

Non-invasive identification of plastic materials in museum collections with portable FTIR reflectance spectroscopy: Reference database and practical applications

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abstract

In this work, portable Fourier transform infrared (FTIR) reflectance spectroscopy was used for the contactless, non-invasive, and in situ analysis of historic plastics. For the first time, this paper presents the complete database of polymer spectra of a set of reference materials widely used in the cultural heritage community. Over 100 samples from the ResinKitTM and SamCo (Popart Project) collections, which also include samples such as foams, thin films, dark plastics, and other challenging materials, were analyzed. The extensive database of spectral signatures that was acquired for this work represented the departure point for a field study aiming at the identification of the components of a variety of plastic artifacts in the collections of Architecture and Design and Contemporary Art of the Art Institute of Chicago. Reflectance FTIR spectroscopy was confirmed in situ to be a fast and effective method of identification of historic plastics. In some cases, in addition to the main polymers, it was also possible to identify additives in plastic blends, such as plasticizers and inorganic fillers.

Keywords:

FTIR reflectance spectroscopy, Plastics, Non-invasive analysis Museum collections Database of polymer spectra Cultural heritage

1. Introduction

Polymers are increasingly used to create modern and contemporary artworks, and today, objects partially or completely made of plastic are an integral part of numerous museum collections. New synthetic polymer-based objects are acquired in high numbers in museums, especially in architecture and design collections, often with incomplete or non-existent materials information. Thus, methods for rapid and non-invasive assessment of the composition of plastic-based collections are greatly needed. Plastic objects may have a short life expectancy because of their susceptibility to degradation as they are constantly exposed to air, moisture, light, and heat [1]. Hence, in order to set up proper strategies for treatment and preventive conservation, it is necessary to understand degradation patterns, assess artworks' condition, and estimate risks. To achieve these goals, the identification of the composition of plastics is the first, fundamental step [2].

A complete identification is often challenging because plastics are available in a wide range of formulations where base polymers are mixed with both organic and inorganic materials including additives, metal powders or glass fibers. Moreover, invasive sampling and

destructive testing are often required for full characterization, and this approach is not always feasible or permitted. A non-invasive approach is preferred, especially in cases of contemporary artworks, whose large size and fragility may preclude safe transport to the laboratory or micro-sampling [3].

The wide availability of relatively inexpensive portable spectroscopy systems paves the way for fast and reliable identification of the main components of plastics entering museum collections, provided that the quality of data is sufficient for their spectral interpretation. Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) has been used for the analysis of plastic objects or other synthetic materials utilized in the field of conservation and restoration of artworks [4,5] but the technique requires contact of the crystal with the object, exposing the artwork to the risk of visible indentation, mainly in the case of degraded polymers. Portable ATR spectroscopy has been used coupled with near infrared (NIR) spectroscopy for the identification of reference historical polymers [6]. NIR spectroscopy in its own merit proved to be a useful technique for the identification of different kinds of polymers even if it requires statistical approaches for data processing. However this technique has limitations for the analysis of actual museum objects because of their limited reflections in the NIR region, which renders the identification of specific markers for polymers belonging to the same category rather challenging.

In this context, the use of FTIR reflectance spectroscopy in the mid-infrared offers the advantage of portability while enabling non –

invasive and contactless analysis with enhanced spectral features available in the MIR region, when compared to NIR. A recent study by Picollo et al. [7] discusses analysis of 50 thermoplastic resins from the reference collection of the ResinKit™ using three different FTIR instrument configurations: Transmission, ATR, and Total Reflection modes. That previous work addresses the challenging interpretation of reflectance spectra because of distortions of band shape, position and intensity, which depend on several factors, such as surface roughness, absorption and refractive index. While the authors argue that reflectance FTIR spectra are not always comparable to available databases of spectral signatures of polymers acquired in transmission or ATR, yet neither Picollo et al. [7] nor Sustar et al. [6] make available a complete database of reference spectra for full consultation and use.

The work presented here aims to fill this gap, by building upon those previous studies and extending the applicability of the reflectance FTIR approach beyond reference samples to the more complex case of reference objects and museum objects that have complex geometries, pigmentation, filler charges, variable thickness, and transparencies. The analytical challenges posed by these specific morphological and physical properties are not well represented in the widely studied ResinKit™ reference collection, which is composed of bulk, opaque white or off-white polymers. Therefore, in addition to samples from the ResinKit™, in this study, reference materials and objects from the SamCo collection assembled for the European POPART Project [8], including foams, thin colored and transparent films, and oddly shaped objects, were examined with portable mid-IR reflectance FTIR spectroscopy and, where appropriate, complementary Raman and FT-Raman spectroscopies.

This paper makes available the comprehensive database of FTIR reflectance spectra of this wide reference collection of polymeric materials and shares insights into the advantages and limitations of this integrated molecular approach based on the analysis of a broad range of case studies from actual objects, including many examples from the collections of Architecture and Design and Contemporary art at the Art Institute of Chicago. The aim is to provide valuable tools to scientists and conservators interested in the conservation of plastics, offering collection managers a robust approach for the rapid and contactless identification of a wide range of materials in various states of preservation and in any location, from storage rooms to exhibition spaces.

2. Experimental

2.1. Materials

Measurements were carried out on an extensive set of reference samples and objects of increasing complexity in terms of composition, shape, form, and state of preservation

- 50 reference polymer samples from the ResinKit™. This collection comprises samples of the most commonly used thermoplastics resins (Table 1). Polymers with different density grades or different fillers are also included. All samples are in the form of bulk, flat plastic specimens that are whitish, yellowish, or clear.
- 24 reference polymer samples from the SamCo collection (POPART project). These materials show different shapes, textures or thickness, including foams, thin transparent films, or rubbery samples (Table 2). Since the first synthetic polymers were produced in order to imitate natural materials, some reference natural materials such as tortoiseshell and horn are also included [8].
- 33 object samples from the SamCo collection (POPART project). These samples (Table 3) come from everyday objects and are made of the same reference plastics but compounded with pigments, dyestuffs, fillers, plasticizers, antioxidants, and other additives [8].
- Eight museum objects. Several museum objects were also analyzed, mostly in the storage rooms of the Architecture and Design and Contemporary Art collection of the Art Institute of Chicago (Table 4).

Table 1
List of reference materials from the ResinKit™ collection.

