



Reflectance FT-IR spectroscopy as a viable option for textile fiber identification



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FTIR <paper review>

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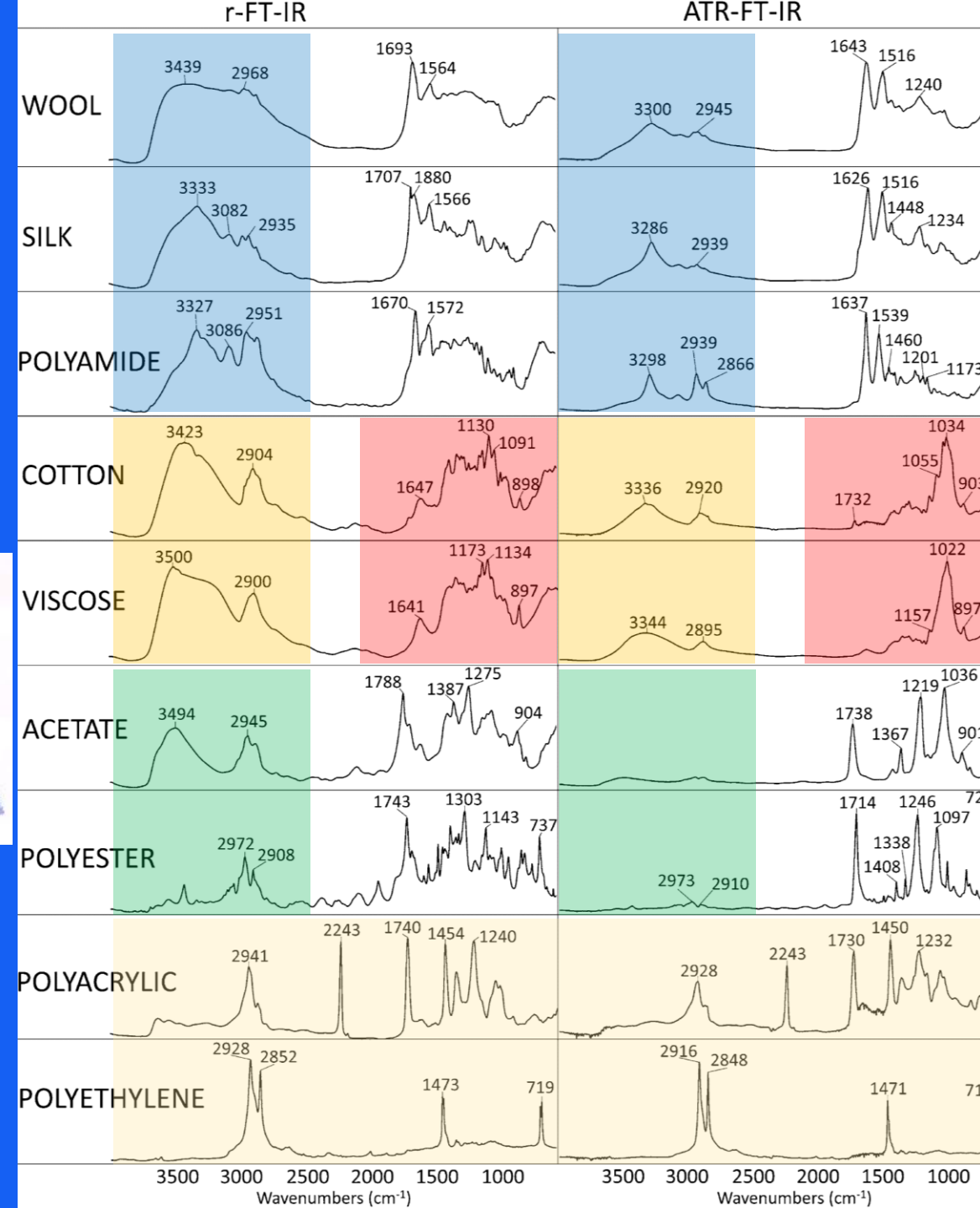
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Infrared Spectroscopy — Paper Review

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1 Paper Review: Reflectance FT-IR spectroscopy as a viable option for textile fiber identification (1)

Fourier Transform Infrared Spectroscopy (FTIR) plays an important role in the identification of textile fibers, due to the forensics and cultural heritage applications. Often samples are unique and/or highly valuable, therefore either extremely small samples or non-destructive characterization techniques are to be implemented during the analysis process. On the other hand, modern regenerated and synthetic fibers are very similar in morphology and are unable to be reliably characterized with microscopic visualization methods (1).

Attenuated Total Reflectance FTIR (ATR-FTIR) is the most popular characterization technique in the analyzes of textile fibers. However, ATR-FTIR requires the application of significant pressure to the textile sample which may damage the unique/valuable sample. Reflectance FTIR (r-FTIR) allows the analyzes of small parts of larger objects without sample removal or manipulation. Nevertheless, r-FTIR only works for flat surfaces (1).

1.1 Chemicals and reagents

For the analysis, Peets et al. worked with 61 single-component textile fibers from 16 different types were used: wool, silk, cotton, linen, jute, sisal, viscose, acetate, lyocell, fiberglass, polyester, polyamide, polyacrylic, elastane, polyethylene and polypropylene. Textile samples were obtained from different companies from Estonia, fabric stores, and private collections (1).

1.2 Instrumentation & Method

For r-FTIR, samples were placed on a gold plate, which was also used as back-ground. For ATR-FTIR, the ATR objective was a conical germanium crystal with 60–75% sample pressure

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strength. To evaluate both techniques, the authors compare the r-FTIR spectra against the ATR-FTIR spectra for the same materials (1).

1.3 Results

The r-FTIR vs. ATR-FTIR spectrum comparison revealed general similarity with small variations. In most cases, the absorbance bands in r-FTIR are wider, with wave numbers shifted to higher values and intensity peaks vary from the ATR-FTIR equivalents. Peets et al.'s general conclusion states that the performance of r-FTIR is comparable to ATR-FTIR (1).

More specifically, r-FTIR works better than ATR-FTIR in the identification of polyamide-based fibers, but it's less successful in differentiating cellulose-based fibers. The authors presented a side-by-side r-FTIR vs. ATR-FTIR spectra comparison of the most common textile fibers, as shown in Figure 1. The figure implies that:

1. r-FTIR spectra seem to contain more absorbance maxima compared to the ATR-FTIR technique. In particular in the region of $3000 - 4000\text{cm}^{-1}$ the bands are wider and more intensive.
2. r-FTIR shifts the bands toward higher wave numbers, compared to ATR-FTIR.
3. The characteristic $C - O$ stretching band of viscose (and cotton) near 1022cm^{-1} is easily identified in the ATR spectra, which has merged into a wide absorbance range in the r-FTIR spectra.
4. r-FTIR is discovered to better classify polyamide-based fibers (silk, wool, and synthetic polyamide) than ATR-FTIR (1).

