

# ATR-FT-IR spectral collection of conservation materials in the extended region of 4000–80 cm<sup>-1</sup>

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**Abstract** In this paper, a spectral collection of over 150 ATR-FT-IR spectra of materials related to cultural heritage and conservation science has been presented that have been measured in the extended region of 4000–80 cm<sup>-1</sup> (mid-IR and far-IR region). The applicability of the spectra and, in particular, the extended spectral range, for investigation of art-related materials is demonstrated on a case study. This collection of ATRFT-IR reference spectra is freely available online ([http://tera.chem.ut.ee/IR\\_spectra/](http://tera.chem.ut.ee/IR_spectra/)) and is meant to be a useful tool for researchers in the field of conservation and materials science.

**Keywords** ATR-FT-IR spectroscopy · Spectral database · Cultural heritage · Paints · Conservation materials

## Introduction

Investigation of cultural heritage objects, including art and conservation materials, using different analytical methods has become an increasingly prominent field of analytical science [1, 2]. Identification of constituents of different types of

artefacts (paints, coatings, mortars, textiles, etc) can provide valuable information for conservation and art history.

Infrared (IR) spectroscopy has served conservation scientists well during several decades and continues to do so [3]. Several important trends have emerged during the last decade in Fourier transform (FT)-IR spectroscopy, which have impact also on conservation and archaeology applications.

Attenuated total reflectance (ATR) has firmly established itself as the dominating sampling technique in IR spectroscopy for analysis of materials. It is suitable for the analysis of a wide range of paints, coatings, and related materials because it is almost nondestructive, can work with very small samples, is fast and convenient, enabling analysis of a diverse range of samples with little or no sample preparation [4].

Furthermore, micro-ATR and microscope accessories enabling analysis of very small samples have evolved from scientific curiosities into mainstream instruments. This is again very beneficial for art and archaeology studies because almost all samples from art objects (if any samples can be taken at all) as well as many archaeological objects are very small.

The wave number range routinely used by researchers has widened considerably. Traditionally, IR spectra have been scanned from 4000 to 400 cm<sup>-1</sup>, but now more and more instruments also enable using the far-IR range (sometimes also called as the low wave number range), loosely defined as ca 500 to ca 50 cm<sup>-1</sup>. This is achieved by using in the interferometer a beamsplitter made of CsI or the so-called solid substrate beam splitter, DTGS detector with polyethylene (PE) window and diamond as the ATR crystal material [5, 6]. In the far-IR region, numerous inorganic pigments (cinnabar, orpiment, cadmium yellow, etc.) and fillers (different minerals and silicates) have characteristic absorption bands that are absent in the mid-IR region. For this reason, the far-IR region is very interesting for conservators (see below for more details).

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The essence of the ATR phenomenon is different from that of absorption of radiation, used in measurements of conventional transmittance or absorbance spectra [7]. In absorption measurements, there exists a constant and well-defined path length, which is the same for the IR radiation of all wavenumbers. The situation is very different in ATR-FT-IR. Although the attenuation of radiation can be considered absorption, its dependence on the sample properties is very different from transmittance measurements. The extent of attenuation is dependent on radiation wavelength (the longer the wavelength the stronger the attenuation) and on the refractive index of the sample (the higher the refractive index the stronger the attenuation) [5, 8]. To make things more complex, refractive index in turn is dependent on wavelength, and its value changes sharply near absorbance maxima [7]. Because of these reasons, although similar in broad terms, the ATR spectra have differences from transmission spectra, especially in relative band heights, but also in band positions [7]. Occasionally the differences are significant enough to cause danger of misinterpretation of spectra of complex objects. For this reason, it is recommended to use for interpretation of ATR-FT-IR reference spectra that also have been recorded in the ATR mode. However, in spite of the constantly increasing popularity of ATR sampling in IR spectroscopy, the majority of available IR spectral databases are still in transmission mode.

In this paper, we present a spectral collection of over 150 ATR-FT-IR spectra of materials related to cultural heritage and conservation science that have been measured in the extended region of 4000–80  $\text{cm}^{-1}$  (mid-IR and far-IR region). We demonstrate on a case study the applicability of the spectra and, in particular, the extended spectral range for investigation of art-related materials. This collection of ATR-FT-IR reference spectra is freely available online ([http://tera.chem.ut.ee/IR\\_spectra/](http://tera.chem.ut.ee/IR_spectra/)). The usefulness of the spectra is demonstrated by the more than 30,000 visits to the database from more than 100 countries during the last year.