ResinKit™ reference polymers		
Acrylonitrile butadiene Styrene (ABS) flame	Nylon 6 Nylon 6,6_33% glass	Polypropylene_glass filled Polystyrene medium impact
Retardant	Nylon transparent	Polystyrene_general purpose
ABS high impact	Nylon 6,6	Polystyrene high impact
ABS medium impact	Polyallomer	Polysulphone
ABS nylon alloy	Polybutylene	Polyvinyl chloride, flexible
Acetal resin_co-polymer	Polycarbonate	Polyvinyl chloride, rigid
Acetal resin_homopolymer	High-density polyethylene	Styrene acrylonitrile
Acrylic resin	Low-density polyethylene	Styrene butadiene block cop.
Cellulose acetate butyrate	Medium density polyethylene	Styrenic terpolymer
Cellulose acetate propionate	Polyphenylene oxide	Synthetic elastomer_styrene-Block co-polymer
Cellulose acetate	Polypropylene	Block co-polymer
Ethylene vinyl acetate	Polypropylene, BaSO ₄ reinf.	Thermoplastic polyester_PBT
Glass fiber reinf. polyester	Polypropylene, CaCO ₃ reinf.	Thermoplastic polyester_PETG
Ionomer	Polypropylene_co-polymer	Urethane elastomer
Modified acrylic	Polypropylene_flame retard.	

Snotty Vase is a digital 3D nano-scan vase designed in 2001 and produced by Marcel Wanders Personal Editions. *Jingzi Lamp* is a suspension light fixture produced by Herzog and de Meuron for Belux. *Polyvase* is a 3D printed vase designed by Dan Yeffet in 2006 and produced by MGX for Materialise. *XO laptop* is a subnotebook computer for children designed by Yves Behar and Bret Recor in 2006 and produced by Quanta Computer. *Y Water bottles* are recyclable and reusable bottles used as creative developmental aid, designed by Yves Behar in 2007 and produced by Y Water Inc. *3Com Audrey* is a home internet appliance designed in 2000 by Don Fotschand and Ray Winninger and produced by 3Com. *Alti Compass Watch* is a watch designed specifically for hardcore outdoors physical training by Scott Wilson in 2003 and produced by Oregon in collaboration with Nike Inc. These objects came into the collection of the Art Institute of Chicago at different times and were identified by the conservator in charge of the collection as having too little information about their constituent materials to be properly stored and preserved.

Additionally, an artwork in the Contemporary collection of the Art Institute was analyzed, "Pitchfork lady," made by the American artist Don Baum (1922–2008) in 1964. The latter is a mixed-media work containing metal, plastic, and wood components. The analytical challenge here was to determine what was the composition of the different plastic elements of the sculpture.

2.2. Portable FTIR reflectance spectroscopy

Analyses were performed using a Bruker Alpha small footprint portable FTIR spectrometer, with reflectance mode sampling module for contactless analysis of artworks and integrated video camera. The spectral range available is 375–7500 cm⁻¹ with a measurement spot of

Table 2
List of analyzed reference materials from SamCo collection.

SamCo reference materials		
Baltic amber	Melamine formaldehyde	Shellac dark red
Bone	Natural rubber	Shellac yellow brown
Casein formaldehyde	Phenol formaldehyde	Silicone rubber
Cellulose nitrate	Polyetheretherketone	Tortoiseshell
Epoxy resin	Polytetrafluoroethylene	Urea formaldehyde
Glass-reinforced plastic	Polyurethane ester foam	Vulcanite
Horn	Polyurethane ether foam	
Ivory	Polyvinylidene fluoride	

Table 3
List of analyzed reference materials from SamCo collection.

Object	Constituent material
Lego brick	Acrylonitrile styrene butadiene (ABS)
Egg cup	Acrylonitrile styrene (SAN)
Fork handle	Casein formaldehyde (CS)
Transparent grey screwdriver	Cellulose acetate (CA)
Knitting needles	Cellulose acetate (CA)
Orange screwdriver	Cellulose acetate butyrate (CAB)
Screwdriver XCelite	Cellulose acetate butyrate (CAB)
Orange ruler	Cellulose nitrate (CN)
Ruler degraded	Cellulose nitrate (CN)
Light blue spoon	Melamine formaldehyde (MF)
Construction material—degraded	Polyamide (PA)
Ikea spoon	Polyamide (PA)
Lamp shade	Phenol formaldehyde (PF)
Bracelet	Unsaturated polyester (UP)
Dutch clog	Thermoplastic polyurethane (TPU)
Ziplock bag	Low-density polyethylene (LDPE)
Cola bottle	Polyethylene terephthalate (PET)
Eiffel Tower model	Poly(methyl methacrylate) (PMMA)
Shark	Polypropylene (PP)
Disposable drinking glass	Polystyrene (PS)
Septum	Polytetrafluoroethylene (PTFE)
Coin holder	Poly (vinylchloride)/Poly (vinyl acetate) (PVC/PVAc)
LP record	Poly (vinylchloride)/Poly (vinyl acetate) (PVC/PVAc)*
Photo pocket	Poly (vinylchloride) (PVC)
Mounting board	Poly (vinylchloride) (PVC)
Cupcake mould	Silicone rubber (SI)
Kitchen spoon holder	Styrene acrylonitrile (SAN)
Cookie Le petit Beurre	Styrene butadiene rubber (SBR)
Coaster	Natural rubber (NR)
Orange container	Urea formaldehyde (UF)
Fake leather fabric (new)	Thermoplastic polyurethane (TPU)
Fake leather fabric (3 years)	Thermoplastic polyurethane (TPU)
Telefunken record	Shellac

5 mm in diameter and working distance of approximately 15 mm in front of the spectrometer. 256 scans were acquired at a resolution of 4 cm^{-1} . Kramers–Kronig transform (KKT) was applied to the spectra with the aim to correct spectral distortions by using Bruker's OPUS software 7.0. When necessary, acquired spectra were pre-treated by an atmospheric compensation, including water vapor and carbon dioxide, and then smoothing (5–13 points) and baseline correction (rubberband correction) were applied.

2.3. Raman and FT-Raman microspectroscopy

A Jobin Yvon Horiba Labram 300 confocal Raman microscope was used, equipped with Andor multichannel Peltier cooled open electrode charge-coupled device (CCD) detector (Andor DV420-OE322; 1024×256), BXFM open microscope frame (Olympus), holographic notch filter, and dispersive grating with 1800 grooves/mm.

The excitation line of a solid state diode laser ($\lambda_0 = 785.7\text{ nm}$) was focused through a $100\times$ objective on to the samples and Raman scattering was back collected through the same microscope objective. Power at the samples was kept very low (below 1 mW) by a series of neutral density filters in order to avoid any thermal damage.

Table 4
List of the analyzed objects of the Architecture and Design collection of the Art Institute of Chicago.