Peets et al. report a table (Table 1), which compares the used FTIR spectroscopy characterization techniques for textile samples. The reflectance mode has the advantage of being non-invasive and non-destructive, especially in the case of valuable/fragile samples. However, r-FTIR does not work well with uneven surfaces, as less radiation is reflected into the detector. To compensate the drawbacks, the authors suggest using a higher number of scans, and a larger measurement area/aperture (1).

It can be concluded that r-FT-IR is a suitable technique for quick, easy, non-destructive and non-invasive analysis of different types of textile samples (1).

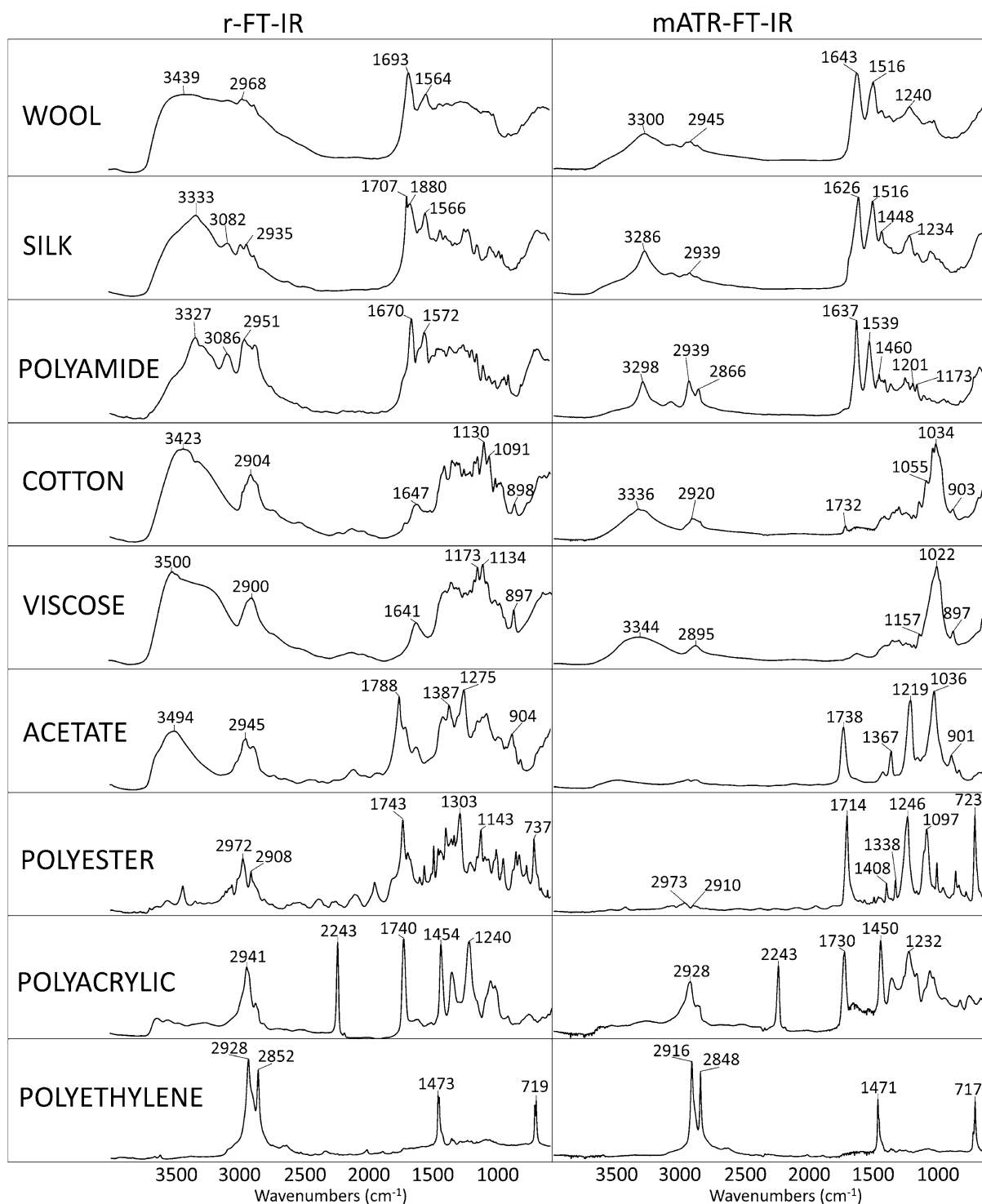


FIGURE 1

r-FT-IR and mATR-FT-IR spectra of most common textile fibers. Spectra in figure represent normalized and averaged results of each. The vertical axis represents absorbance. (1)

TABLE 1

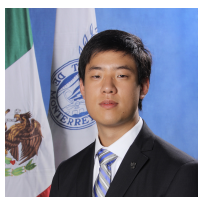
Comparison of different FT-IR approaches for analyzing textile fibers (1)

Textile sample type/property	ATR-FT-IR spectrometer	r-FT-IR microspectrometer Non-contact
Fragile sample	Applying pressure can damage the sample. High pressure should not be applied; spectrum quality might decrease.	Non-contact approach. Enables analyzing the sample with- out any alteration.
Thick sample	Penetration depth is few μm to few tens of μm . Fibers inside the fabric are not likely missed.	Spectrum is recorded only from the surface. Fibers in the inner part of the thread might be missed.
Uneven sample surface	Not a problem if enough pressure is applied, but high pressure may damage the sample.	More difficult to get high-quality spectrum. Scattering from the surface is extensive.
Extraneous material on sample fib- ers (additives or contaminants)	Penetration depth is few to few tens of μm . Surface contamination can have influence on the spectrum.	Spectrum is recorded only from the surface. Extraneous material on the surface can completely mask some fiber's bands and show additional bands.
Very small thread (less than 10 individual fibers)	Quality of the spectrum can be poor.	Spectrum may be distorted if the measured area (aperture) is larger than the sample thread itself.

References

- [1] Pilleriin Peets, Karl Kaupmees, Signe Vahur, and Ivo Leito. Reflectance FT-IR spectroscopy as a viable option for textile fiber identification. *Heritage Science*, 7(1):93, dec 2019. 10.1186/s40494-019-0337-z

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RESEARCH ARTICLE

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Reflectance FT-IR spectroscopy as a viable option for textile fiber identification

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Abstract

In this study, the reflectance-FT-IR (r-FT-IR) spectroscopy is demonstrated to be a suitable option for non-invasive identification of textile fibers. A collection of known textile fibers, 61 single-component textiles from 16 different types, were analyzed, resulting in more than 4000 individual spectra. The r-FT-IR method was compared with ATR-FT-IR spectroscopy using two instrumental approaches: FT-IR-microspectrometer with ATR mode (mATR-FT-IR) and ATR-FT-IR spectrometer (ATR-FT-IR). Advantages and drawbacks of these methods were discussed. Principal component based discriminant analysis and random forest classification methods were created for the identification of textile fibers in case-study samples. It was concluded that in general, the performance of r-FT-IR is comparable with ATR-FT-IR. In particular, r-FT-IR is more successful than ATR-FT-IR in differentiating between the amide-based fibers wool, silk and polyamide. As an additional result of this work, a collection of r-FT-IR spectra of different textile fibers was compiled and made available for the scientific community.

