

Determination of the polymer composition of mid-twentieth century purses by Raman spectroscopy

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Abstract

A database was constructed of 134 reference plastic samples and their Raman spectra to aid in the rapid and accurate identification of the polymer composition of mid-twentieth century plastic purses and their component parts from the Plastics Artifacts Collection at Syracuse University Libraries. Work began by making and testing the database, which led to the determination that matching artifact spectra to reference sample spectra worked well for artifact spectra having signal-to-noise ratios down to 30:1. This finding allowed for using reduced laser power as necessary to protect delicate and pigmented artifacts. These studies enabled the definitive chemical identification of seven selected artifacts, showing that each is composed of polystyrene, polymethyl methacrylate, and/or cellulose acetate. The compositions of three artifacts of unknown composition were discovered, corrections to the existing records were made for three other artifacts, and the composition of one artifact was confirmed. Furthermore, it was discovered that one of the purses was composed of both polymethyl methacrylate and cellulose acetate. This decisive study will contribute to the archival processing and preservation of these artifacts.

Introduction

The Plastics Artifacts Collection (PAC) was established by the Special Collection Research Center at Syracuse University Libraries (SCRC-SUL) in 2007 and is composed of 5,000 + plastic artifacts as well as periodicals, books, manuscripts, and other media documenting the history of plastics. The majority of the plastic objects in this collection were donated by the National Plastics Center and Museum when it closed in 2008. These items were manufactured from the late 1800s to the early 2000s and encompass everything from consumer products to military gear and industrial parts.(1) This eclectic collection is an important record of our modern cultural history.

The earliest artifacts in the PAC are composed of semi-synthetic plastics such as celluloid and cellulose acetate (CA), while more recently manufactured pieces are made with a wide range of polymers including polystyrene, vinyl, acrylic, and polycarbonate. In addition to polymers, many of these plastics contain additives such as pigments, composite materials, and plasticizers. Knowledge of an artifact's chemical composition is an essential part of its preservation since plastics are known to degrade over time with different plastics having different degradation pathways. For example, the primary degradation reaction for CA is the hydrolysis of its acetyl groups, which produces acetic acid. This acetic acid then catalyzes further hydrolysis and causes additional degradation in both the degrading artifact and any nearby artifacts that are sensitive to acids.(2–9) Surveys of plastic artifacts in British museums in the 1990s showed that the most actively degrading plastics were cellulose nitrate, CA, plasticized polyvinyl chloride, and polyurethane foam.(2, 10) When artifacts are identified as containing vulnerable plastics such as these, inhibitive conservation may then be practiced, decreasing degradation rates and prolonging the useful lifetimes of those artifacts. In the case of conserving artifacts made of CA, efforts would include mitigating acetic acid.(2, 3, 9) Thus, to support archival processing and preservation of the PAC, a major goal of this study is to identify artifacts composed of plastics that are vulnerable to degradation.

Artifact records obtained by the SCRC-SUL when it acquired the PAC lack a description of chemical composition for some of the artifacts, while the composition of others is listed but not known definitively. The process of decisively identifying the polymer composition of the collection's artifacts has begun using Raman spectroscopy with laser excitation at 785 nm. We chose this technique for its significant advantages. First, Raman spectroscopy is nondestructive and noninvasive, making it a safe process for delicate artifacts.(11–13) Raman spectroscopy is also very sensitive to a variety of different polymers and can be used to distinguish among them relatively quickly and with great accuracy.(6) Finally, modern Raman spectrometers provide a portable solution for examining artifacts *in situ*, making it unnecessary to move artifacts to a laboratory.(11–14) While using this technique, we do not expect to be able to identify the complete chemical makeup of all the artifacts. Even though many polymers can be identified using Raman spectroscopy, some polymers as well as component materials in the plastics are not good candidates for these studies because they fluoresce during the experiment. Fluorescence overpowers the relatively weak Raman scatter, obfuscating spectral features.(12, 15) Another difficulty is the identification of additives, impurities, and degradation products in plastics since they may either complicate the spectral results or be relatively difficult to detect.(8, 15) Even with these limitations, we anticipate success with identifying the polymer composition of many artifacts in the PAC, and in this manuscript, we report on our first investigations.

For this initial study of the PAC objects, we examined plastic purses and their component parts. Women's handbags, a fascinating component of cultural history, became popular in Europe during the late 1790s when pockets in dresses were eliminated as the result of emerging slimmer styles of dress.(16, 17) Over time, the design and construction of purses evolved reflecting changes in fashion, women's practical needs, available materials, and manufacturing techniques. In the early twentieth century, with the availability of plastics for manufacturing domestic goods, handbags started to be crafted of plastics. The type of plastics used in these bags changed as new polymers were invented and manufacturing techniques evolved from skilled handcrafting to injection molding.(16–18) Design and construction features combined with knowledge of an object's chemical composition can aid curators and researchers in establishing the origin of artifacts lacking complete documentation of provenance.(2) Having more complete records about artifacts in the PAC will make the collection a more valuable resource for scholars and enhance the appreciation of these artifacts.

Records of the purses studied within this manuscript, all containing transparent plastic parts, indicate manufacturing dates from the 1940s-1970s. During this mid-century period, acrylic purses were popular, but other types of plastics were being used as well.(16–18) It is difficult to accurately identify plastic composition by eye. So, to ease identification of the chemical composition of the purses, as well as looking to future studies of the PAC, we first obtained Raman spectra for many standard plastics and developed a reference database of those spectra. Once a sufficiently large database was constructed, it was tested on plastic objects of known composition. When we had confidence in our database, we began investigating the purses and their component parts by obtaining their Raman spectra and performing spectra matching to the reference plastics in the database. Finally, to ensure a definitive identification, we

manually analyzed the spectral fingerprint of each artifact, ensuring its peaks correspond to the correct chemical functional groups for the matched reference polymer.