Object	Accession no.	Listed as	Description
Snotty Vase	2007.61	Polyamide	Whitish plastic of complex, tortuous shape
Jingzi Lamp	2007.332	Silicone	Composite object including whitish, soft and slightly textured, curved surfaces)
Polyvase	2009.11	Epoxy	Green egg-shape vase, with porous surface and rigid structure
XO laptop (One Laptop Per Child)	221773	Medical grade plastic	Green and white smooth and opaque surfaces
Y Water bottles	198845	Plastic, biodegradable rubber	Transparent tortuous shape bottles with soft whitish rubber junctions and colored caps
3Com Audrey	198806	Various plastics	Light greyish opaque plastic with smooth surface
Alti Compass Watch	2008.685	Plastic, polyurethane	Digital watch made with soft black plastic with smooth surface

A high-resolution (0.4 cm^{-1}) Fourier transform infrared spectrometer (VERTEX 70-BS) coupled with Ramscope III FT-Raman microscope was used. The instrument is equipped with a (D418-T/R) high-sensitivity Ge detector and $\text{Nd}^{3+}/\text{YAG}$ laser, with excitation wavelength at 1064 nm. 100–1000 scans were accumulated at 4 cm^{-1} resolution, using a $40\times$ objective, with a nominal laser power of 150 mW.

3. Results and discussion

3.1. Reflection mid-FTIR of ResinKit™ reference materials

Good-quality spectra were obtained overall, with few cases where a slight band shift was noted in comparison with literature values for spectra acquired in transmission or ATR mode, as already described by Picollo et al [7]. In general, the excellent spectral quality allowed the unambiguous identification of the polymer present, as evident from the whole database of spectra available in the Supporting Information section.

The main value of the reflectance FTIR method for practical applications lays in the fairly large sampling area, and the operation in the mid-infrared region, which is rich in information for both the organic and inorganic components that are often present in composite plastic objects. Thus, even in the reference ResinKit™ materials, in addition to the identification of the main components of the plastic, in some cases, additive and fillers could also be identified. For example, spectra acquired for flexible PVC also included characteristic bands of the plasticizer (Fig. 1). Indeed, peaks at 2957, 1601, 1581, 1464, 1380, 1286, 1274, 1123, 1073, 1039, and 743 cm^{-1} can be ascribed to bis (2-ethylhexyl) phthalate (DOP), in accordance with literature data [9]. Characteristic bands of the isolated reference additive usually shift upon plasticization because of the interactions between the plasticizer and PVC, leading to the observation of the typical $\nu(\text{C}=\text{O})$ of phthalate esters at 1724 cm^{-1} in the plasticized PVC, compared to the value of 1730 cm^{-1} for the free DOP [9,10].

The presence of additives can sometimes significantly affect the quality of the spectra, ultimately hindering the positive identification of the polymer resin. For example, as illustrated in Fig. 2, when polypropylene is reinforced with CaCO_3 , the obtained spectra (Fig. 2a) are of lower quality, and they are strongly dominated by the reflections of the carbonate (centered at 1785, 1424, and 872 cm^{-1}), leading to shifts in the characteristic bands of polypropylene, rendering identification challenging (Fig. 2b).

3.2. Reflection mid-FTIR of the SamCo reference collection

Fig. 3 shows a selection of the reflection mid-FTIR spectra collected from the polymers of Table 2, where both reflectance and absorbance spectra obtained by applying the KK transform are displayed. On average, spectra of variable quality were obtained, which were mostly affected by color and shape of samples, but this did not impair identification by comparison with library spectra recorded in transmission mode.

In addition to the positive identification of the polymer, in some cases, the observed bands allow to make hypothesis on the structural conformation of the polymer. For example, the spectrum of

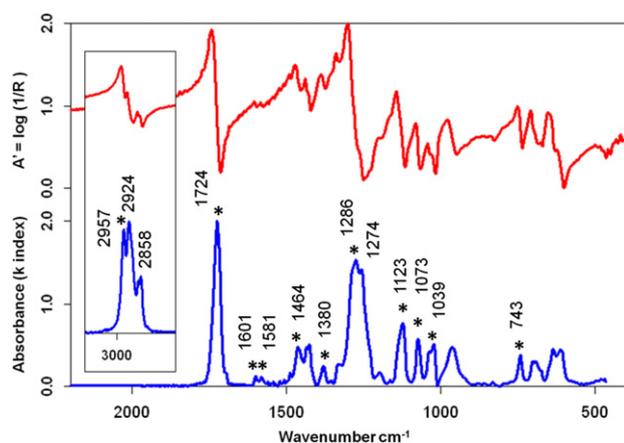


Fig. 1. Reflectance ($A' = \log(1/R)$) (top, red), and calculated absorbance after KKT (bottom, blue) spectra of Polyvinyl chloride plasticized with bis (2-ethylhexyl) phthalate (DOP: main peaks marked with an asterisk). In the box, the area between 3100 and 2700 cm^{-1} is reported.

polyvinylidene fluoride (PVDF, Fig. 3a) shows its characteristic bands as detailed in Table 5. The frequencies of the bands suggest an α crystalline form for PVDF instead of β [11,12].

Bands ascribable to the fillers are also evident in some cases, like for example for glass fiber reinforced polyester (GRP) (Fig. 3b). This material shows characteristic bands of a styrene-based polyester resin (the most commonly used in GRP) (Table 5) [13]. Moreover, a weak band at 1374 cm^{-1} was also observed, which could possibly be ascribed to borate-based glass fiber [14].

In the calculated spectrum of poly (ether ether ketone) (PEEK, Fig. 3c) it is possible to identify the characteristic bands of the three

main functional groups for this polymer: benzene, ketone, and aromatic ether, respectively, at 1600 and 1491, 1651 and 1223 cm^{-1} [15]. The spectrum of urea formaldehyde (UF, Fig. 3d) shows the characteristic functional groups of the resin (Table 5) bands at 3332 and 1254 cm^{-1} should be ascribed to intra- and intermolecular hydrogen bonds [16,17].

Polyurethane foams are challenging materials for portable FTIR reflectance spectroscopy because of their porous texture. Indeed, spectra of both ester and ether have the poorest spectral quality compared to those of the other materials listed in Tables 1 and 2 being affected by diffuse noise due to the low signal back collected by the detector. Still it is possible to find some characteristic peaks such as the sharp $\nu \text{C}=\text{O}$ of PUR ester at 1740 cm^{-1} , the stretching of CH and CH_2 between 3000 and 2600 cm^{-1} , and the CN stretching at 1375 cm^{-1} so as to allow qualitative discrimination of the two foams [18]. Both spectra are in the Supporting Information section. In these cases, analysis with FT-Raman and Raman spectroscopy is advantageous because, due to the small spot size (variable depending on laser line and numerical aperture of the objective used, but in general smaller than 1 mm), it is possible to focus the laser light on the rim of a cell and get good quality spectra from the planar surface (Fig. 4a,b).

3.3. Reflection mid-FTIR of SamCo collection objects samples.

In order to fully validate the applicability of the reflection FTIR technique and related reference spectral database derived from analysis of the ResinKit™ and SamCo reference set, it was necessary to test real objects, which often present particular shapes, irregular surfaces, and several additives in the blend. Object samples from the SamCo collection were analyzed for such purpose.

The qualitative parameters that were selected for the objective evaluation of the applicability of the method were the quality (S/N) of the spectrum and the ability for positive identification based on a successful match with the reference spectra. Table 6 shows the list of analyzed objects from the SamCo collection and the relative quality of the spectra as well as match results. In this well-characterized collection, the constituent materials of the objects are known [8].