Keywords: Reflectance-FT-IR, ATR-FT-IR, Textile analysis, Non-invasive, Classification

Introduction

Textile fibers are by their chemical composition complex materials, commonly classified by their origin as natural (e.g. cotton, linen, silk, wool), regenerated (e.g. viscose, cellulose acetate) and synthetic (e.g. polyester, polyamide, polyacrylic) [1, 2]. Textile fibers can be used in making items like clothes, carpets, furniture, ropes and bags. The identification of textile fibers is of great importance as textiles are a major international commodities, form a significant part of cultural heritage and can be an important physical evidence in forensics [3–5]. Due to the wide variety of fibers used to make textiles, analysis and identification of the fibers is often challenging [1]. In many cases in forensics and cultural heritage, the samples are unique and/or highly valuable. Thus, either non-invasive approaches or extremely small samples have to be used for the analysis. Otherwise the analyzed object would be damaged. Also, the time needed to perform the analysis might be an important factor. Thus, it is often desirable to use express methods.

The easiest and most used way to identify fibers is probably using optical microscopy. This method is well suitable to detect the presence of natural fibers like wool, cotton, linen. Unfortunately, most of the modern fibers (regenerated and synthetic) are almost identical in their morphology and thus cannot be identified reliably with microscopic visualization [2, 6]. For fast analysis of textile fibers, often in (almost) non-destructive way, different vibrational spectroscopy approaches—Raman, near-infrared spectroscopy (NIR) and mid-infrared spectroscopy (IR)—have been used [1, 4, 5, 7–11]. Raman spectroscopy, while being widely used method in cultural heritage, [4, 12, 13] has a serious limitation when it comes to the identification of textile fibers. The main obstacles are the textile dyes. Several studies [4, 9, 14] have shown that most of the Raman bands come from the dyes and represent only a small part of textile fibers. Due to a fact that cloths are usually dyed, this significantly hinders the use of Raman spectroscopy in identification of textile fibers.

When it comes to the analysis of textile fibers, Fourier transform infrared (FT-IR) spectroscopy in the attenuated total reflectance (ATR) mode is the most acknowledged analytical technique [1, 8, 15–20]. The main

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drawback of ATR-FT-IR is the need to apply significant pressure to the textile, which in cases of e.g. unique artifacts can be unacceptable as they can break under ATR pressure. FT-IR analysis of textiles can be performed in a contactless non-invasive way when reflectance mode is used instead of ATR. Using reflectance FT-IR (r-FT-IR) with a microspectrometer [21, 22] enables analysis of miniature objects or small parts of larger objects without sample removal, i.e. local analysis. This is possible because of the small measurement area and accurate control of the position from where the spectra are measured. Thus, it becomes possible to collect a number of spectra across the surface for spectral mapping, e.g. for assessing the homogeneity of the sample. Despite these advantages, r-FT-IR has previously been overlooked for fiber identification as it is classically considered suitable only for flat surfaces [23, 24].

The aim of this work was to evaluate the ability of reflectance-FT-IR to identify textile fibers using FT-IR microspectrometer in reflectance mode. In this study comparison between r-FT-IR and ATR-FT-IR spectra of textile fibers was made and the main advantages and limitations of these techniques have been highlighted. Different data science tools were used for data analysis and classifying textile fibers. Additionally, a collection of r-FT-IR spectra of different textile fibers was composed and made available for the scientific community [25].

Experimental

Analyzed textile samples

For the analysis, 61 single-component textile fibers from 16 different types were used: wool, silk, cotton, linen, jute, sisal, viscose, cellulose acetate (acetate), TencelTM (lyocell), fiberglass, polyester, polyamide, polyacrylic, elastane, polyethylene and polypropylene. For classification analysis 59 single-component textile samples were used (two TencelTM samples were excluded). Real-life textile samples (fabrics from fabric manufacturers, clothing items, shopping bags, etc.) were used, obtained from different companies from Estonia (Kreenholm Manufaktuur OÜ, Estonian National Opera), fabric stores (AS Abakhan Fabrics Estonia) and private collections. Most of the standard samples were pieces with a size of few cm², cut off from the fabric, clothing items or bags. Others were yarns or threads. Sample of standards were significantly larger than needed, in order to be able to map larger area for our reference spectral collection. Obtained standard spectra were afterwards used for creating classification models. This approach was also needed to verify that the standard samples are homogeneous and do not contain any other fiber types or additives. The measurement area (sampling area) of the specific sampling techniques (see next section of spectrometers' parameters) is

the parameter that indicates how much sample is needed to identify real-life samples. Problems with very small sample sizes are discussed more thoroughly in "Results and discussion" section.

Case-study samples in this work were small textile pieces or threads that were analyzed directly without cutting or altering the sample.

Analysis with FT-IR-microspectrometer using reflectance and ATR modes

Thermo Scientific Nicolet iN10 MX integrated FT-IR microscope (FT-IR microspectrometer) was used in reflectance and ATR modes. Measurements were done using MCT detector cooled with liquid nitrogen, spectral range 600–4000 cm⁻¹, resolution 4 cm⁻¹ and 64 number of scans. For reflectance mode, sample was placed on the gold plate, which was also used as background. In the ATR mode, the slide-on ATR objective with a conical germanium crystal (Slide-On MicroTip Ge ATR crystal) was used with 60–75% pressure strength. For all the samples, multiple spectra from different parts of each sample piece were recorded. The micro-ATR tip allows analyzing samples as small as 3 microns. In the reflectance mode measurement area is adjustable: in most cases aperture 150 × 150 µm was used. For smaller sample pieces aperture down to 25 × 25 µm was used. With FT-IR microspectrometer using ATR mode (mATR-FT-IR) 2068 spectra and using reflectance mode 1677 spectra were recorded altogether. The data were collected and processed using Thermo Electron's OMNIC PICTA software.