## Materials and methods

### Materials

A number of museums, conservation institutions, and companies have donated their materials and samples (see the Acknowledgements section). Some materials were purchased from Safran OÜ, Kremer Pigmente GmbH and Co. KG, Maimeri, Winsor and Newton, Sennelier, Tempera OY, Lefranc and Bourgeois, Old Holland Classic Colours, Sigma-Aldrich, Reakhim, Tartu Flora, Kemasol, Eskaro, Fisher Scientific Company, AS keemiakaubandus, AS Hermseal, and Distrei Goup OÜ.

### Analysis with ATR-FT-IR spectroscopy

ATR-FT-IR spectra were acquired on Thermo Scientific Nicolet 6700 FT-IR spectrometer with the “Smart SplitPea” and “Smart Orbit” diamond (refractive index  $n_D=2.418$ ) micro-ATR accessories. The spectrometer has Vectra aluminum interferometer and sealed and desiccated optical bench with CsI optics. In order to protect the spectrometer from atmospheric moisture, it is constantly purged with dry air.

ATR-FT-IR spectra were measured in two ranges: 4000–225  $\text{cm}^{-1}$  (with DLaTGS detector and CsI beamsplitter) and 500–80  $\text{cm}^{-1}$  (with DTGS detector with PE window and Solid Substrate far-IR beamsplitter). The following spectrometer parameters were used: resolution: 4  $\text{cm}^{-1}$ , number of scans: 256 (for solids), 128 (for non-volatile liquids), and 16 (for volatile liquids), level of zero filling: 0, apodization: Happ-Genzel.

The sample was placed directly on the ATR crystal. Solid samples were pressed against the ATR crystal and the ATR-FT-IR spectrum was scanned. If necessary, they were powdered beforehand.

Reference materials (mostly inorganic pigments), which have high  $n_D$  (higher or close to diamond) and have bands in the far-IR region were dispersed in linseed oil (matrix with low  $n_D$ ), and ATR-FT-IR spectra were recorded from the mixture. Mixing the pigment with linseed oil decreases the  $n_D$  of the mixture and makes it possible to obtain better quality ATR-FT-IR spectra. Linseed oil does not have characteristic bands in the far-IR region and is thus a suitable matrix material [8, 9]. Thermo Electron’s OMNIC software for FT-IR spectrometer was used to collect and process the IR spectra.