Materials And Methods

Raman instrument & data analysis software

A B&W Tek (Newark, NJ) iRaman Plus portable spectrometer equipped with a 785 nm laser and a fiber optic probe (85 μm spot size) was used for excitation and data collection. The system is also equipped with a microscope for collecting data when microscopic sampling is required. Its CCD detector has a 65–3200 cm^{-1} range and 4.5 cm^{-1} resolution. Spectra were averaged over 225 acquisitions with a 1-second exposure time at room temperature. The full laser power (100%) at the probe is approximately 200 mW, but laser power was varied, with lower powers used to avoid damaging pigmented and delicate artifacts. BWSpec software (B&W Tek, version 4.11) was used for instrument control and data collection.

The plastics spectral database for use in chemical analysis was constructed using BWID software (B&W Tek, version 2.03). BWID software uses line smoothing, followed by first derivative analysis, and finally peak correlation analysis to match spectra from artifacts to reference samples. The spectral region of 200–2600 cm^{-1} is used by the BWID software for data matching. This region contains peaks arising from the vibrations of common chemical functional groups found in plastics.

Reference polymers and plastic samples

Reference polymers used in the creation of our database were obtained from multiple sources. One kit came from Scientific Polymer Products Inc., Ontario NY; scipoly.com (Polymer Sample Kit #205). A second polymer sample kit was obtained from ResinKit.com (currently available from Plastics Group of America, Woonsocket, RI; plasticsgroup.com). Additional reference plastics in the form of industrial samples of known composition including the Chroma Corporation samples were obtained from the Plastic Artifacts Collection and the Plastics Pioneers Association donations. We refer to these industrial samples as our Historical Sample Library. Test samples with recycling codes were taken from campus recycling. See the **Supplementary information** section for a comprehensive list.

Artifacts

The artifacts analyzed within this manuscript are housed in the SCRC-SUL and are shown in Table 1 with their accession numbers and known manufacturing information. The manufacturing information in the curatorial records is incomplete.

Results And Discussion

Creation of the Syracuse Chemistry of Artifacts Project (SCOAP) plastics reference database

Spectra were obtained for a large variety of reference plastics, for a total of 134 different samples that are identified in the **Supplementary information** section. These specific reference plastics were chosen to comprise those used in manufacturing from the late 1800s through the early 2000s, which is the manufacturing time span of the artifacts in the PAC. The reference spectra were compiled using BWID to form the SCOAP plastics reference database.

After constructing the database, we tested it using spectra of plastic marketing samples produced by the Chroma Color Corporation and some discarded consumer items marked with recycling codes. The analyses produced correlations to the database references of 93–99+% match quality, and the results can be seen in Table 2. We generally consider correlations greater than 90% match quality to be successful. Even when obtaining high correlations, complete analysis of the artifact spectrum includes looking for anomalies both within the 200–2600 cm^{-1} spectral window that BWID uses for matching and also outside of that window. The presence of all spectral fingerprint features is verified in the artifact spectrum. Any anomalies are carefully considered, and best attempts are made for attributions to sample-specific aspects such as the presence of pigments.

Table 2

Samples used to test the SCOAP plastics reference database and their correlations to reference plastics.

Sample ID	Known composition (pigment)	Correlation match quality (reference)
ChromaAC24030	Acrylonitrile-butadiene-styrene terpolymer (25.5% TiO_2)	97.0% (acrylonitrile-butadiene-styrene)
ChromaHC2200B	Polystyrene (26.5% TiO_2 + 13% CaCO_3)	99.0% (polystyrene)
ChromaNC2667A	Nylon (32% TiO_2)	93.3% (nylon-6)
ChromaZC2606B	Polycarbonate (23% TiO_2)	97.0% (polycarbonate)
RecycleCode1 (bottle)	Polyethylene terephthalate (colorless)	96.6% (polyethylene terephthalate)
RecycleCode2 (tub)	High-density polyethylene (white pigment)	98.8% (high-density polyethylene)
RecycleCode5 (bottle)	Polypropylene (colorless)	98.9% (polypropylene)

When testing and using the SCOAP database, we expect some variations in the correlation between the references and test samples. The presence of additives or impurities, which may have been incorporated during manufacture or as a result of degradation may reduce correlation quality. Additionally, a lower

correlation quality is expected for composite materials, chemically modified polymers (e.g., CA), and copolymers due to their innate variations in composition. Finally, lower correlation qualities are seen when the baseline of a spectrum is not flat, such as when fluorescence occurs.

Successful matching of the database references to artifact spectra demands a high correlation between the sample and reference spectra. Mathematically, obtaining a high correlation is in part reliant on having a spectrum with a high signal-to-noise ratio, which is generally maximized at higher laser powers. Yet when an artifact is darkly pigmented, aged, or degraded, it is prudent to use a reduced laser power to avoid surface damage. We tested the BWID software with spectra of CA, a plastic commonly found in older artifacts, taken with reduced laser powers. This analysis (Fig. 1, Table 3) shows that the match correlations remain above 91% until the laser power is reduced from 20–10% (approximately 40 mW to 20 mW) at which point the correlation to the reference drops to 27%. At the same time, the signal-to-noise ratio for the 1729 cm^{-1} peak drops from 31 to 15. This result shows that we are able to perform reliable spectra matching when the signal-to-noise ratio exceeds approximately 30:1, and in the case of CA, we can use laser powers reduced to 20% and still achieve a high correlation match.