Fig. 5 shows three representative examples of low, medium, and good match, respectively. A bad match was obtained for the “dutch clog” whose FTIR spectrum has just few peaks in common with the reference thermoplastic polyurethane (Fig. 5a). The FTIR spectrum of the “Lamp Shade” showed a medium match with the reference phenol formaldehyde (Fig. 5b) with differences in peaks shape and intensity possibly due to differences in texture and color. Moreover, the presence/absence of some peaks is ascribable to different additives and fillers inside the two materials. A very good match was obtained between FTIR spectra of “Eiffel Tower Model” and poly(methyl methacrylate) as shown in Fig. 5c.

A bad or an incomplete match could be attributed to a different formulation of the polymeric bends including different additives or fillers as well as different features of the polymeric structures or to a degradation of the plastic material. Moreover, different textures or characteristics of the compared materials could affect the reflectance spectrum and the resulting calculated absorbance one.

Low-quality spectra were obtained for just five samples out of the 33 analyzed: two fake leathers (black surface), a coin holder (thin green transparent material), and a photo pocket (extremely thin, transparent film). The disposable drinking glass (transparent material) had better-quality spectra than the last ones mentioned and it was possible to confirm polystyrene (PS) as base material despite the noise.

Overall, good-quality spectra and reliable matches were obtained for more than 80% of the analyzed samples, each of them with different shapes, textures, and colors.

Expected challenges were offered by excessively thin transparent materials, foams and other dark-colored porous materials because of the physics of the interactions of infrared light with the substrate leading to low amounts of radiation reflected back into the detector. In the

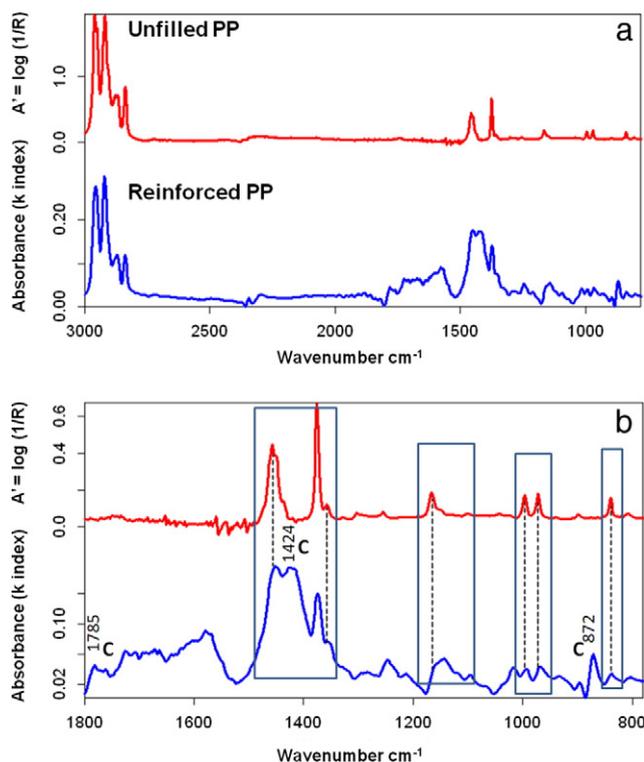


Fig. 2. Comparison between KK calculated spectra of unfilled polypropylene (top, red) and polypropylene reinforced with calcium carbonate (C) (bottom, blue) (a). Enlargement of the spectra in the spectral range between 1800 and 800 cm^{-1} to better understand the shifts of the peaks. (b) The boxes refer to the corresponding main bands of unfilled PP in the reinforced one. The dashed lines indicate the shifts. No baseline correction was applied.

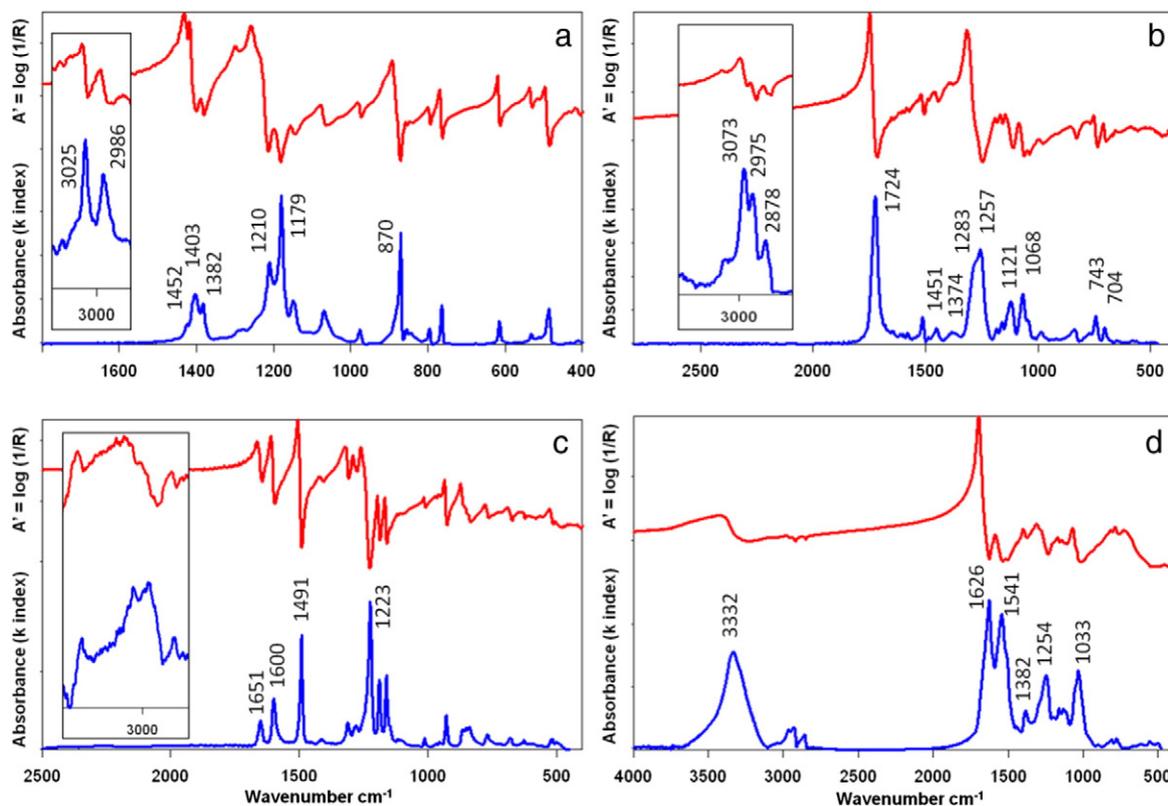


Fig. 3. Reflection mid-FTIR (red, top) and calculated absorbance (blue, bottom) spectra of (a) polyvinylidene fluoride, (b) glass fiber reinforced polyester, (c) poly(etherether ketone) and (d) Urea formaldehyde.