Analysis with ATR-FT-IR spectroscopy

Thermo Scientific Nicolet 6700 FT-IR spectrometer with Smart Orbit micro-ATR accessory was used. The instrument has DLaTGS detector, Vectra Aluminium interferometer and sealed and desiccated optical bench with CsI optics. Smart Orbit is a single-bounce diamond crystal ATR accessory with a refractive index of 2.4, active sample area diameter 1.5 mm. Parameters used in measurements were: resolution 4 cm⁻¹, spectral range 225–4000⁻¹, zero filling factor 0, apodization window was Happ-Genzel and number of scans 128. Thermo Electron's OMNIC 9 software was used to collect and process the IR spectra. ATR-FT-IR spectra were recorded directly from the textile piece, textile fiber or clothing. Sample was placed on the ATR crystal, pressure was applied, and the ATR-FT-IR spectrum was scanned. Together with the spectra acquired in this work our collection of ATR-FT-IR spectra contains now altogether 614 spectra of different samples.

Classification

Classification analysis was done with the “native” data analysis suite of the used FT-IR spectrometer—Thermo Scientific TQ Analyst™ Professional Edition 9.0 (utilizing the discriminant analysis)—as well as with an in-house written Python script. The script utilizes the random forest classification with the *sklearn* library [26] and was introduced in part for achieving greater flexibility and in part as an independent method for increased reliability of identification.

In the case of discriminant analysis the problem of absence of uniform pathlength (penetration depth) that occurs with ATR [1], exists also in the reflectance mode. Unlike in transmission mode, it is not possible to adjust or equalize the IR beam penetration depth for different samples because of their different refractive indices. In order to correct that, TQ Analyst™ Professional offers different pathlength correction possibilities like standard normal variate (SNV), multiplicative signal correction (MSC), peak ratio (normalization) and constant. For experiments that have different pathlengths and pathlength is difficult or impossible to measure accurately, MSC and SNV are suggested when using classification. With ATR-FT-IR measurement, previous experience [1] showed that MSC gave the best results for the classification of textile fibers, so that approach was also used in this study. When using reflectance mode instead, SNV corrections seem to be more useful, which also corresponds to suggestion from the TQ Analyst™ Professional [27], which indicates that SNV is suggested for usage if scattering due to differences in particle size can produce significant variation in the standard spectra. The range for classification was 600–3700 cm^{-1} . Altogether 1600 reflectance spectra and 2022 mATR-FT-IR spectra with FT-IR microspectrometer in ATR mode were used (with elimination on Tencel™ samples, see below for reasons).

In the case of random forest, altogether 1589 reflectance spectra and 2010 mATR-FT-IR spectra were used in the process. In addition to elimination on Tencel™ samples, some spectra were erased because at data analysis stage the respective files were found to be corrupt. Prior to building the model, all spectra were normalized (i.e. subtracted the mean and divided by standard deviation). In addition, for optimizing the computation time, three regions 600–1800 cm^{-1} , 2200–2300 cm^{-1} and 2600–3800 cm^{-1} of the spectra were used, because only these spectral regions contained useful information. For training the model default parameters of *sklearn.ensemble.RandomForestClassifier* [26] were used, the only exceptions being the number of trees (set at 100) and the maximum depth (set at 20). For evaluating the accuracy of the approach, the initial spectra were divided into training and test set, so that the test set would have

5 random spectra from each class. The final models that were used to classify the case-study samples were trained using all the available spectra for both modes, not just the training set.

Results and discussion

Reflectance spectra of different single-component textile fibers

The best way to evaluate the ability of r-FT-IR to identify textile fibers is by comparison with the widely used ATR-FT-IR technique. To accomplish that, FT-IR spectra from 16 different types of individual single-component textile materials (altogether 61 different textile samples) were recorded using FT-IR microspectrometer with reflectance (r-FT-IR) and ATR (mATR-FT-IR) modes and ATR-FT-IR spectrometer (ATR-FT-IR). Comparison between r-FT-IR spectra and (m)ATR-FT-IR spectra for the same materials revealed that in spite of general similarity, at detail level the spectra are markedly different. In many cases absorbance bands in r-FT-IR spectra are wider, wavenumbers shifted towards higher values, and intensity ratios of peaks are different from the corresponding ATR-FT-IR spectra. Variations in r-FT-IR spectra from the corresponding ATR-FT-IR spectra are caused by different reflectance modes (specular, diffuse) that are contributing simultaneously to the detected signal due to the uneven surface of the textile samples. Because of the “mixed-mode” reflectance, the usual Kramers–Kronig and Kubelka–Munk corrections are not useful [28]. Although full interpretation may be complicated, each fiber type still has its unique r-FT-IR spectrum, which enables differentiating between the materials and identifying the material of an unknown textile sample with reflectance mode. In Fig. 1 r-FT-IR and mATR-FT-IR spectra of the most common textile fibers are shown for comparison. All the reflectance mode spectra in full size are presented in Additional file 1 as well. ATR-FT-IR spectra of different textile fibers recorded with ATR-FT-IR spectrometer are reported in authors’ previous articles [1, 25].

In Fig. 1, it can be seen that the reflectance mode spectra seem to contain more absorbance maxima compared to the ATR mode. In particular, in the region of 3000–4000 cm^{-1} the absorbance bands are much wider and more intensive. In this wavenumber region, the O–H and N–H stretching bands are found [23]. As in reflectance mode the extent of light penetration into the sample is smaller, it was hypothesized that these wider and more intensive peaks are due to the humidity on textile surface (water strongly absorbs in the region of 3000–4000 cm^{-1}). This was however not confirmed as drying experiments (textile piece was dried for 2 h at 70 °C) showed no significant variations between dried and