Table 3
Effects of laser power on the Raman spectral match quality and signal-to-noise ratio for CA.

Laser power (%)	Correlation match quality (%)	Signal-to-noise ratio ^a (1729 cm^{-1} peak)
100	98.1	121
80	98.0	96
60	97.9	74
40	97.1	53
20	91.0	31
10	27.0	15

^a $\text{SNR} = \frac{\bar{E}}{s}$ where \bar{E} is the mean value of the peak height and s is the standard deviation of the noise.

Work on the SCOAP plastics reference database is an ongoing project. We intend to increase the variety of both modern and historical references with the goal of enhancing our ability to identify the composition of artifacts in future studies of the PAC. As synthetic chemistry and plastics formulation is an evolving and creative science, we need to prepare for studies which uncover artifacts with unusual polymer compositions. A further goal of expanding the database is to incorporate degraded samples and

better identify the chemical fingerprints of degradation products. Finally, the incorporation of known additives such as plasticizers and pigments would benefit our work.

Analysis of the artifacts

The clear, colorless handbag covers, **Artifact A**, are identified in the SCRC-SUL records as being composed of polystyrene (PS). This information is confirmed by Raman analysis with a 99+% correlation to the PS reference. In Fig. 2, the artifact spectra are dominated by the aromatic ring-breathing mode band at 1000 cm^{-1} . As expected for PS, the peaks associated with in-plane ring deformation (620 cm^{-1}) and in-plane ring stretching (1455 cm^{-1} , 1600 cm^{-1}) are present as well. Beyond the BWID search region, we can identify the characteristic aromatic CH stretching at 3060 cm^{-1} and aliphatic CH stretching at $2854\text{--}2923\text{ cm}^{-1}$.(19–21) The BWID analysis combined with our peak inspection confirms that **Artifact A** is PS, as was listed in the SCRC-SUL artifact description.

Artifact B is a purse with a top, bottom, and handle made of colorless, clear plastic and metal sides. Its plastic composition was previously unidentified in the SCRC-SUL records. The three plastic parts were analyzed individually by Raman spectroscopy and examined with BWID software. Spectra matching revealed that all three parts were manufactured using an acrylic polymer, which is chemically known as polymethyl methacrylate (PMMA), with a 94+% correlation match quality to the PMMA reference. The spectra for the three parts of **Artifact B** as well as that of the reference plastic from the database are shown in Fig. 3. An inspection of the traces shows that they all have similar features. Within the BWID analysis range we can see vibrational modes characteristic of the ester functional group including the carbonyl stretch at 1735 cm^{-1} . Also, there is the spectrally dense region from $1100\text{--}1525\text{ cm}^{-1}$ containing combination modes of C-O stretching and CH bending and rocking. At approximately 800 cm^{-1} , a sharp peak is observed, which is a C-C stretch and C-O stretch combination band.(20, 22) Outside of the BWID analysis range, we observe a broad group of bands from $2850\text{--}3040\text{ cm}^{-1}$ indicating the presence of both methyl and methylene groups. Thus, the previously unknown plastic used in manufacturing all three parts of the handbag is identified as PMMA.

Artifact C is a clear, colorless plastic purse with glitter embedded in the plastic, and it was constructed of three molded plastic pieces: the top, bottom, and handle. The SCRC-SUL artifact description did not contain information about the plastic composition used in the purse manufacture. The Raman spectra and BWID analyses of all three pieces identify the plastic as PS, all having a 99+% correlation to the reference. The artifact spectra are shown in Fig. 4 along with the PS reference spectrum. An inspection of the data in the BWID search range shows that the purse spectra contain the characteristic modes for aromatic groups as seen for **Artifact A** including the intense aromatic ring-breathing mode band (1001 cm^{-1}), the in-plane ring deformation (620 cm^{-1}), and in-plane ring stretching (1455 cm^{-1} , 1600 cm^{-1}). Likewise, beyond the BWID search region, we can identify the characteristic aromatic CH stretching at

3060 cm^{-1} and aliphatic CH stretching at 2854–2923 cm^{-1} .(19–21) This combined evidence allows us to positively identify the plastic used to manufacture **Artifact C** as PS.

The colorless and orange plastic bamboo-like handles (**Artifacts Da** and **Db**) were previously identified as PS in the SCRC-SUL records. Spectra shown in Fig. 5 and BWID analysis show that both of the handles are actually composed of CA with a 90+% correlation to the reference. Clearly the artifact spectra do not match the PS reference spectra since they are devoid of the characteristic aromatic peaks for PS around 620 cm^{-1} , 1000 cm^{-1} , and 3055 cm^{-1} . Rather, the spectra for **Artifacts Da** and **Db** have spectral features consistent with the presence of the ester group of CA including the C = O stretching (1728 cm^{-1}) and C = O in-plane rocking (648 cm^{-1}). Also, we see a spectrally dense region of 1060–1200 cm^{-1} consistent with peaks arising from C-O stretching due to the ester, the cellulose rings and (non-acylated) hydroxyl groups.(20, 23) The chemical composition identities of these handles have been corrected by this study, showing that **Artifacts Da** and **Db** are composed of CA rather than PS.