Table 5

Principal assignments for calculated FTIR spectra of polyvinylidene fluoride, glass fiber reinforced polyester, poly(ether ether ketone), and urea formaldehyde.

Polymer	Peak position (cm ⁻¹)	Assignment
Polyvinylidene fluoride	3025, 2986	CH ₂ stretching
	1452	CH ₂ bending
	1403	Combination of wagging of CH ₂ and stretching of CC
	1382	Combination of twisting and wagging of CH ₂
	1210	Combination of CF ₂ and CC stretching
	1179	Combination of asymmetrical stretching and rocking of CF ₂
Glass fiber reinforced Polyester	870	
	3073, 2975, 2878	Stretching of CH and CH ₂
	1724	Stretching of C=O
	1374	Stretching of B-O
	1451	Stretching of aromatic ring
	1283-1257	Stretching of CO
	1121	Combination of stretching of C-O and bending of CH
	1068	Bending of =CH
Poly(ether ether ketone)	743	Out of plane deformation of =CH
	704	Out of plane deformation of aromatic ring
	1651	Stretching of CO
Urea formaldehyde	1600	Stretching of aromatic ring
	1491	Stretching of aromatic ring
	1223	Asymmetric stretching of C-O-C
	3332	Stretching of OH
	1626	Combination of CO and NH stretching
	1541	Combination of CN and NH stretching
	1382	Bending of CH in CH ₂ /CH ₂ OH/NCH ₂ N
	1254	In-plane bending of OH
	1033	Stretching of CO

case of thin, transparent, or colored materials, an integrated approach using Raman or FT-Raman spectroscopy led to the successful identification of these plastics. In Fig. 5, two examples are reported, polyurethane flexible ether foam and disposable drink glass (transparent

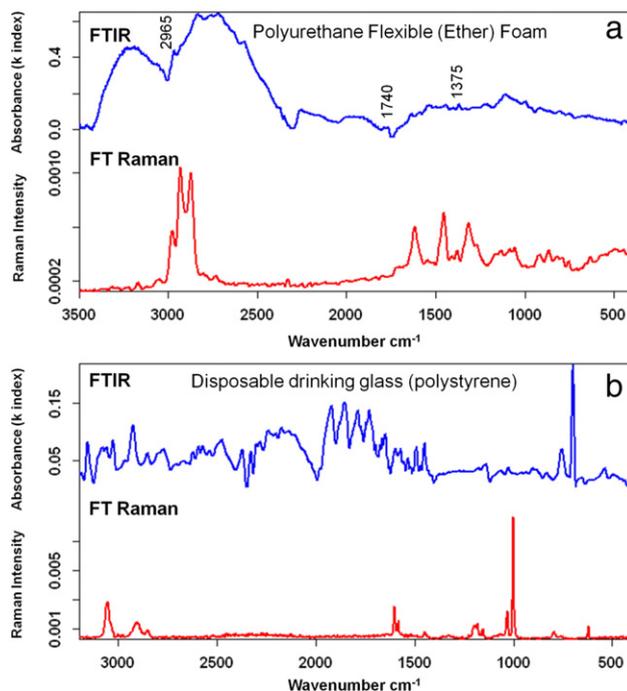


Fig. 4. Comparison between mid-FTIR (top, blue) and FT-Raman (bottom, red) spectra of polyurethane flexible foam (a) and disposable drinking glass made of polystyrene (b).

Table 6

List of analyzed objects samples from the SamCo collection with evaluation of spectral quality and ability to achieve a correct match with library spectra (G: good, M: medium, L: low). Spectra of polymer marked by an asterisk were compared with reference ones in literature as no reference spectra are available from the reference collections examined.

Object	Constituent material	Quality of spectrum	Quality of matching with reference
Lego brick	Acrylonitrile styrene butadiene (ABS)	G	G
Egg cup	Acrylonitrile styrene (SAN)	G	G
Fork handle	Casein formaldehyde (CS)	M	G
Transparent grey screwdriver	Cellulose acetate (CA)	G	G
Knitting needles	Cellulose acetate (CA)	G	G
Orange screwdriver	Cellulose acetate butyrate (CAB)	G	G
Screwdriver XCelite	Cellulose acetate butyrate (CAB)	G	G
Orange ruler	Cellulose nitrate (CN)	G	G
Ruler degraded	Cellulose nitrate (CN)	G	G
Light blue spoon	Melamine formaldehyde (MF)	G	G
Construction material—degraded	Polyamide (PA)	G	G
Ikea spoon	Polyamide (PA)	G	G
Lamp shade	Phenol formaldehyde (PF)	G	M
Bracelet	Unsaturated polyesterUP	G	G
Dutch clog	Thermoplastic polyurethane (TPU)	M	L
Ziplock bag	Low-density polyethylene (LDPE)	G	M
Cola bottle	Polyethylene terephthalate (PET)	G	G
Eiffel Tower model	Poly(methyl methacrylate) (PMMA)	G	G
Shark	Polypropylene (PP)	G	G
Disposable drinking glass	Polystyrene (PS)	M	G
Septum	Polytetrafluoroethylene (PTFE)	G	G
Coin holder	Poly (vinylchloride)/Poly (vinyl acetate) (PVC/PVAc)*	L	L
LP record	Poly (vinylchloride)/Poly (vinyl acetate) (PVC/PVAc)*	G	G
Photo pocket	Poly (vinylchloride) (PVC)	L	–
Mounting board	Poly (vinylchloride) (PVC)	L	L
Cupcake mould	Silicone rubber (SI)	G	G
Kitchen spoon holder	Styrene acrylonitrile (SAN)	G	G
Cookie Le petit Beurre	Styrene-butadiene rubber (SBR)	M	G
Coaster	Natural rubber (NR)	M	L
Orange container	Urea formaldehyde (UF)	G	G
Fake leather fabric (new)	Thermoplastic polyurethane (TPU)	L	L
Fake leather fabric (3 years)	Thermoplastic polyurethane (TPU)	L	L
Telefunken record	Shellac	G	G

polystyrene). Fig. 4a and b show on the top (in blue) the FTIR spectra while on the bottom (in red) the FT-Raman spectra are shown.

3.4. In situ identification of plastics in the Architecture and Design collection of AIC

Portable FTIR reflectance spectroscopy successfully identified the components of several plastic objects belonging to the Architecture and Design collection of the Art Institute of Chicago (see Table 4). For each object, the constituent materials were identified, and in some cases also the additives, such as fillers, pigments or plasticizers, were recognized.

Jingzi Lamp, made of a soft, whitish plastic in a bulbous, biomorphic shape, gave the spectrum shown in Fig. 6.