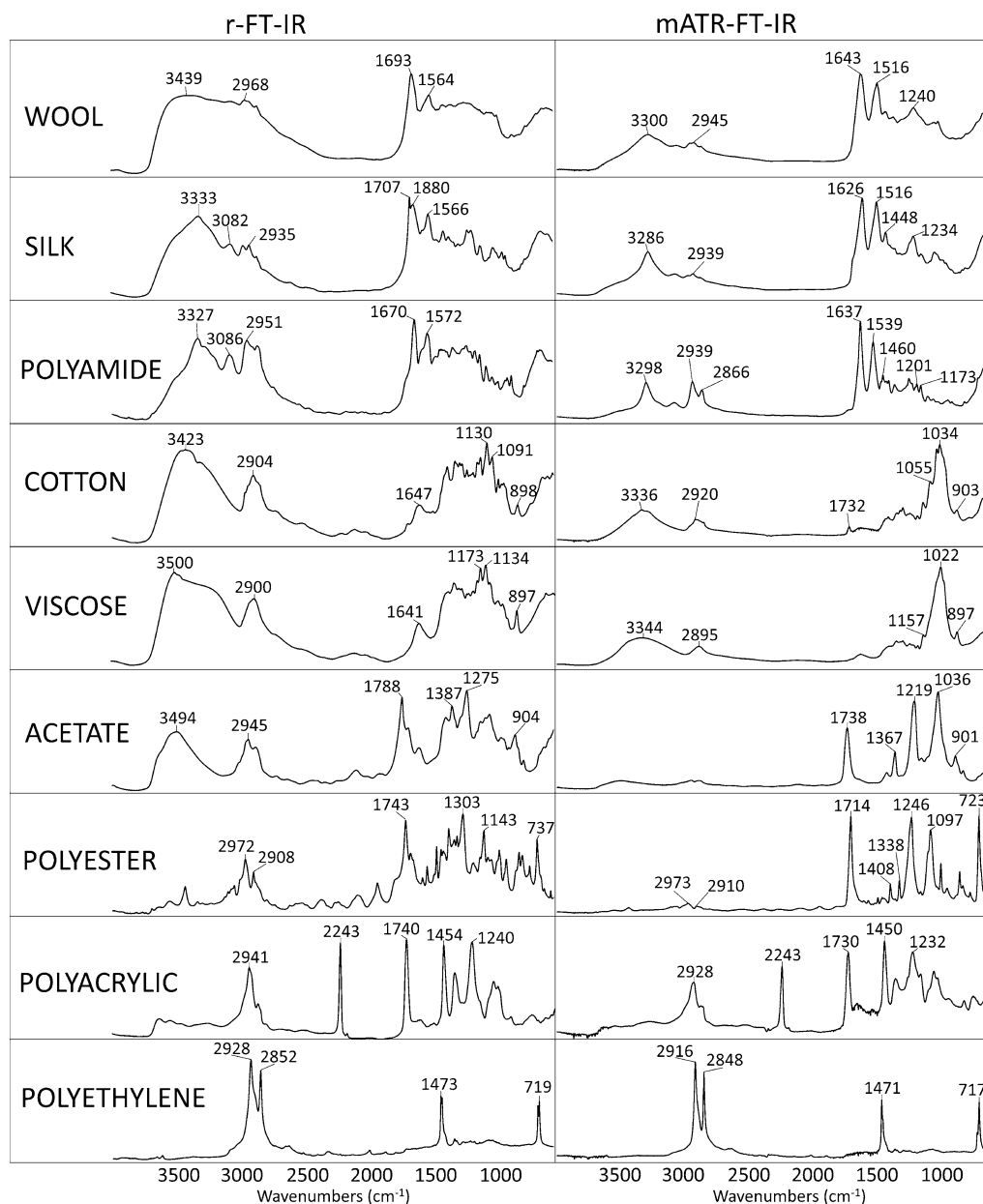


Fig. 1 r-FT-IR and mATR-FT-IR spectra of most common textile fibers. Spectra in figure represent normalized and averaged results of each class. The vertical axis represents absorbance. As natural cellulose-based fibers have very similar spectra, only cotton is presented. Spectra of other natural fibers like linen, jute and sisal are shown in Additional file 1

undried textile sample spectra. Most likely these vibrations in the region of $3000\text{--}4000\text{ cm}^{-1}$ are characteristic to the reflectance mode. In the reflectance mode, the bands are in many cases shifted toward higher wavenumbers, compared to the ATR mode. For example, for cellulose-based viscose fiber, O–H stretching band maximum in the ATR mode is at 3344 cm^{-1} , but in the reflectance mode a wide band with narrower tip can be

seen at 3500 cm^{-1} . The characteristic C–O stretching band that is prominently visible in the ATR mode (near 1022 cm^{-1}) has merged into a wide area of absorbances ($1400\text{--}1100\text{ cm}^{-1}$) in the reflectance mode, with bands at 1173 and 1134 cm^{-1} .

An unexpected advantage of the reflectance mode was revealed in distinguishing between polyamide-based fibers: silk, wool and synthetic polyamide. In the ATR

mode, the ATR-FT-IR spectra of these three materials look very similar. Absorbance maxima are only slightly shifted and the main difference is the width of N–H/O–H stretching (~ 3500 – 3000 cm^{-1}), amides C=O stretching ($\sim 1630\text{ cm}^{-1}$) and C–N–H bending ($\sim 1520\text{ cm}^{-1}$) absorbance bands. These differences are usually sufficient for identifying single-component fibers that are in good condition by ATR-FT-IR but not for partially degraded and/or contaminated real-life samples, because of the possible changes in band shapes and emerging of new bands. In the reflectance mode, the spectra of these three fiber types are considerably more different. For example, all five different silk standard samples investigated in this work, obtained from different sources, had an intensive and sharp absorbance maximum near 1710 cm^{-1} , which is absent in the spectra of wool and polyamide.

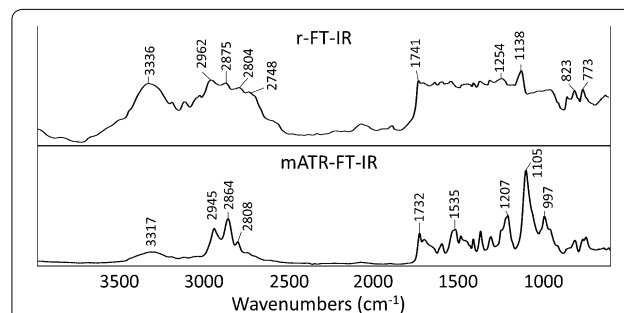
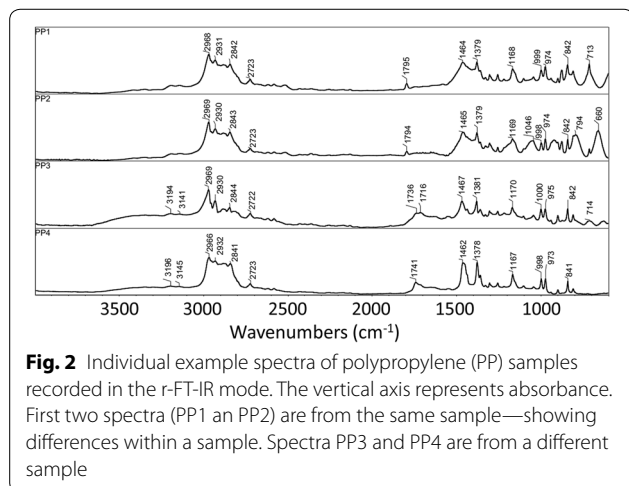
Interestingly, the polyester spectrum had several extra absorbance bands in the reflectance spectrum compared to the ATR-FT-IR spectrum. Relative intensity for C–H stretching in reflectance mode (at 2972 and 2908 cm^{-1}) was considerably higher compared to ATR mode spectrum, where the corresponding bands (at 2973 and 2910 cm^{-1}) were almost unnoticed due to low intensity. The aromatic overtones/combinations area between 2500 and 1800 cm^{-1} , which in case of the other studied fibers contains only minor bands, was surprisingly rich in the case of polyester. These bands are characteristic to polyester fibers as all the analyzed samples gave similar results.