The polymer composition of **Artifact E**, the clear, colorless clamshell purse was identified in the SCRC-SUL records as PMMA. However, Raman analysis by the BWID software indicates that this information is incorrect and that **Artifact E** is composed of PS with a 99+% correlation to the reference spectrum. A comparison was made of the PMMA and PS reference spectra with the artifact spectrum, all shown in Fig. 6. The artifact spectrum is dominated by the strong aromatic peak centered at approximately 1000 cm^{-1} that is characteristic of PS. The artifact spectrum also contains the other characteristic peaks for PS as described in the analysis of **Artifact A**.(19–21) In contrast, the PMMA reference contains the characteristic carbonyl stretch at approximately 1730 cm^{-1} , which is lacking in the artifact spectrum. This analysis shows that **Artifact E** had been previously misidentified as PMMA, and we are able to definitively show that this purse is manufactured from PS.

Artifact F, the flattened cylindrical purse, is constructed of four parts: the lid, the base, the handle, and the feet. No information about the materials used in manufacturing this artifact was provided in the SCRC-SUL artifact description. Each part of this artifact was analyzed separately, and unlike other purses we studied, two different polymers were used in its construction (Fig. 7). The lid, base, and handle were all determined to be PMMA by BWID analysis with correlations to the reference Raman spectrum exceeding 96%. The similarities between the spectra for the handle, top, base and PMMA reference are readily observed with the characteristic C = O stretch at approximately 1730 cm^{-1} . The spectra of the handle, base, and top contain the other peaks characteristic of PMMA described in the analysis of **Artifact B**.(20, 22) In contrast, the feet of the purse have a different spectral fingerprint, which matches the CA reference spectrum with 94+% correlation. Like the spectra for **Artifacts Da** and **Db**, this complicated spectrum shows features originating from the C = O and C-O stretching of the ester and cellulose rings.(20, 23) Thus, the feet are determined to be constructed from CA, unlike the other parts of the purse.

The results of this Raman spectroscopic study of plastic purses and purse parts are summarized in Table 4. These results provide definitive identifications of the polymer compositions of all seven artifacts, with correlations ranging from 90–99+%. Those with the lower correlations, **Artifacts Da**, **Db**, and **F**, are

composed of CA. These lower correlations are to be expected since CA is a chemically modified polymer that is vulnerable to degradation. Chemical modifications can be accomplished to different degrees and degradation can add impurities, both causing anomalies in the sample spectrum. The artifact spectra with the highest correlations are **Artifacts A, C, and E**, all of which are composed of colorless PS. This is due in part to the sample spectra having flat baselines and lacking interference peaks resulting from additives or impurities. Yet in all cases, we carefully analyzed the Raman fingerprints of the artifacts to ensure they contained the important characteristic peaks resulting from the functional groups of the identified polymer.

Table 4

Summary comparing SCRC-SUL catalog descriptions of polymer composition with Raman spectroscopy results.

Artifact	SCRC-SUL accession number	SCRC-SUL catalog description of polymer composition	Polymer composition determined by Raman spectroscopy	Correlation to SCOAP database reference
A	2010_055.147	PS	PS	99+ %
B	2005.17	Unidentified	PMMA	94+%
C	2003.207	Unidentified	PS	99+%
Da (colorless)	2010_055.016	PS	CA	90+%
Db (orange)				
E	2003.206	PMMA	PS	99+%
F	2003.208	Unidentified	PMMA (body, handle) CA (feet)	96+% 94+%

Conclusions

The construction of a 134-reference plastics database of Raman spectra provides a robust system for rapid and accurate identification of the composition of plastic artifacts. We show that our methodology is effective at lower laser power, which is sometimes necessary to protect pigmented and delicate artifacts and find that a signal-to-noise ratio above 30:1 provides data with the quality required for successful (> 90% correlation) spectra matching. Use of this approach uncovered the polymer composition of mid-twentieth century plastic purses and purse parts from the PAC, showing that these purses are composed of PS, PMMA, and/or CA. This study confirms the chemical identity of **Artifact A**, identifies the previously unknown polymers in **Artifacts B, C and F**, and corrects the mislabeling of **Artifacts Da, Db, and E**.

Furthermore, it was revealed that the body and handle of **Artifact F** are composed of a different polymer than its feet, highlighting the necessity to test the component parts of compound artifacts. Of these artifacts, we identified three with unknown compositions that contain CA, a polymer that is vulnerable to degradation. This discovery, which was unanticipated, provides the SCRC-SUL an opportunity to practice inhibitive conservation on **Artifacts Da, Db, and F**. An important component of this conservation would involve mitigating the acetic acid emitted from these aging CA-containing artifacts to prevent autocatalytic degradation.(2, 8, 9) This mitigation would not only protect **Artifacts Da, Db, and F** but also other artifacts archived in the PAC that are sensitive to acids.

We believe that Raman spectroscopy is a powerful tool in the non-destructive materials characterization of plastic artifacts and that application of this methodology can provide new insights into museum and library collections. Within this study, the definitive identification of the polymer composition of the PAC purses and component parts delivers more complete documentation to manufacturing, fashion, and chemistry researchers seeking information about these mid-twentieth century artifacts. It also provides an opportunity to improve conservation of the collection for future scholarly inquiry.

Abbreviations

PAC: Plastics Artifacts Collection

SCRC-SUL: Special Collections Research Center at Syracuse University Libraries

SCOAP: Syracuse Chemistry of Artifacts Project

PS: Polystyrene

PMMA: Polymethyl methacrylate

CA: Cellulose acetate

Ref.: Reference

Declarations

Availability of data and materials

The datasets used and/or analyzed in this manuscript are available from the corresponding author upon request.

Competing interests

The authors declare that they have no competing interests.

