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Development of FTIR spectra database of reference art and archaeological materials

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Fourier Transform Infrared (FTIR) spectroscopy is a reliable analytical technique to study both organic and inorganic materials. FTIR spectroscopy has been widely applied in investigation of art and archaeological objects. The specificity and complexity of such analysis require the availability of comprehensive database containing standards of cultural heritage materials. In this paper, the development of FTIR spectra database of art and archaeological materials is presented. The database provides absorption FTIR spectra, total attenuated reflectance (ATR) spectra, as well as information on a number of pigments and dyes, adhesives, oils, resins, gums and other binders, bulk components, fillers and etc. The composition of several ancient art and archaeological materials was determined by means of our spectral database.

Key words: art and archaeological materials, database, FTIR, ATR

INTRODUCTION

Globally, there is a huge interest in preservation of the cultural heritage. The care, maintenance and investigation of the Bulgarian museums' collections play significant role in the conservation of the Bulgarian cultural heritage. Protection, conservation and restoration of cultural valuables are needed in order to preserve them ensuring national and worldwide appreciation. Archaeological, historical and artistic objects bear not only aesthetical value but also can be considered for their historical and cultural context. [1,2] In the field of fine arts, archeological and monumental conservation, science and technology play fundamental role for the characterization of the materials constituting the cultural heritage (historical buildings, monuments, archaeological objects, works of art, ancient papers, manuscripts, etc.) [3]. FTIR spectroscopic techniques are widely used in investigation of both organic and inorganic art and archaeological materials [1,3,4]. The main advantages of this spectroscopic method are the speed, accessibility and the requirement for very small sample amount, the latter being very important factor when studying artworks. Thanks to these characteristics and the broader scope of application for analysis of cultural heritage objects, the FTIR spectroscopy has been selected as main analytical method in many different types of artwork investigations [3,4]. A large number of papers have been published showing the importance of FTIR spectroscopy and covering all kinds of specimens and materials used in different art techniques in wall paintings [5-7], icons [8-11] pottery [12,13], metal artifacts [14,15], polychromed sculptures [16,17], etc.

In the process of artwork creation, various inorganic and organic materials are used. Natural aging and changes in environmental conditions have specific impact on the cultural heritage objects In order to have an appropriate identification of an artwork material, it is essential to use spectral database of standard art and archaeological materials. In general, the available spectral databases [4,18-20] provide one spectrum per compound, typically as an image file, thus the spectra cannot be used with the appropriate spectroscopic software and the information given about the material is not sufficiently detailed.

The scope of the paper is focusing on developping FTIR spectra database of art and archaeological materials. All tested samples of reference materials and Bulgarian art and archaeological artwork samples are classified according to their type, chemical composition and historical period in which they were used. A matter of particular interest is the availability of their FTIR-ATR spectra.

This paper illustrates the usefulness of FTIR spectroscopy as an applied method for the study of cultural heritage presenting example spectra of

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some reference and artefacts materials. The e-library would be a particularly useful tool for analysing unknown cultural valuables by comparison with similar artworks available in the database.

MATERIALS AND METHODS

Commercially available materials have been selected on the basis of their chemical properties, and their application as art and archaeological materials. The main part of standard materials (pigments and dyes, some natural and synthetic resins and gums) has been kindly provided by the conservator-restorers Yoana Kancheva and Elitsa Tzvetkova and by the National Academy of Art, Sofia. The remaining materials under study have been purchased from Aldrich (e. g. calcium carbonate, barium sulphate, gypsum) and from food supermarkets (e. g. egg, honey, beeswax, oils produced from walnut, sunflower, almond, sesame, soybeans, etc.). Some substances were synthesised in the laboratory (e.g. Punic wax) or obtained from natural sources (e.g. cherry gum).