For polypropylene significant differences were observed between reflectance spectra of different samples (See Fig. 2), both between samples as well as within one sample. In Fig. 2 four most different reflectance spectra from two different samples are shown to illustrate the differences. The C–H stretching area has

several absorbance bands at the same wavenumbers (~ 2970 , ~ 2930 , $\sim 2840\text{ cm}^{-1}$), but the bands' shape and relative intensities are different. For example, sample PP4 contains all the same absorbances, but they are merged into one wide band, while in the spectrum PP3 the band at 2969 cm^{-1} is clearly more intensive than 2930 cm^{-1} and 2844 cm^{-1} . The same situation applies to C–H bending bands around 1460 and 1380 cm^{-1} —same bands, different shapes. The most prominent difference appears to be in the wavenumber range of 800 – 600 cm^{-1} . As it can be seen in Fig. 2, the spectrum PP1 contains intensive band with absorbance maxima at 713 cm^{-1} , spectrum PP2 has very small band in this area but instead has wide and intensive bands at 660 cm^{-1} . The other two spectra PP3 and PP4 contain nothing or bands with very low intensity in this area. The reasons for these differences in reflectance spectra are most likely small amounts of co-monomers or additives that are often used in manufacturing of real-life polypropylene items [29]. As no analytical fiber standards could be obtained, no reflectance spectra were left out of the data analysis.

Elastane is mostly used in textiles, as an additive to make materials more elastic. While pure elastane as a textile is quite rare, elastane thread was used as a standard. Obtaining good quality r-FT-IR spectrum of elastane was problematic. Reflectance spectra of the used elastane thread and other very thin pieces (see “Different textile samples and practical aspects” section) were distorted and differed strongly from the mATR-FT-IR spectra. Absorbance bands were wide, and the tips of the bands seemed to be cut off in the region of 1750 – 1100 cm^{-1} (See Fig. 3). C–O stretching band is the most intensive in the ATR mode (1105 cm^{-1}) and is still well seen in the reflectance mode spectrum at 1138 cm^{-1} .

Characteristic ATR-FT-IR spectra of Tencel™ (containing lyocell fiber) recorded with ATR-FT-IR spectrometer [1], showed absorbance bands belonging to cellulose-based fibers, but also to amide groups. Analysis with

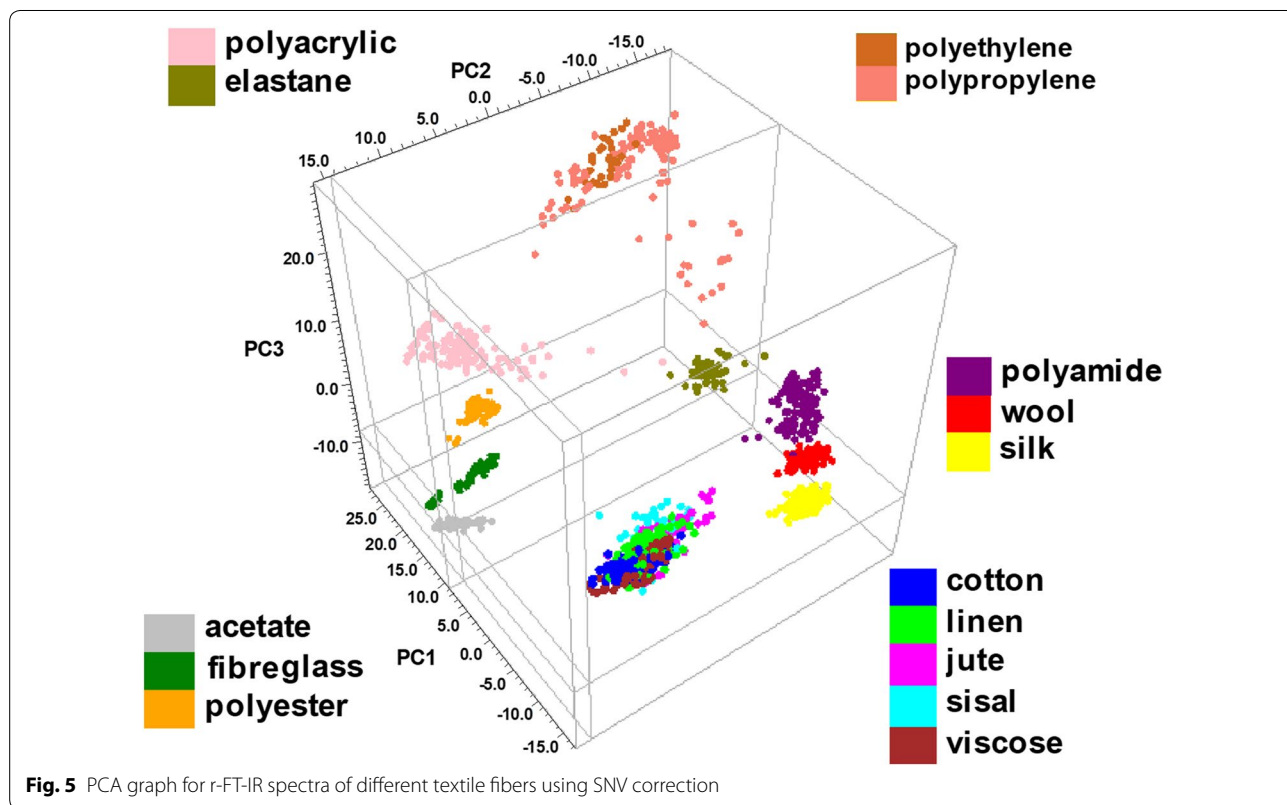
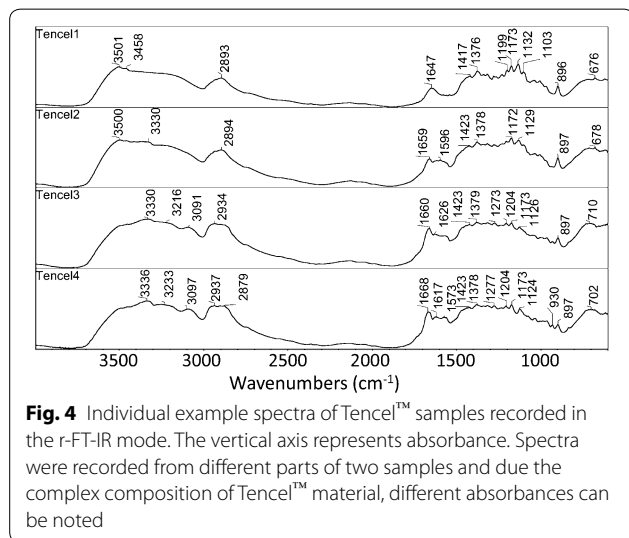


FT-IR microspectrometer in both reflectance and ATR modes revealed that the two Tencel™ samples used in this work were actually mixtures of at least two fibers (See Fig. 4). Only few of the recorded spectra (like Tencel 1 in Fig. 4) were similar to pure cellulose-based fiber as lyocell ought to be [30–32]. Most of the spectra contained in addition to lyocell bands (~ 3500 , ~ 3460 , ~ 1130 cm^{-1}) also N–H stretching absorbances (~ 3330 cm^{-1}) and

amide C=O stretching bands at ~ 1660 cm^{-1} , better seen in Fig. 4 spectra Tencel 3 and Tencel 4. As Tencel™ is not always 100% pure lyocell [32] the identification can often be difficult. Due to these difficulties, Tencel™ was removed from the classification training set.