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Authors' Contributions

Data acquisition and analysis were performed by MNB, EMK and TMK. CKA selected the artifacts and helped identify the historical reference samples for the study. MNB wrote the first draft of this manuscript and all co-authors collaborated on subsequent drafts and editing. All authors read and approved of the final manuscript.

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Figures

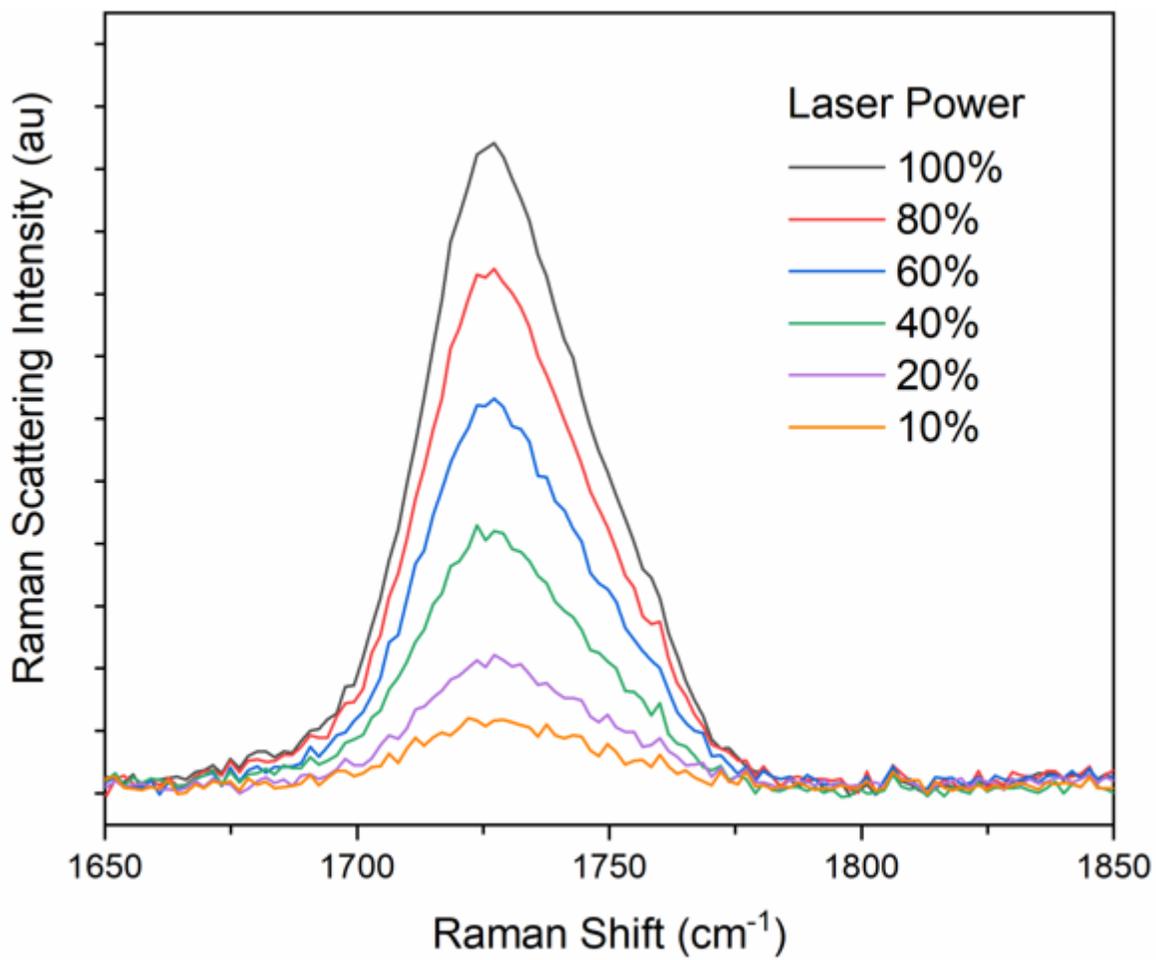


Figure 1

The relative intensity of the CA 1729 cm⁻¹ peak as a function of power.