All samples were characterized by means of FTIR spectral methods. Vibrational spectra were taken at standard conditions:

(a) Absorption spectra in the middle IR region (4000-400 cm^{-1})

(b) Reflection (ATR) spectra in the middle (4000-600 cm^{-1}) IR region

Reference art and archaeological materials of pigments and/or dyes, waxes, oils, resins, proteins, gums, and different carbonates, sulphates, silicates, etc., as well as ancient art and archaeological materials were studied. The ancient art and archaeological materials of organic origin were obtained from the samples by extraction with a suitable solvent. Commercially available spectral quality solvents were used. The extracted solutions were kept at room temperature for several days and the dry materials were analysed.

All samples were measured in solid state (KBr pellet) and/ or in the case of ATR technique they were directly applied on a diamond crystal. The spectra were recorded on Bruker Tensor 27 FT spectrometer with MIRacle-Diamond ATR accessory (Pike technologies). For KBr pellet technique, a resolution of 2 cm^{-1} and 64 scans were applied with background spectrum of pure KBr. In the ATR measurements, the spectra were recorded with a resolution of 2 cm^{-1} and 128 scans referencing to the air as background spectrum.

DATA PROCESSING

All spectra were recorded and processed by OPUS software (Bruker Optics). The absorptions of the atmospheric moisture and carbon dioxide were removed in all cases by automatic compensation which is included in the software package OPUS, version 6.5.

Spectral data were saved in several formats (spectral-JCAM-DX and ASCII, and graphics-GIF, JPG or PDF) in order to be easily compared with the spectra of materials from real artistic and archaeological objects, as well as to be processed with the available spectrum software. For each spectra the frequencies and intensities of the characteristic bands were described.

RESULTS AND DISCUSSION

Multi-layered structure of each cultural heritage object is a complex and complicated issue for analysis. FTIR spectroscopy provides molecular and structural information for the organic as well as for inorganic materials. FTIR spectra of art and archaeological standards (reference materials) were measured. In order to provide more detailed spectroscopic information, it is necessary to record more than one spectrum for each sample.

Total attenuated reflectance (ATR) is a very suitable and useful technique for the analysis of artefacts, especially using high refractive index crystal such as diamond. Due to its durability and chemical inertness, it allows direct deposition on the crystal without sample preparation for a wide range of solid and liquid samples. Furthermore, the ATR accessory available in our laboratory has a very small diamond crystal, 2 mm across.

It diminishes the amount of sample required for analysis to a few milligrams. When obtaining spectra with this technique, it should be taken into account that the absorption peak intensity shows wavenumber dependency. As a result, the spectral bands in the low wavenumber region appear with enhanced intensity compared to those obtained with absorption measurement with KBr technique. Also peak deformation toward the first-order differential form is possible in the ATR spectra of inorganic and other high-refractive-index samples due to the anomalous dispersion of the refractive index. Some differences in the intensities, bands shapes and peak’s position could appear depending on the different spectra collection technique or sample origin. As an example, the spectra of Gum Arabic obtained by absorption measurement with KBr and ATR are illustrated in Fig. 1. The stretching of polysaccharides O-H group at 3429 cm^{-1} is shifted at 3291 cm^{-1} in the case of ATR spectrum. Other notable FTIR pattern differences are the two intense C-O stretching bands at 1073 cm^{-1} and 1032 cm^{-1} in the absorption spectrum and the corresponding shoulder at 1063 cm^{-1} and peak at 1026 cm^{-1} in the ATR spectrum.

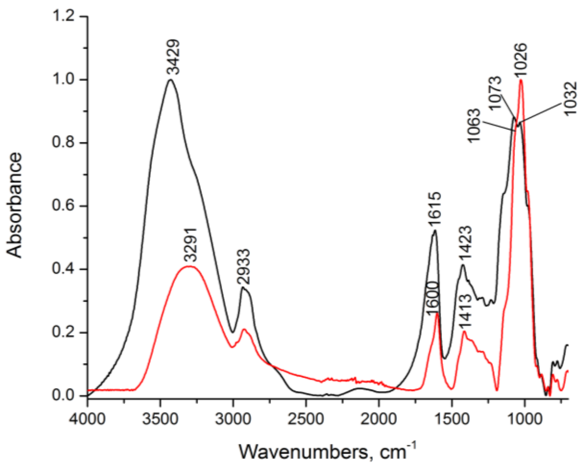

Fig. 1. Normalized FTIR spectra of Arabic gum: KBr pellet (black line), ATR-FTIR on a diamond crystal (red line).