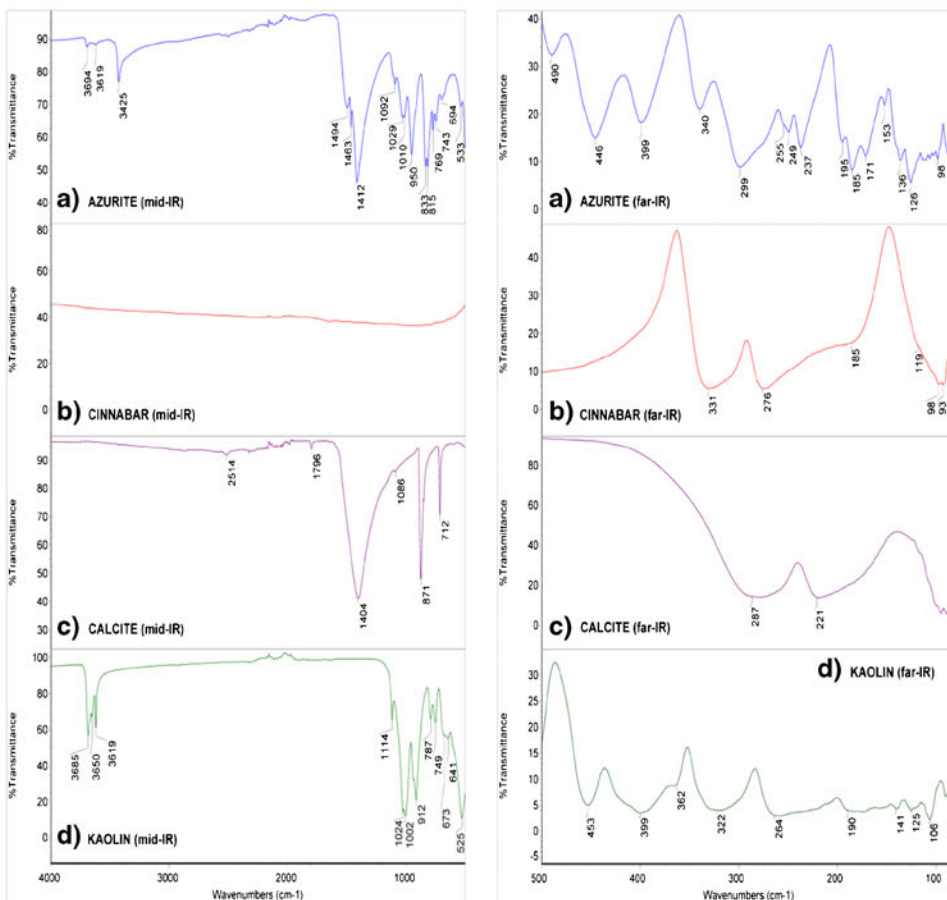
## Results and discussion

Cultural heritage materials are complex multicomponent and multi-layered mixtures and their IR spectra are generally not easy to interpret, especially in complex samples where the absorption bands of different components overlap [9, 10]. The availability of reference spectra of pure materials is very important for the interpretation. In addition, when analysis of a sample is carried out with ATR-FT-IR spectroscopy, as discussed above, it is important to use ATR-IR reference spectra for interpretation.

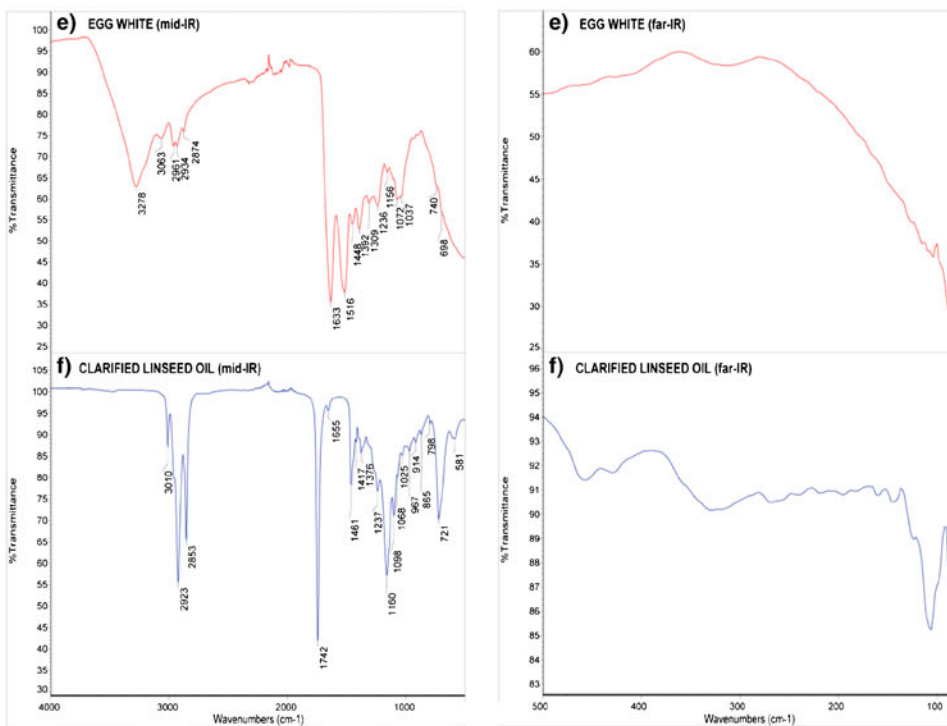
During the last 9 years ATR-FT-IR spectra of various materials were acquired in the course of different projects on historic, industrial, and construction paints and coatings, as well as for B.Sc., M.Sc., and Ph.D. theses. We have assembled all these ATR-FT-IR spectra of different materials into a library of ATR-FT-IR spectra of various materials. This library now contains over 150 IR spectra and is meant to be a useful tool for students and scientists.

**Fig. 1** ATR-FT-IR spectra of reference materials in the mid-IR and far-IR region

**Pigments and Fillers**



**Binders**



Besides ATR-FT-IR spectra recorded in the mid-IR region, there are ATR-FT-IR spectra of pigments and fillers that are measured in the far-IR region (500–80  $\text{cm}^{-1}$ ). These spectra are quite unique: there are not many spectral databases where ATR-IR spectra of inorganic materials in the far-IR region are available.

The strength of FT-IR, that the large majority of substances absorb in the mid-IR region (4000–500  $\text{cm}^{-1}$ ), is also its weakness: in complex paint samples (usually binders and also some fillers), serious overlap of bands can be seen in the mid-IR region and it is often impossible to determine some constituents in the presence of others.