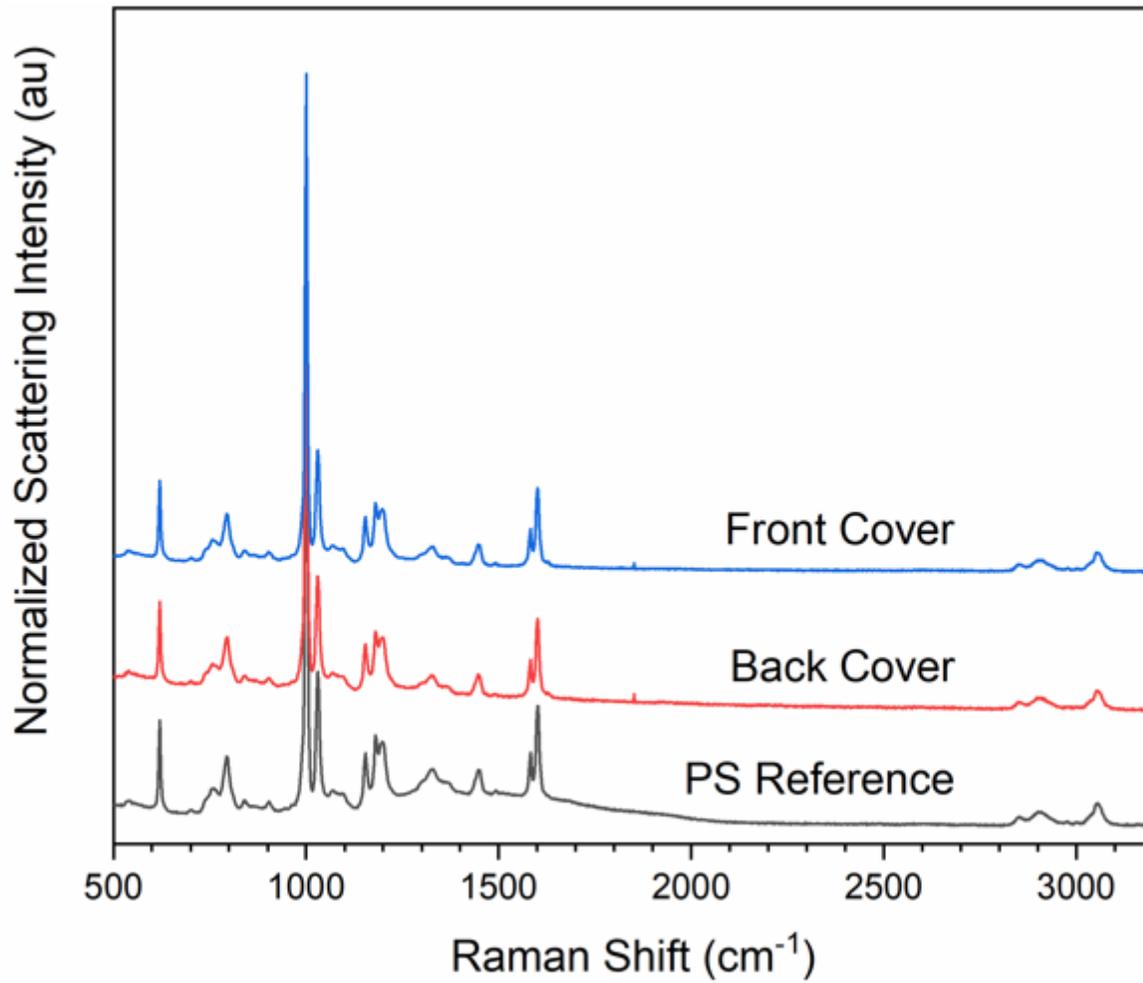


Figure 2

Raman spectra of **Artifact A** (front and back handbag covers) and the PS reference

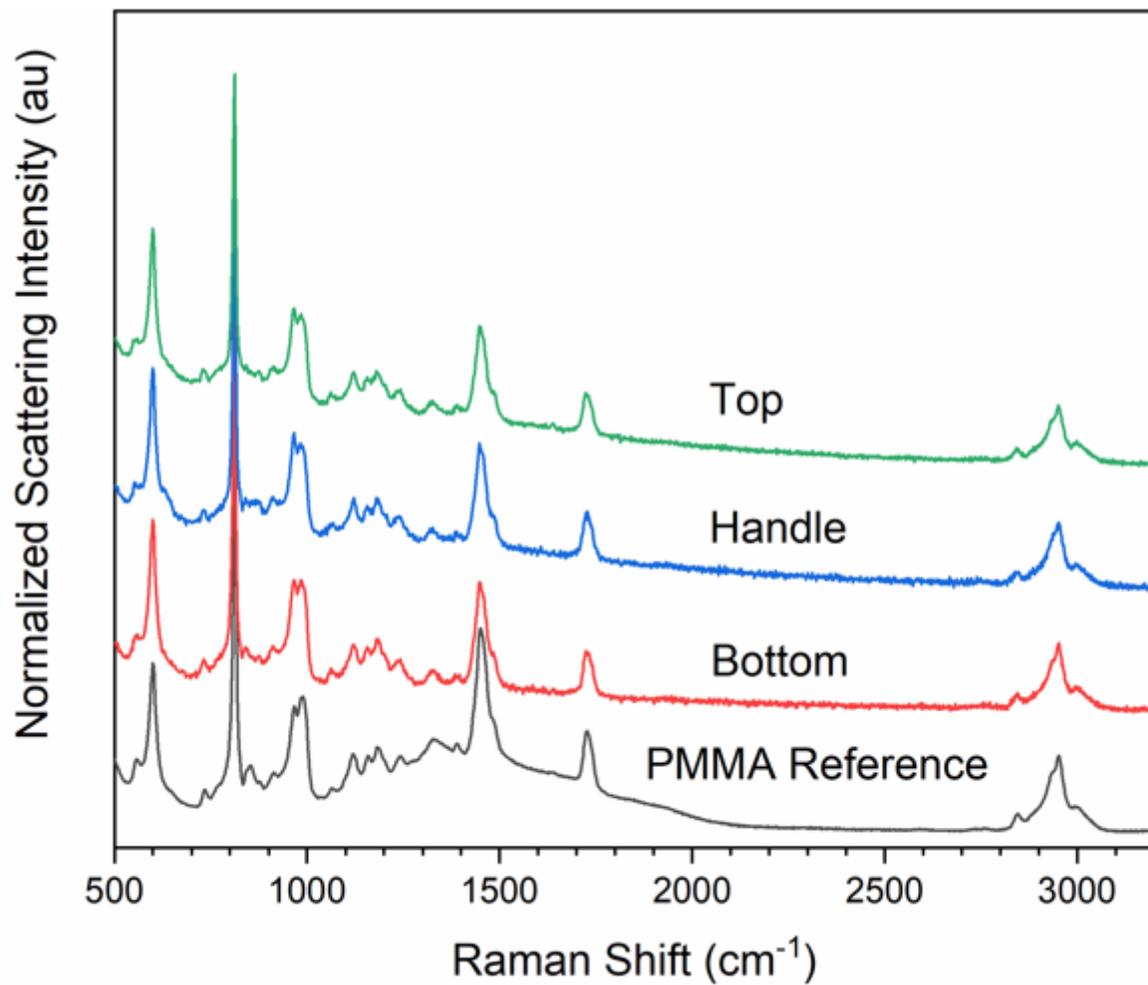


Figure 3

Raman spectra of **Artifact B** (handbag top, handle and bottom) and the PMMA reference.