The data for each standard contains spectral and additional (name, synonyms, origin, etc.) information (example- Gum Arabic Fig. 1 and Animal glue Table 1). The presence of such additional information is quite helpful. For example, identical names have been used to describe more than one pigment in antiquity. In Roman times, minium was reserved for cinnabar (HgS) but was applied increasingly to red lead (Pb_3O_4) by the Renaissance [21]. On the other hand, most of the varnishes, binders, dyes, pigments and etc. included in the artworks have their own history of occurrence and certain (historical) periods of use as well as geographical areas of distribution. This information can be added to the results of chemical analyses (and sometimes by the method of exclusion) in order to specify and limit the search. Some materials used in artworks are not commercially available. Such example is the Punic wax, which is produced by boiling beeswax with alkaline carbonates or hydroxides. In this way, the esters and free fatty acids in the beeswax are partially converted into alkaline salts (soaps). Emulsions of Punic wax in water were used as paint vehicle. In order to provide a reference spectrum of Punic wax, a sample of beeswax purchased from the local market was subjected to saponification by potassium carbonate (potash) according to a literature recipe [22]. The obtained emulsion was dried on glass and the spectrum was measured by ATR technique. The superimposed spectra of beeswax and Punic wax are presented in Fig. 2. The main difference between the spectra of beeswax and Punic wax is the appearance of IR bands for the carboxylate stretching vibrations at 1561 and 1414 cm^{-1}. Saponification was carried out also by potassium hydroxide and led to the same spectral changes.

Table 1. Animal glue information.

Name	Animal glue
Obsolete and synonym names/Varieties	Hide glue, bone glue, skin glue, fish glue, etc. tutkal (in Bulgarian)
Origin	Animal (rabbit, fish, goats, sheep, etc.)
Chemical composition	Natural organic product extracted from animal tissues and bones. It consists primarily of gelatine and other proteins, residues of collagen, karate or elastin.
Compatibility and permanence	It swells when it is soaked in cold water and it may be dissolved by gentle heating. When dry it hardens but do not change chemically. Thus it can be dissolved again in water.
Use and applications	Adhesive, binder of pigments and grounds (primers), consolidating agent.
Possible adulterations and mixtures	The addition of a bulking agent to the glue causes some changes in the chemical and physical properties of the protein network, most of these correlate to changes seen in cross-linked polymers.
FTIR Spectrum	sample 1, sample 2, sample 3,….
ATR-FTIR Spectrum	sample 1, sample 2, sample 3,…

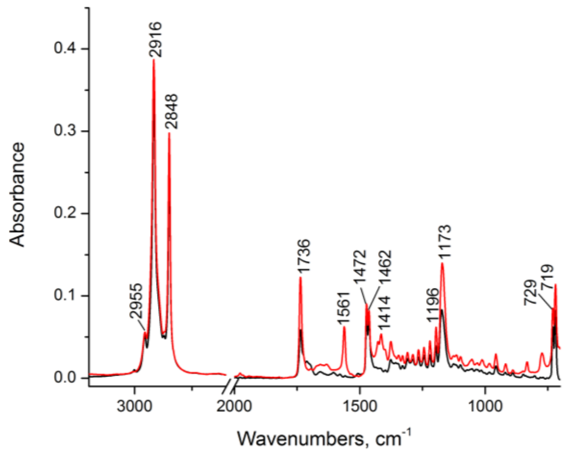

Fig. 2. ATR-FTIR spectra of reference beeswax (black line) and Punic wax (red line).