Silicone rubber was identified as diagnostic bands at 2962 (asymmetric CH stretching of CH_3), 1261 (CH_3 symmetric deformation of $\text{Si}-\text{CH}_3$), 1101 (asymmetric stretching of $\text{Si}-\text{O}-\text{Si}$), 1068 (asymmetric stretching of $\text{Si}-\text{O}-\text{Si}$), 806 (symmetric stretching of $\text{Si}-\text{O}-\text{Si}$), 678 (stretching of $\text{Si}-\text{C}$), and 482 cm^{-1} ($\text{O}-\text{Si}-\text{O}$ bending) were detected [19,20]. Several additional peaks are present. Bands at 2916, 2848, 1710, and 1472 cm^{-1} can be ascribed to stearic acid, usually added to silicone and other polymers as stabilizing agent [21].

Fig. 7 shows the four different areas of XO laptop (One Laptop Per Child) which were analyzed. This object was listed in the museum files simply as medical-grade plastic.

The spectra of points a, b, and c matched the reference spectrum of polycarbonate (shown in S.I.) and highlighted the presence of some fillers added to the base resin, although not identified. In fact, spectra of points a and b (b not shown) showed two additional peaks at 960 and 689 cm^{-1} (Fig. 7a) which remain not assigned. The FTIR analysis of point d, the green-colored cord of the charger (Fig. 7b), allowed the identification of polyvinylchloride (PVC) as constituent polymer. The thin, curved nature of the analyzed area led to a spectrum with

relatively low S/N; however, it was still possible to match the unknown with reference PVC (shown in S.I.). Some additional peaks could also be detected at 1789 , 1427 , and 874 cm^{-1} that are diagnostic for the presence of calcium carbonate, usually used as filler in PVC; and bands at 1729 and 1654 cm^{-1} that can be ascribed to a phthalate plasticizer. The spectrum showed some noise and it wasn't possible to detect the green pigment bands, even if two weak peaks at 1336 and 1043 cm^{-1} were noticed, possibly diagnostic for a phthalocyanine-based pigment. In order to unambiguously identify the pigment, Raman spectroscopy ($\lambda_0 = 785\text{ nm}$) was carried out, leading to the identification of PG7, a phthalocyanine-based green pigment, and also to confirm the presence of calcium carbonate (1087 cm^{-1}) as filler (Fig. 7c).

The inset in Fig. 8a shows the two selected points analyzed for Y Water bottles, a porous white (a) and a thin transparent (b) plastic.

Spectrum of point a (Fig. 8a) shows some noise because of low signal due to the porous, heterogeneous nature of the plastic material probed. However, the analysis suggests that the material could be styrene-butadiene rubber (SBR) because signals of such rubber are clearly identifiable at 3027 , 2924 , 2852 , 2717 , 1659 , 1447 , 1347 , 1304 , 1121 , 1087 , 889 cm^{-1} [22]. Some of the peaks are shifted compared to reference spectra of libraries, but in this case, these shifts could be ascribed to a different composition of the blend (different amount of monomers) rather than to the KKT calculations. Not all the bands have been assigned as in the case of the band at 1533 cm^{-1} . Micro-destructive analysis such as Py-GC/MS may help in further elucidating all the different components of the plastic.

The FTIR analysis of point b (Fig. 8b) allowed the identification of a blend made of polyethylene terephthalate (PET) and polyethylene terephthalate glycol (PETG) as constituent materials. The spectrum matches with reference PET (see S.I.) and the peaks at 1119 and 958 cm^{-1} suggest the presence of PETG. The band at 1271 cm^{-1} , which is not visible in the spectra of the individual polymers PET or PETG, is actually characteristic of the co-polymer (PET/PEG) [23].

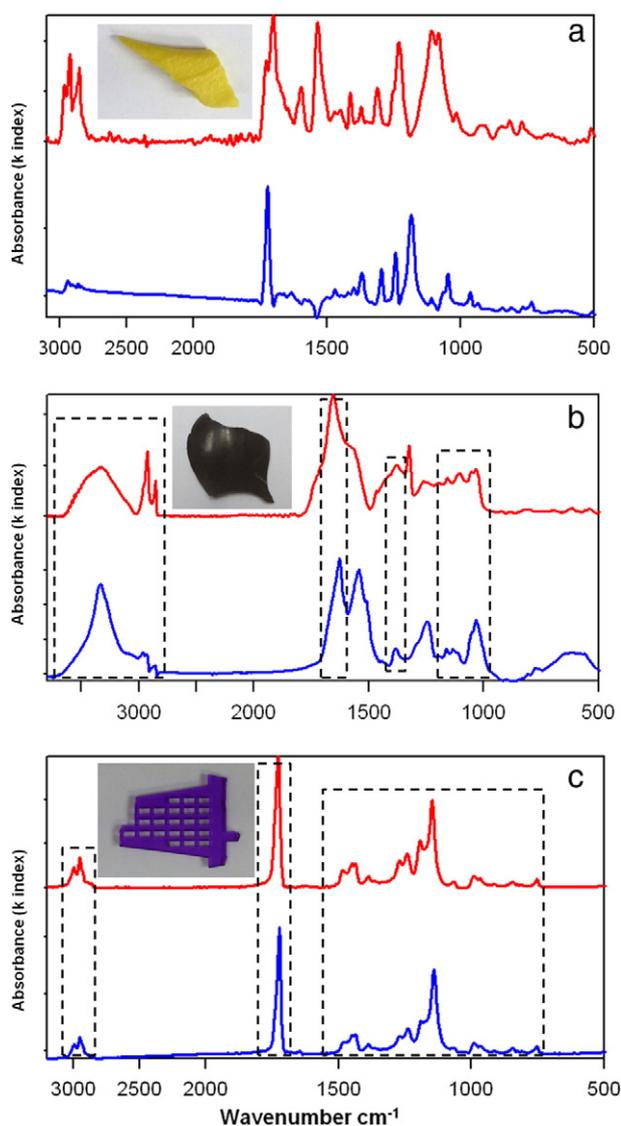


Fig. 5. Representative indication of quality of matching, low, medium, and good. Low match (a): Dutch clog (red) vs thermoplastic polyurethane (blue). Medium match (b): lamp shade (red) vs phenol formaldehyde (blue). Good match (c): Eiffel Tower model (red) vs poly(methyl methacrylate) (blue). The dotted boxes indicate the corresponding bands between the spectra of the object and the relative reference material.

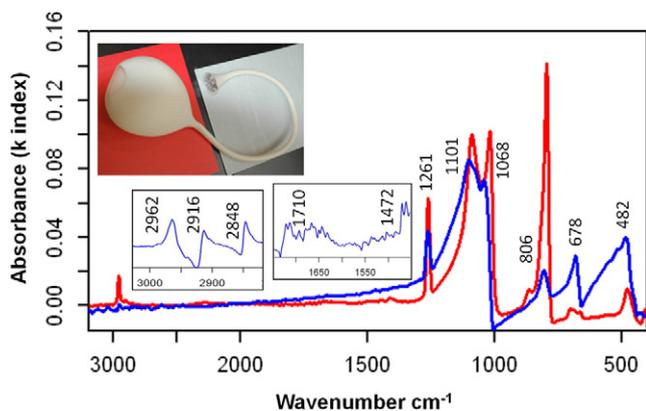


Fig. 6. Calculated (KKT) absorbance FTIR spectrum (blue) from 3000 to 400 cm^{-1} of Jingzi Lamp (in the box) identifying a silicone rubber. In the boxes, the enlargement of the spectrum between 3000 to 2800 and 1750 to 1450 cm^{-1} . The red spectrum is the reference silicone rubber (see S.I., this work).