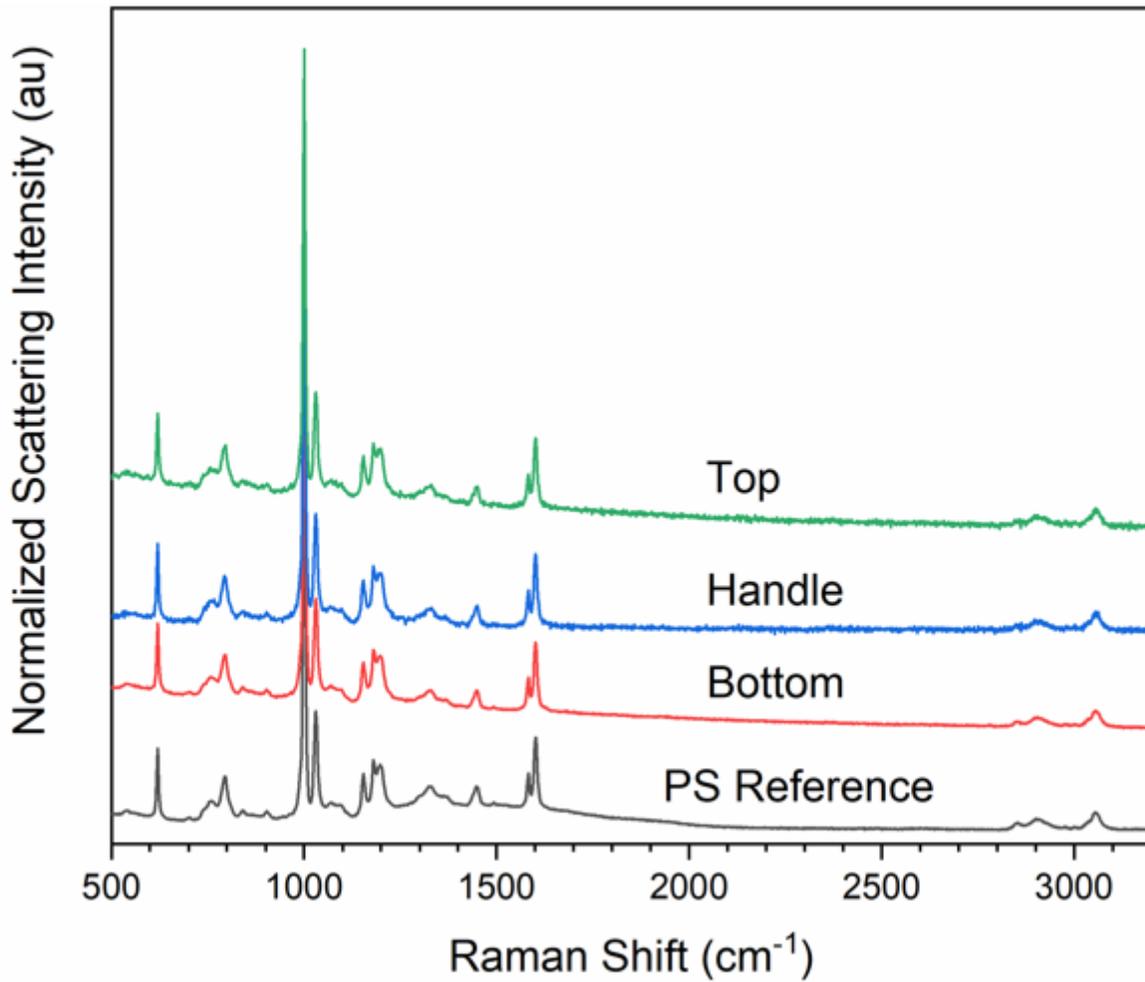


Figure 4

Raman spectra of **Artifact C** (purse top, handle and bottom) and the PS reference.

Figure 5

Raman spectra of **Artifacts Da** (colorless) and **Db** (orange) and the CA and PS references.