Vegetable drying oils (sometimes with or without the addition of siccative) were used in the paintings as binding media. In order to provide more versatile examples, including some oils typically used in Bulgarian artistic objects, several reference spectra were recorded. This group includes linseed oil which is commonly used in the painting art in many countries and oils from some other locally grown seeds - sunflower, walnut, corn etc. Vegetable oils consist basically of triglycerides with different substitution patterns whose main differences are the degree and the form of unsaturation of the acyl groups and their length. Despite of these differences, the IR spectra of vegetable oils show a great similarity (Fig. 3). The discrimination is possible based on the position of band of the C-H stretching of the *cis*-double bond above 3000 cm^{-1}. The oil composition affects the exact position of this band which for vegetable oils rich in polyunsaturated fatty acids such as linseed oil, is about 3010 cm^{-1}. In oils with higher content of monounsaturated fatty acids, such as olive and almond oil, the band appears about 3005 cm^{-1}. The ratio of the absorbance of the bands responsible for the C-H stretching of the *cis*-double bonds and the asymmetric C-H stretching the methylene bonds at 2925 cm^{-1} could also be used for differentiation.

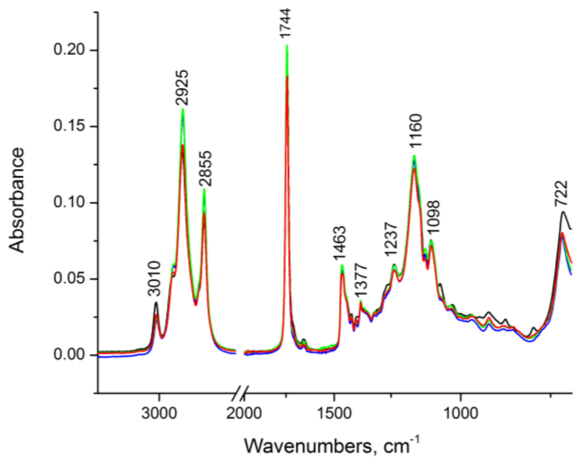

Fig. 3. FTIR-ATR spectra of linseed (black line), walnut (red line), sunflower (blue line) and corn oils (green line).

The interpretation of the spectra of art and archaeological samples were carried out by comparing the spectra of the reference materials. This allows identification of the materials of interest in actual samples and establishing their age. When it was impossible to use "automatic search" for analysing the vibrational spectra from the available electronic spectral database (since this method is only reliable for pure samples and the investigated materials usually are complex mixture of different substances), it was more appropriate to apply an analytical approach, namely: "peak by peak" comparison of the spectrum of the sample with the characteristic bands in the spectrum of reference material taking into account aging, atmospheric and degradation process, as well as applying of the fundamental analytical approach in IR spectral analysis. This method is slower but gives much better results and usually all peaks of the samples could be identified. As an illustration the spectrum of a red sample from the Thracian tomb wall paintings at Alexandrovo, Bulgaria (fourth century BC), is given in Fig.4, together with spectra of $CaCO_3$ and red ochre standards. It is obvious that this archaeological sample contains both materials $CaCO_3$ (characteristic bands at 2512, 1797, 1427, 876 and 712 cm^{-1}) and red ochre (characteristic bands at 3698, 3621, 3427, 1092, 1032, 1009, 913, 799, 778, 538 and 472 cm^{-1}).

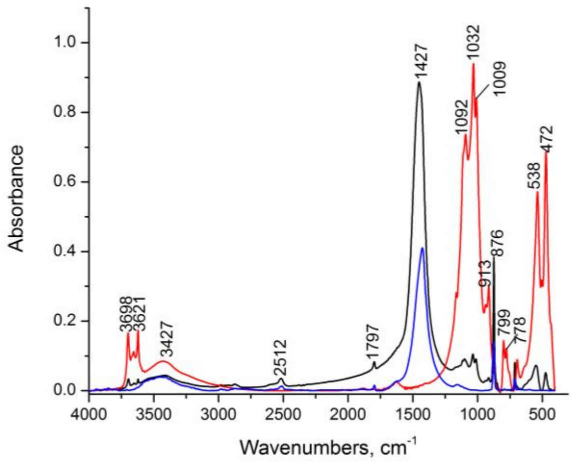

Fig. 4. FTIR spectra (KBr pellet) of Alexandrovo Thracian tomb wall paintings red sample (black line); standard $CaCO_3$ (blue line) and standard red ochre (red line).