The far-IR region (specifically 500–80  $\text{cm}^{-1}$ ) can be very instrumental in such cases. It has to date found limited use in FT-IR analysis because it has traditionally been less accessible for common instrumentation, and most organic compounds do not have characteristic absorption bands of sufficient intensity in that region, limiting the number of compounds that can be determined [8, 9, 11]. However there are many factors that make far-IR region very interesting for analytical chemistry:

- (1) There are a number of interesting inorganic compounds (pigments, some fillers, and minerals) that have characteristic absorption bands in the region of 500–80  $\text{cm}^{-1}$  and are often present in samples or on their surfaces at

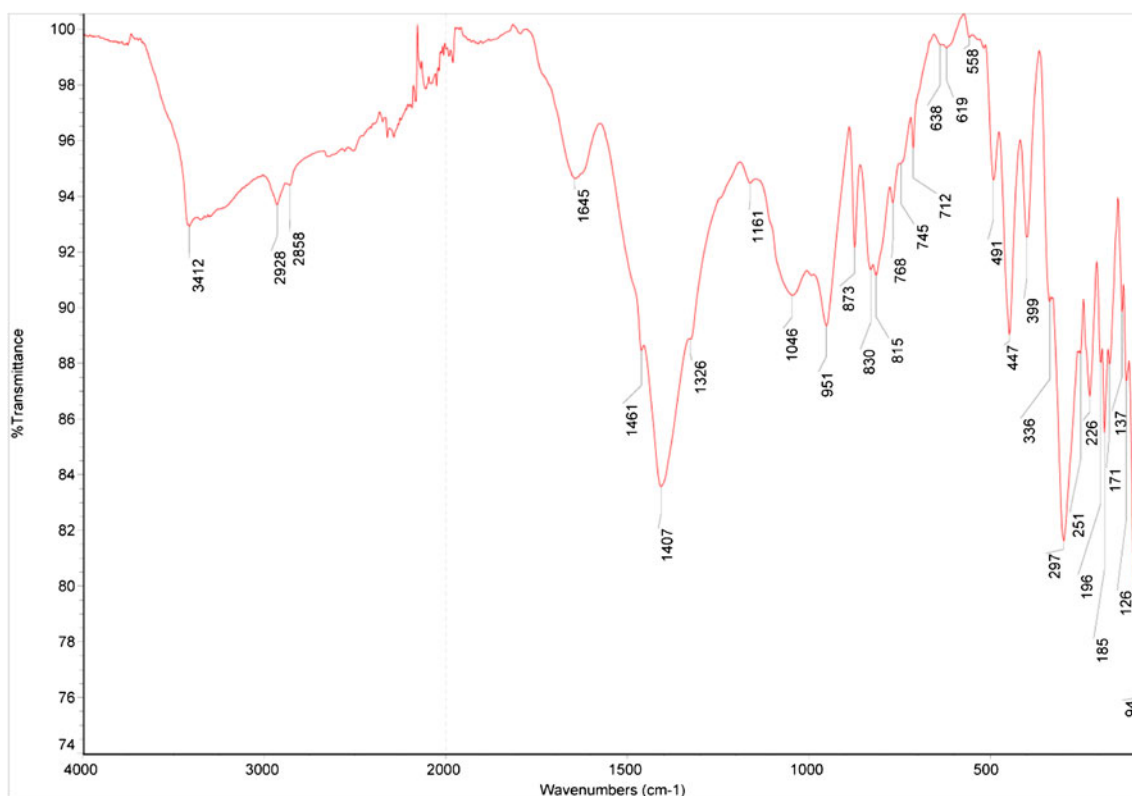
concentrations high enough for ATR-FT-IR analysis [8, 9, 12, 13]. In general, vibrations involving heavy atoms as well as lattice vibrations in crystals are found in that region. Furthermore, some inorganic pigments (cinnabar, orpiment, etc.) that can be detected in the far-IR region do not in fact have useful absorption bands in the mid-IR region [8, 9].

- (2) Absence of characteristic absorption bands of most organic constituents in the region of 500–80  $\text{cm}^{-1}$  significantly decreases problems due to bands overlap, which are so common in the mid-IR region [14]. For example, esters (oils, alkyds etc.) and proteins (glues, egg-tempera, etc.) are essentially devoid of characteristic absorption bands in that region, and carbohydrates have only low-intensity bands.

Figure 1 presents the ATR-FT-IR spectra of some paint components in the mid-IR and far-IR region. Using both of these regions makes interpretations much more reliable.

Our spectral database contains ATR-FT-IR spectra of the following groups of materials (recorded in the mid-IR and far-IR region):

- (1) Paint components (inorganic pigments, fillers, binders)
- (2) Oil paints (self-made oil paints – pigments mixed with linseed oil)
- (3) Coating materials (varnishes, tars, etc.)