Classification of single-component fibers

Two distinct approaches were used for classification: principal component analysis (PCA) based discriminant analysis (DA) and random forest based machine learning algorithm. Classification with DA shows that similarly with our previous work, where classification was performed using IR spectra recorded with ATR-FT-IR spectrometer [1], the fibers can be easily distinguished on the basis of their spectra recorded in reflectance mode. PCA graph for analyzed textile fibers (see Fig. 5), using the first three principal components, is presented to help visualize how much the fiber classes actually differ from each other. Scores for each PC in reflectance mode are: PC1=69.7%, PC2=12.1%, PC3=6.2% describing all together 88.0% of the variance. Scores for mATR-FT-IR are: PC1=57.1%, PCA2=21.3%, PC3=9.4% describing all together 87.8% of the variance. The performance of the random forest classifier was evaluated based on training and test set classification accuracy scores. For r-FT-IR, the test and training set classification accuracy scores



were both 0.99 (1.0 is the maximum). For mATR-FT-IR, the test and training set classification accuracy scores were 0.96 and 1.0, respectively.

As previous research has shown, cellulose-based fibers (cotton, linen, jute, sisal, viscose), which are very similar by their chemical composition, are difficult to differentiate from each other with IR-based methods [1]. Differences between IR spectra of several cellulose-based fibers have been found by Garside and Wyeth [15], but in our work, we found that the reflectance spectra of cotton and linen fibers were too similar for unambiguous identification. Thus, still additional methods, like microscopy, have to be used for confident analysis. Viscose is clustered quite closely with natural cellulose-based fibers, but the shapes of the bands are slightly different making the identification and correct classification of viscose possible. Apart from the cellulose-based fibers that are clustered together, the PCA-based discriminant analysis enables successful classification of the textiles analyzed in this work.

Different textile samples and practical aspects

Table 1 presents a comparison of the used FT-IR spectroscopy sampling techniques in the identification of different types of textile fibers.

When using FT-IR microspectrometer in reflectance mode, the key factor is selection of suitable sample

area (aperture) and good focusing of the radiation on the sample surface, which is often challenging. Some samples can be very thick, shredded, fragile or contain additives. In this work multiple old, partially deteriorated, thick or thin, small pieces and whole clothing with uneven surface were analyzed to test the accuracy of identification despite the sample condition.

r-FT-IR has the strong advantage of being a non-contact approach, especially in the case of fragile and/or valuable samples. The downsides of the r-FT-IR method are the problems encountered with uneven surfaces and extraneous material (additives or impurities) on sample surface. With uneven surface, less radiation is reflected into the detector and thus the spectrum quality is decreased. To compensate for that, it is advised to use higher number of scans, larger measurement area (aperture) and the best possible detector like nitrogen-cooled MCT. In the case of extraneous materials on the surface, scanning the surface for cleaner spots is the only option to mitigate the risks of misidentification. Very small thread pieces with width less than 10 individual fibers were difficult to identify with r-FT-IR. Depending on the fiber type, the spectra were sometimes distorted and uncharacteristic, e.g. in the case of thin elastane (discussed above) and silk thread (discussed below). In this case, the ATR approach must be used.

Table 1 Comparison of different FT-IR approaches for analyzing textile fibers

Textile sample type/property	ATR-FT-IR spectrometer	ATR-FT-IR microspectrometer	r-FT-IR microspectrometer
Fragile sample	Applying pressure can damage the sample High pressure should not be applied; spectrum quality might decrease	Applying pressure can cause damage, but since the sampling area is significantly smaller than regular ATR, the damage is very small	Non-contact approach Enables analyzing the sample without any alteration
Thick sample	Penetration depth is few μm to few tens of μm Fibers inside the fabric are not likely missed		Spectrum is recorded only from the surface Fibers in the inner part of the thread might be missed
Uneven sample surface	Not a problem if enough pressure is applied, but high pressure may damage the sample		More difficult to get high-quality spectrum Scattering from the surface is extensive
Extraneous material on sample fibers (additives or contaminants)	Penetration depth is few to few tens of μm [33] Surface contamination can have influence on the spectrum		Spectrum is recorded only from the surface Extraneous material on the surface can completely mask some fiber's bands and show additional bands
Very small thread (less than 10 individual fibers)	Quality of the spectrum can be poor	Micro-ATR tip area of few μm diameter enables obtaining spectra from very small samples Using MCT detector ensures good spectral quality	Spectrum may be distorted if the measured area (aperture) is larger than the sample thread itself

Case-study samples

In this section, the analysis results of textile samples taken from two different cultural heritage objects are discussed and different FT-IR spectroscopy approaches (r-FT-IR, mATR-FT-IR and ATR-FT-IR) are compared.

Scarf from twentieth century

The analyzed artifact from Estonian History Museum was a twentieth-century scarf with many embroideries. A conservator detected different textile fibers by visual observation (with an optical stereomicroscope). The aim of this analysis was to identify the textile fibers and help the conservator to determine the technology used in making the scarf. Small parts of threads, as well as cloth pieces (altogether five samples), were taken from the scarf and used for identification. Additional file 1: Figure S23 presents the scarf together with the locations of the samples.

Two samples—3 and 5—both contained two slightly visually different textile pieces. The mATR-FT-IR method was used as a benchmark for r-FT-IR. From each sample, several spectra were recorded and each of these were identified individually. Table 2 summarizes the results. Full results with chemometric accuracy scores are given in Additional file 1. All the r-FT-IR and mATR-FT-IR spectra of analyzed textile samples and their microscopic images are presented in Additional file 1.

Using FT-IR microspectrometer with ATR and reflectance modes combined with classification approaches and supplemented with optical microscopy, four out of seven fiber samples were successfully identified (see Table 2). Samples 3.2 and 5.2 were reliably identified as silk, thanks to the characteristic spectra. The cellulose-based fibers in samples 3.1 and 5.1 were found to be cotton and viscose, respectively. Optical microscopy was needed for these two samples as a confirmatory method because the IR results alone were inconclusive. Sample

3.1 was identified as linen/cotton/jute using IR and for sample 5.1 the results oscillated between viscose and natural cellulose-based fibers. Samples 3.1 and 3.2 were both threads from the embroidery. As one of them was identified as viscose instead of the expected silk, conservator concluded that viscose threads were used as assistance threads to mark the centerline of the pattern.