Thanks to the high sensitivity for organic compounds, FTIR spectroscopy is indispensable when studying organic materials used in artworks and archaeological sites. However, since usually the analysed sample is a complex matrix of several materials, FTIR spectrum often includes collective information for the primer, pigment and/or binder, etc. This leads to complications when identifying individual components due to overlapping of spectral bands and relative signal intensity. As an example, the spectra of archaeological sample (decoration with white incrustation paste) from Deneva Mogila (dated in the early or in the late Chalcolithic period), located south-east from the village of Salmanovo, Bulgaria are presented (Fig. 5). The predominant compound in the studied archaeological sample is $CaCO_3$. The binder was extracted with distilled water. After water evaporation white medium was obtain. The exact composition of the binder is under investigation. According to historical information and the FTIR spectrum of water-extracted mass (aggregation) (Fig. 5, red line) the closest presumable binder compound is gum from a plant origin (such as Gum Arabic or Cherry gum).

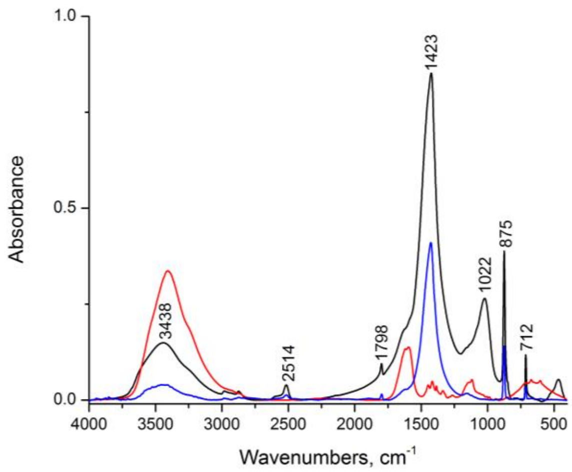

Fig. 5. FTIR spectra (KBr pellet) of Devina Mogila white sample (black line); reference $CaCO_3$ (blue line) and binder in Devina Mogila sample (red line).

CONCLUSION

The necessity and usefulness of FTIR database of reference art and archaeological materials have been demonstrated using various examples. Taking into account the collected spectroscopic, art, archaeological and historical information, it is possible to gain appropriate and complete artefact information.

The currently available FTIR database of reference art and archaeological materials needs to be constantly updated. Also fluorescence spectroscopic analysis, additional information and materials (modern art materials, conservation products, mixtures, etc.) will be included. The provision of a much wider and more comprehensive database of standards would facilitate more accurate study and description of art and archaeological materials. Moreover, the data on newly studied cultural heritage objects will be included in order to create artefacts' database which will be useful in investigation of other art and archaeological objects. This will be of great benefit to the cultural heritage preservation science and society in Bulgaria and worldwide.