**Fig. 2** ATR-FT-IR spectrum of the blue paint sample from the crucifix of the Kolga-Jaani church

**Table 1** Analysis results of the blue paint sample from the crucifix of the Kolga-Jaani church

ATR-FT-IR ANALYSIS (Band wavenumbers (cm <sup>-1</sup> ) in the ATR-FT-IR spectra)		
Pigment		
Azurite [2CuCO <sub>3</sub> Cu(OH) <sub>2</sub> ]	3412 1461, ~1407 <b>951</b> <b>830, 815</b> <b>491, 447, 399, ~297</b> 251, <b>196, 185, 171, 137, 126</b>	O-H stretch asym. C-O stretches in the CO <sub>3</sub> <sup>2-</sup> O-H bend sym. C-O stretch in the CO <sub>3</sub> <sup>2-</sup> Cu-O skeleton stretching bands Cu-O skeleton bending bands
Fillers		
Calcite (CaCO <sub>3</sub> )	Band in the region of 1450-1400 <b>873</b> <b>712</b> ~297, ~226	asym. C-O stretch in the CO <sub>3</sub> <sup>2-</sup> C-O <i>out-of-plane</i> bend in the CO <sub>3</sub> <sup>2-</sup> C-O <i>In-plane</i> bend in the CO <sub>3</sub> <sup>2-</sup> probably lattice vibration modes
Silicates	Bands in the region of 1100-1000 <b>768, 745</b>	Si-O stretches Si-O bends
Binder		
Probably protein	2928, 2858 <b>1645</b>	C-H stretches C=O stretch (amide I)

- (4) Conservation materials (glues, solvents, diluents, etc.)  
(5) Textile fibers

### Case study: Investigation of blue paint sample from the crucifix from Kolga-Jaani church

The usefulness of ATR-FT-IR reference spectra in the region of 4000–80 cm<sup>-1</sup> for identification of material components is demonstrated via a case study of a paint sample from the crucifix from Kolga-Jaani (Estonia) church. The parish church of Kolga-Jaani is located in central Estonia. One of its main attractions is a medieval crucifix, one of the oldest preserved in Estonia, which has been dated to the 14th century. The crucifix has been overpainted several times. One of the aims of the scientific examination was determining the survival of the original paint layers, the painting technique, and pigment range. The blue paint sample was taken from the figure's loincloths at the lowest polychrome levels. The ATR-FT-IR spectrum of the blue paint sample is presented in Fig. 2 and the results of interpretation in the Table 1.

The ATR-FT-IR spectrum of blue paint agrees very well with that of azurite (see Figs. 1a and 2). The mid-IR and far-IR range support each other and are both useful for the interpretation of IR spectrum of blue paint. The absorption bands in the mid-IR region give a hint that the pigment could be azurite but do not enable conclusive statements. The bands in the far-IR region confirm the assignment (azurite has a number of characteristic absorption bands in the region of 500–80 cm<sup>-1</sup> (see Fig. 1a).

Importantly, if one would use transmission spectra, the identification of the paint components would be more difficult because the wave numbers can be shifted. This can happen due to abrupt changes of the sample's refractive index near the absorbance maxima. Refractive index of a material depends on the wavelength, and in the IR spectral region the change of refractive index with wavelength is not monotonous, and large nonlinearities can be observed. Absorption bands that occur near such nonlinearities can be shifted from those observed in the transmission mode (see reference [7] for physical background). Occasionally the wavenumber difference can reach 10 cm<sup>-1</sup>.

In addition, the sample contains chalk and some silicates as fillers. It is difficult to identify the binder because of its extensive decomposition and overlap of the bands with other components but the characteristic “triangular” band in the region of 3600–3000 cm<sup>-1</sup> and the band at 1645 cm<sup>-1</sup> enable stating that the binder is protein with high probability.

The conclusion that the pigment is azurite is fully supported by the SEM-EDS results (see Fig. S1 in the Electronic Supplementary Material, ESM). Additional elements in the EDS spectrum may belong to the components from other layers. Identification of azurite indicates that scarce fragments of original polychrome paint layer might be present under the overpaintings.

### Conclusions

The usefulness of reference ATR-FT-IR spectra in the extended wavenumber region of 4000–80 cm<sup>-1</sup> is

demonstrated and the spectral database of historical and conservation materials, available at [http://tera.chem.ut.ee/IR\\_spectra/](http://tera.chem.ut.ee/IR_spectra/) is presented.

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#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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