The inset in Fig. 9a shows the three selected points analyzed for 3Com Audrey laptop, front (a), base (b), and backside (c).

The KKT calculated spectra of point *a* and *c* allowed to identify polycarbonate as constituent material. It was not possible to assign any specific vibration to the peak at 961 cm^{-1} (Fig. 9b). The FTIR analysis of the grey pin (point *b*) allowed the identification of polyethylene as constituent material when compared to the reference spectrum (shown in S.I.) (Fig. 10c). In particular, the shape and the height of peaks at 1474–1464 and 731–720 cm^{-1} would suggest that such kind of polyethylene could be high-density polyethylene (HDPE) [24].

3.5. Identification of plastics in a contemporary artwork

Analysis of “Pitchfork Lady” 1964 by Don Baum (American, 1922–2008; 70.5 × 35 × 28 cm; AIC 1979.351, Gift of Mr. and Mrs. Samuel W. Koffler) (Fig. 10) was conducted in the storage rooms of the Contemporary Art collection of AIC. The object is simply listed as metal, plastic, and wood in the Museum’s collection database. In order to identify the specific plastic, portable FTIR reflectance spectroscopy was used on the top head and on the legs. It is a very useful case study given both the challenging shape and the date of production of the object, a time when many new plastic materials were introduced on the market.

For the head, the FTIR analysis allowed the identification of cellulose nitrate (CN) as constituent material (Fig. 11) when compared to the reference spectrum of cellulose nitrate (reported in the S.I.). In this particular case, it was important to optimize the data collection as much as possible by orienting the instrument on a tripod so as to conform to the curvature of the piece. This allowed the most efficient collection of back-scattered radiation, dramatically increasing the spectral quality. Additional peaks are observed at 1018 and 673 cm^{-1} , which could be ascribed to talc, used as filler, even if the peak at 3670 cm^{-1} is not clearly distinguishable from the noise of the spectrum in that area. The presence of two bands with frequencies characteristic of νCO (1734 with a shoulder at 1718 cm^{-1}) suggests that a plasticizer could be present. Since there aren’t any characteristic band of the most used plasticizers for CN, such as camphor (2963 and 2874 cm^{-1}) and phthalate ester (2861, 1579, and 1602 cm^{-1}) [4], it is possible that there could be another kind of plasticizer as well as it is possible that the CO stretching could be ascribed to products of degradation of the constituent material.

The FTIR analysis of the legs (Fig. 11) allowed the identification of polyethylene as constituent material, matching the reference spectrum (reported in the S. I) with additional peaks that can be ascribed to talc (1021 and 676 cm^{-1}). The band at 1094 cm^{-1} could be ascribed to silica. The presence of CO stretching bands (1710–1730 cm^{-1}) could indicate the presence of a plasticizer or the occurrence of products of degradation of polyethylene.

4. Conclusions

In recent years, increasing attention has been devoted to the study and characterization of large reference collections of plastic materials of relevance to the production of works of art and design. Here for the first time, the complete mid-IR spectral database for a large set of widely used plastics is presented in its entirety (Supp. Info) both as reflectance data as well as calculated absorbance after Kramers–Kronig transformation. The study demonstrated that in most cases in situ analysis with reflectance mid-FTIR spectroscopy successfully identifies the main plastics with good-quality spectra obtained irrespective of an object’s shape or color, as verified on a reference collection of everyday objects (SamCO collection). A notable exception is the case of thin transparent films and foams that remain extremely challenging to characterize with this technique but render very good quality spectra when analyzed with Raman or FT-Raman spectroscopies, which remain a very important complementary technique. In some cases, in addition to the main

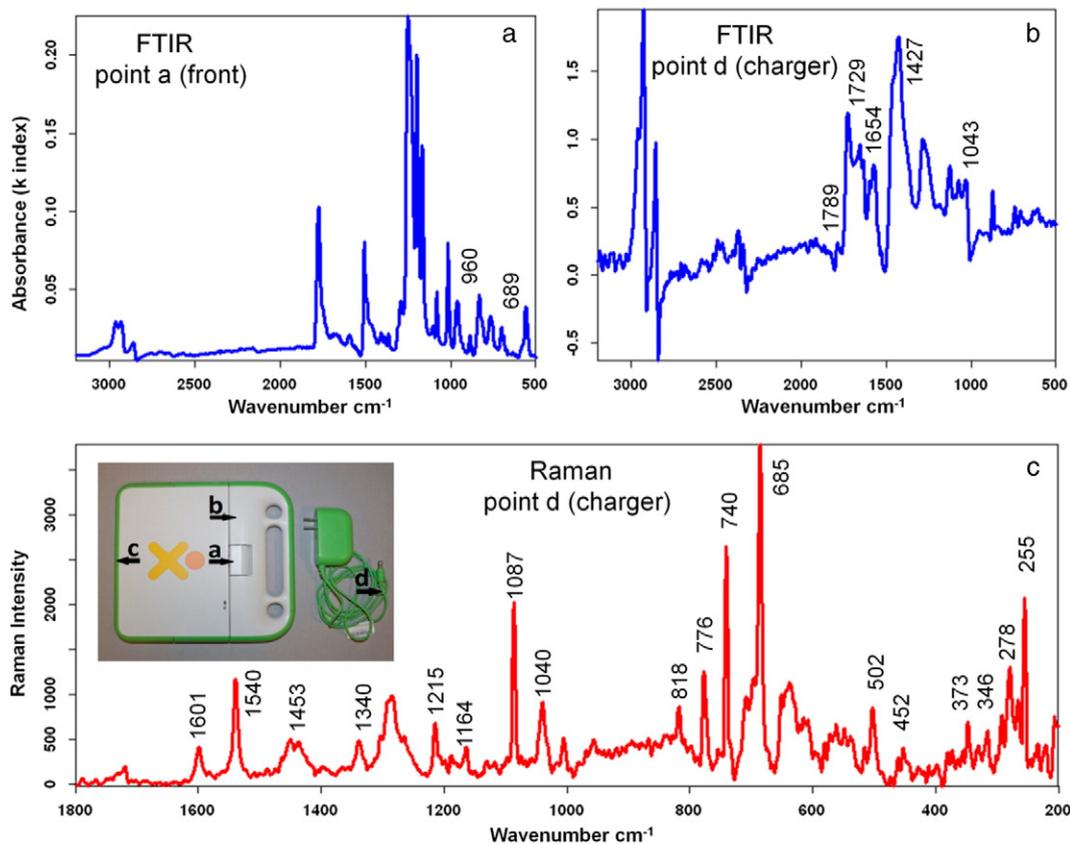


Fig. 7. Calculated (KKT) absorbance FTIR spectrum of (a) point a (polymer identified as polycarbonate) and (b) point d (polymer identified as PVC) of XO laptop (One Laptop Per Child) showing polycarbonate and plasticized PVC, respectively. (c) 785 nm Raman spectrum of point d (green charger) identifying copper phthalocyanine green PG7 pigment and calcium carbonate filler.