REFERENCES

1. I. Kuleff, Archaeometry, Sv. Kliment Ohridski, Sofia, 2012.
2. H. G. M. Edwards, J. M. Chalmers, Raman Spectroscopy in Archaeology and Art History, Royal Society of Chemistry, Cambridge, 2005.
3. G. Bitoss, R. Giorgi, M. Mauro, B. Salvadori, L. Dei, *Appl. Spectros. Rev.*, **40**, 187 (2005).
4. M. R. Derrick, D. Stulik, J. M. Landry, Infrared Spectroscopy in Conservation Science, The Getty Conservation Institute Los Angeles, 1999.
5. C. Maruţoiu, I. Bratu, A. Trifa, M. Botiş, V. C. Maruţoiu, *Int. J. Conserv. Sci.*, **2**, 29 (2011).
6. J. Cuní, P. Cuní, B. Eisen, R. Savizky, J. Bové, *Anal. Methods*, **4**, 659 (2012).
7. M. L. V. de Ágredos Pascual, M. T. D. Carbó, A. D. Carbó, *J.Cult. Herit.*, **12**, 140 (2011).
8. D. Kovala-Demertzi, L. Papathanasis, R. Mazzeo, M. A. Demertzis, E. A. Varella, S. Prati, *J. Cult. Herit.*, **13**, 107 (2012).
9. I. C. A. Sandu, S. Bracci, I. Sandu, M. Lobefaro, *Microsc. Res. Techniq.*, **72**, 755 (2009).
10. I. C. A. Sandu, C. Luca, I. Sandu, V. Vasilache, M. Hayashi, *Rev. Chem. (Bucuresti)*, **59**, 384 (2008).
11. A. Baciu, Z. Moldovan, I. Bratu, O.F. Măruţoiu, I. Kacsó, I. Glăjar, A. Hernanz, C. Măruţoiu, *Curr. Anal. Chem.*, **6**, 53 (2010).
12. D. Barilaro, G. Barone, V. Crupi, D. Majolino, P. Mazzoleni, G. Tigano, V. Venuti, *Vib. Spectrosc.*, **48**, 269 (2008).
13. S. Legnaioli, F. A. Garcia, A. Andreotti, E. Bramanti, D. D. Pace, S. Formola, G. Lorenzetti, M. Martini, L. Pardini, E. Ribechini, E. Sibilia, R. Spiniello, V. Palleschi, *Spectrochim. Acta A*, **100**, 144 (2013).
14. J. Baeten, K. Romanus, P. Degryse, W. De Clercq, H. Poelman, K. Verbeke, A. Luypaerts, M. Walton, P. Jacobs, D. De Vos, M. Waelkens, *Microchem. J.*, **95**, 227 (2010).
15. W. Luo, T. Li, C. Wang, F. Huang, *J. Archaeol. Sci.*, **39**, 1227 (2012).
16. D. Cauzzi, G. Chiavari, S. Montalbani, D. Melucci, D. Cam, H. Ling, *J. Cult. Herit.*, **14**, 70 (2013).
17. A. Sarmiento, M. Pérez-Alonso, M. Olivares, K. Castro, I. Martínez-Arkarazo, L. A. Fernández, J. M. Madariaga, *Anal. Bioanal. Chem.*, **399**, 3601 (2011).
18. C. Montagner, M. Bacci, S. Bracci, R. Freeman, M. Picollo, *Spectrochim. Acta A*, **79**, 1669 (2011).
19. http://www.irug.org
20. http://www.ut.ee/katsekoda/IR_Spectra/index1.htm
21. H. G. M. Edwards, D. W. Farwell, E. M. Newton, F. R. P. Miium, *Analyst*, **124**, 1323 (1999).
22. H. Kühn, *Stud. Conserv.*, **2**, 71 (1960).

СЪЗДАВАНЕ НА СПЕКТРАЛНА БАЗА ДАННИ ОТ РЕФЕРЕНТНИ ХУДОЖЕСТВЕНИ И АРХЕОЛОГИЧЕСКИ МАТЕРИАЛИ

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(Резюме)

ИЧ спектроскопията е надеждна аналитична техника за изследване както на органични, така и на неорганични материали. Тя намира широко приложение при анализа на художествени и археологически обекти. Спецификата и сложността на подобни анализи изисква наличието на обширна база данни на референтни художествени и археологически материали. Настоящата работа представя създаването на спектрална ИЧ база данни на такива материали. Базата данни съдържа набор от абсорбционни и отражателни (ATR) спектри, както и информация за голям брой пигменти, багрила, лепила, масла, смоли, гуми, и други свързватели, градивни материали, пълнители и т.н. Материалният състав на различни старинни художествени и археологически обекти беше определен с помощта на създадената спектрална база данни.