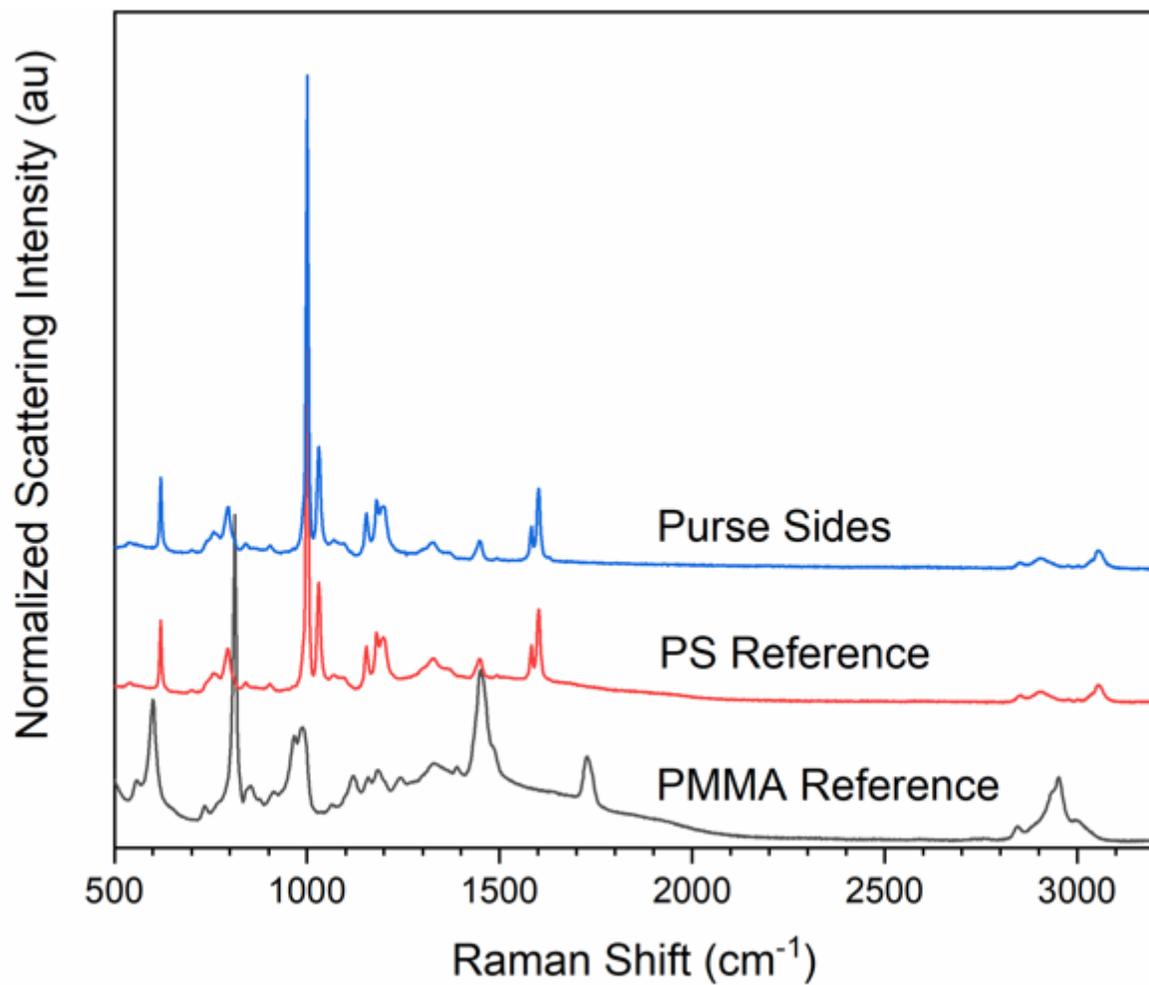


Figure 6

Raman spectra comparison of Artifact E (purse sides) to the PMMA and PS references.

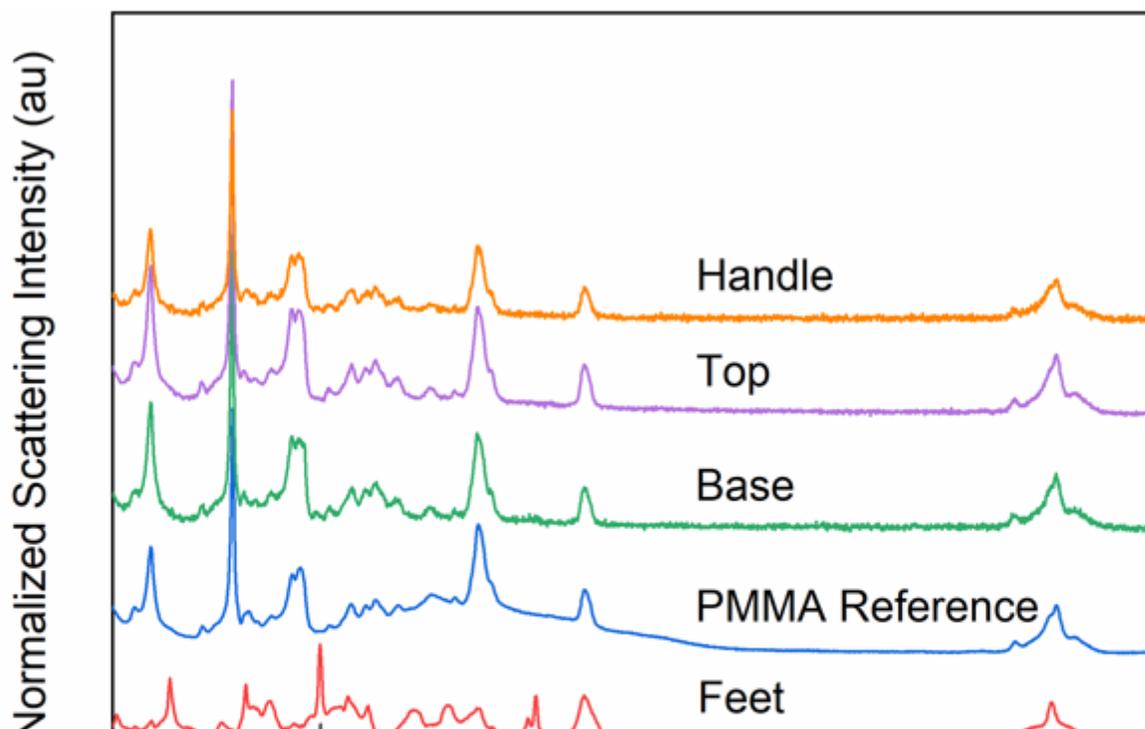


Figure 7

Raman spectra comparison of the four component parts of Artifact F with PMMA and CA references.

Supplementary Files

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