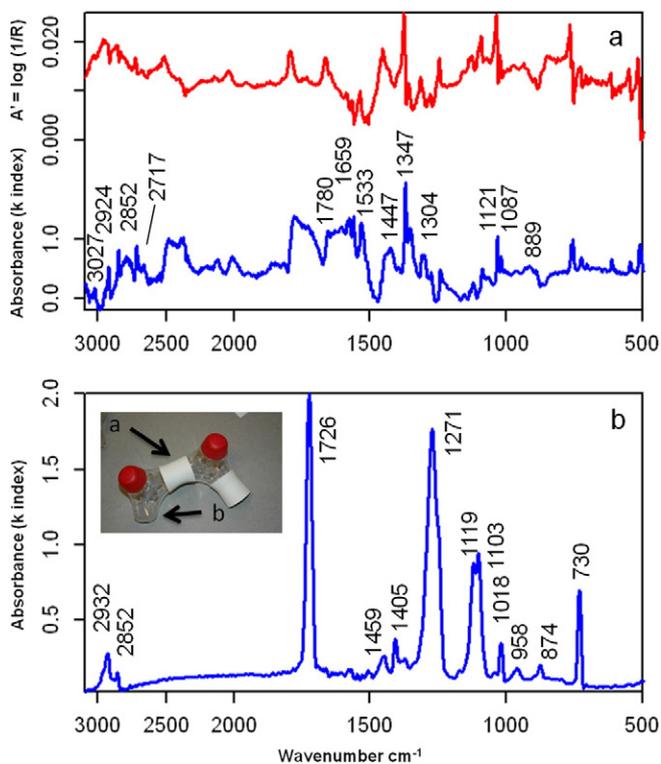


Fig. 8. Calculated (KKT) spectra of Y Water bottles, white part (styrene-butadiene rubber) (a) and transparent part (polymer identified as PET/PETG blend) (b). In the inset of figure a, the analyzed points in Y Water bottles are reported.

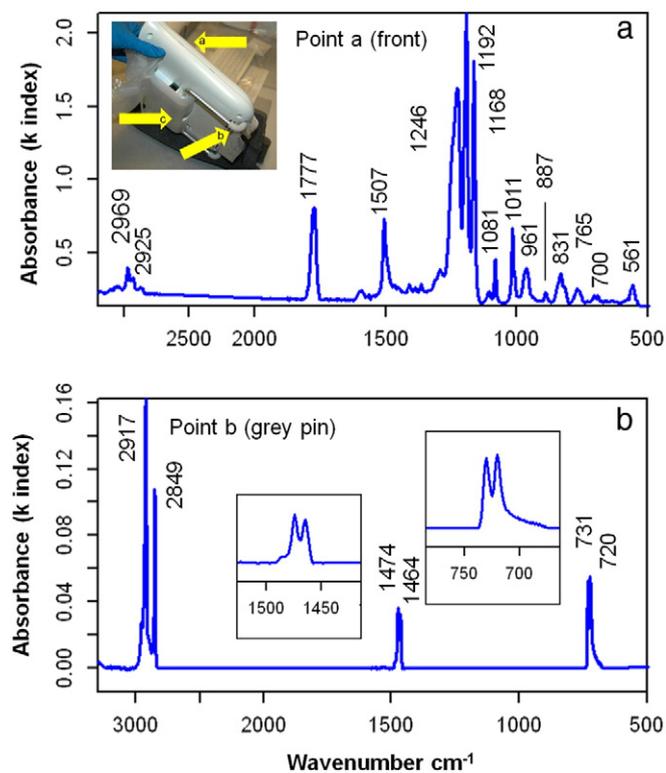


Fig. 9. KKT calculated FTIR spectra of the front (point a, polymer identified as polycarbonate) (a) and grey pin (point b, polymer identified as high-density polyethylene) (b). In the inset of figure a, the 3Com Audrey laptop and the selected analyzed points are shown.



Fig. 10. "Pitchfork Lady" 1964 by Don Baum (The Art Institute of Chicago, Gift of Mr. and Mrs. Samuel W. Koffler, 1979.351).

polymer or polymer blend, it was possible to identify additives in plastics blend, such as plasticizers or inorganic fillers. The use of the Kramers–Kronig transformation is applicable in most cases, in order to correct spectral distortions. The procedure doesn't significantly affect the quality of spectra and bands shifts are recorded in few cases, nevertheless not significantly impairing the positive identification of the base polymer or blend.

The extensive reflectance FTIR database was used for the characterization of the components of plastic objects with incomplete media description belonging to the Architecture and Design collection and Contemporary Art Collection of the Art Institute of Chicago, leading to the successful identification of their constituent materials directly in storage rooms. In one case, the unexpected identification of cellulose nitrate in a composite contemporary art sculpture led to specific

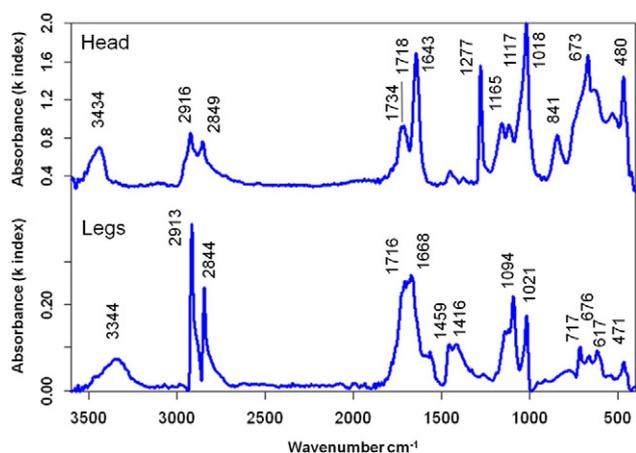


Fig. 11. KKT calculated FTIR spectra from the head (polymer identified as cellulose nitrate) and the legs (polymer identified as polyethylene) of Pitchfork Lady.

recommendations for the storage and preservation of such notoriously fragile material.

Given the relatively low cost and proliferation of portable mid-FTIR spectrometers, it is hoped that the spectral database presented here will become an important resource for the analysis of unknown materials in museum and design collections.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.microc.2015.07.016>.

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