictive ability of the established PLS model. This procedure was repeated five times, selecting new training and validation sets at random with the purpose of assessing the robustness of the obtained data.

According to Figure 4, it should be noted that the predicted PET-recycled content of 0, 25, 50, and 100% wt. PET-recycled samples were quite normally distributed around their real PET-recycled content. The obtained data dispersion in Figure 4 might be due, to some extent, to the inaccurate PET-recycled content provided by the suppliers and assumed as real. In particular, according to the PLS regression results, predictive values for 0% wt. PET-recycled bottles were 3 ± 15% wt. (for the calibration set) and 4 ± 20% wt. (for the validation set). Predictive values for 25% wt. PET-recycled bottles were 30 ± 9% wt. (calibration set) and 35 ± 9% wt. (validation set). Predictive values for 50% wt. PET-recycled bottles were 57 ± 10% wt. (calibration set) and 50 ± 11% wt. (validation set). Predictive values for 100% wt. PET-recycled bottles were 92 ± 13% wt. (calibration set) and 88 ± 22% wt. (validation set). On the contrary, the predicted PET-recycled content of the 15% PET-recycled bottles was underestimated with values of 4 ± 4% wt. (for the calibration set) and 10 ± 1% wt. (for the validation set). This result suggests that further studies increasing the population, specifically of 15% wt. PET-recycled bottles, are encouraged.

4 | CONCLUSIONS

A fast, nondestructive methodology based on Raman spectroscopy and chemometrics was developed to discriminate between recycled-PET (of different percentages) and virgin plastic bottles from diverse manufacturers. In addition, the methodology is solvent-free and does not require sample preparation. Although further investigation regarding the laser focusing, radiation angle and direction, and exposure time during the inline analysis would be required, this methodology could be likely automatized and integrated in the polymer production process to monitor recycling levels. In particular, the combination of Raman spectroscopy and chemometric analysis (PCA, OPLS-DA, and PLS regression) within the range from 600 to 1800 cm^{-1} of PET samples was demonstrated, for the first time, to be a very useful tool to determine the percentage of recycled-PET in PET water bottle samples. This novel analytical approach can be taken to check adulteration of plastic materials to avoid fraud in the recycling plastic area.

ACKNOWLEDGEMENTS

The authors would like to thank the Spanish MICINN (PGC2018-098363-B-I00), the Comunidad Autónoma de la Región de Murcia (CARM, Fundación Séneca, Project 19888/GERM/15) and the European Commission (FEDER/ERDF) for their funding support.

DECLARATION OF COMPETING INTEREST

The authors declare no conflict of interest. The manuscript has been approved for publication by all authors.

ORCID

Natalia Arroyo-Manzanares https://orcid.org/0000-0001-9882-6270

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How to cite this article: R. Peñalver, F. Zapata, N. Arroyo-Manzanares, I. López-García, P. Viñas, *J Raman Spectrosc* **2022**, 1. https://doi.org/10.1002/jrs.6457