Samples 1, 2 and 4 could not be identified using FT-IR classification only. The spectra revealed that those sample pieces were not single-component fibers: the spectra from all of these three samples exhibited absorbances belonging to cellulose but also characteristic amide absorbance bands. Thus, the classification algorithm, which was developed for single-component textiles only, failed. Under the optical microscope the fibers looked shiny and smooth, which implies that the used cellulose fiber could be regenerated cellulose, e.g. viscose and the amide bands probably belong to silk. In conclusion, the textile pieces are likely to be a mixture of silk and some cellulose-based fiber.

Very small piece of thread from painting on the textile from end of the twentieth century

Small thin textile thread (with overall length of 40 mm, of which a 2 mm section was used for the analysis) was taken from an edge of the textile painting, originating from a private collection, with the aim of proving that the textile is silk. The painting is reportedly from China portraying the owner's great-grandmother's sister. Additional file 1: Fig. S52 presents the textile painting together with the location of the sample. Under optical microscope (Additional file 1: S53–S55) textile fibers look smooth implying that it could be either some synthetic fiber, artificial fiber or silk.

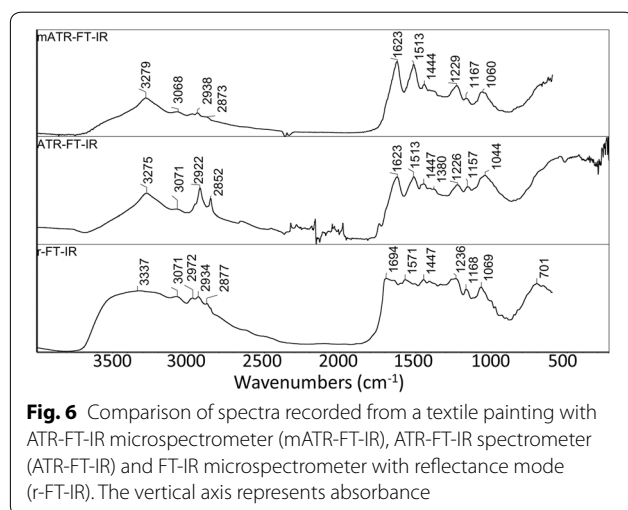
Figure 6 presents IR spectra recorded with different sampling techniques. The spectra are ranked according to quality. The r-FT-IR spectrum is strongly distorted, the

Table 2 Classification results for all five samples from the scarf

Sample nr	r-FT-IR		mATR-FT-IR		Final result
	DA	RF	DA	RF	
1	Jute	Wool/jute	Polyacrylic	Silk/sisal	Unambiguous identification with IR impossible, see text
2	Silk/jute/wool	Jute/silk	Jute/polyacrylic	Sisal/viscose/silk	Unambiguous identification with IR impossible, see text
3.1	Jute/cotton	Linen/cotton/jute	Jute/cotton	Linen/cotton/jute	Cotton ^a
3.2	Silk	Silk	Silk	Silk	Silk
4	Jute	Jute/wool/viscose	Jute	Viscose/jute	Unambiguous identification with IR impossible, see text
5.1	Viscose/cotton/jute	Cotton/viscose/linen	Jute	Viscose	Viscose ^a
5.2	Silk	Silk	Silk	Silk	Silk

DA discriminant analysis classification, RF random forest classification. Assignments separated by "/" correspond to individual assignments from the same textile piece

^a For final identification, additionally microscopic analysis was used



absorbance bands are wide and uncharacteristic. According to this and other (for example thin elastane thread) experiments with very small samples, it can be concluded that it is often impossible to get undistorted spectra from small thread pieces.

The mATR-FT-IR approach turned out to be the best for analyzing very small sample pieces due to its small measurement area (diameter down to 3 micrometers) and sensitive detector (MCT). Using ATR-FT-IR spectrometer, the spectrum quality was poor, absorbance intensity low and baseline noisy, but absorbance bands were still characteristic for some polyamide-based fiber. Based on mATR-FT-IR spectra, the classification methods identified the analyzed textile as silk.

In the case of that specific fiber piece, neither ATR-FT-IR microspectrometer nor ATR-FT-IR spectrometer caused any damages due to pressure. To get better quality IR spectra, in case of ATR-FT-IR spectrometer, the ATR pressure was strong enough to deform the fiber piece but not to break it. Deformation using FT-IR microspectrometer in ATR mode was minimal and cannot be seen with naked eye. Based on this case study, it can be suggested, that when analyzing very small threads (up to 10 individual fibers), non-contact reflectance mode might not be possible and mATR-FT-IR approach should be preferred.

Conclusions

It can be concluded that r-FT-IR is a suitable technique for quick, easy, non-destructive and non-invasive analysis of different types of textile samples. Using FT-IR microspectrometer in reflectance mode allows collecting multiple reflectance spectra from the textile fibers that are characteristic enough for creating classification models and for the identification of unknown textile samples. In particular, r-FT-IR is more successful than ATR-FT-IR

in differentiating between the amide-based fibers wool, silk and polyamide. However, r-FT-IR has also limitations: reflectance spectra can be recorded only from the surface of the sample and surface contamination and additives can markedly influence the spectra, problems occur also with the measurement of very small samples (it may be impossible to obtain good-quality reflectance spectrum). In these cases, ATR-FT-IR microspectrometer is preferred. An additional outcome of the work is a publicly available collection of r-FT-IR spectra (16 textile materials).

Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s40494-019-0337-z>.

Additional file 1. Supplementary information.

Abbreviations

NIR: near-infrared; FT-IR: Fourier transform infrared; ATR: attenuated total reflectance; r: reflectance; mATR: FT-IR microspectrometer in ATR mode; MCT: mercury cadmium telluride; DLaTGS: deuterated, L-alanine doped triglycine sulfate; SNV: standard normal variate; MSC: multiplicative signal correction; SI: supplementary information; PCA: principal component analysis; DA: discriminant analysis; PC: principal component; RF: random forest.

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Declarations

Part of the data generated or analyzed during this study are included in this published article and its additional files. The rest of the datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Authors' contributions

PP performed measurements with FT-IR spectrometric instruments, interpreted the data, did classification with TQ Analyst software and was a major contributor in writing the manuscript. KK developed in-house written Python script for random forest classification, wrote article sections concerning random forest classification and contributed significantly to manuscript writing. SV assisted with FT-IR microspectrometer and ATR-FT-IR spectrometer measurements and manuscript writing. IL participated in discussions and manuscript writing. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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