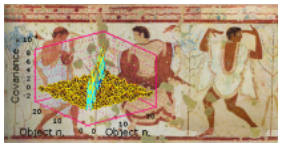

Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Historic Paper Documents as a Preliminary Step for Chemometrical Analysis

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Abstract

The evolution of papermaking from XII century, in Europe, was characterized by continuous changes of fibrous and non-fibrous materials as cellulose, wood pulp, sizing agents, fillers and coatings. In this study, the composition of many ancient paper documents is analysed by means of non-destructive Fourier Transform Infrared Spectroscopy (FTIR) in order to identify the main components of paper and to evaluate the presence of other compounds. The substances that cannot be detected by FTIR analysis are also underlined. The goal of this work is to set up an FTIR database for diagnostic purposes and to identify optimal spectral ranges useful for chemometric analyses.

Introduction

Owing to the variety of their components, conservation and restoration of ancient paper documents often require a preliminary analysis of their composition. To this end the FTIR analysis appear very promising particularly in Attenuated Total Reflectance (ATR) mode. Unfortunately an exhaustive database of IR of ancient papers is not available yet, making it difficult to identify their components. Another difficulty arises from the overlapping of several FTIR bands, that requires some data processing with sophisticated mathematical methods (deconvolution[1], best-fit[2], multivariate analysis [3]). It follows that several components can be identified while others cannot be detected. We present here some examples of FTIR spectra, selected from our database, taking roughly into account the historical development of papermaking.

Materials & Methods

Old paper samples were selected from the last years in our laboratories, while the reference standards were commercially available or appositely prepared.

A Perkin-Elmer Spectrum One FTIR, equipped with the Universal ATR Sampling Accessory (ZnSe cell), was used to obtain 4 cm^{-1} resolution spectra in the 550 - 4000 cm^{-1} region, scanned 10 times (Absorbance vs. wavenumbers mode) at room temperature and humidity. The FTIR data shown in the figures were shifted onto the vertical axis to permit convenient comparisons.

Results

1100-1300 A.D. samples. Rag paper sized with starch can be detected through the characteristic absorption band at 999 cm^{-1}, in the fingerprint region of cellulose (Fig 1b).

1400-1700 A.D. samples. Rag paper sized with gelatine shows the typical amide I and II bands at about 1640 and 1550 cm^{-1} (Fig 1c) while the presence of alum cannot be detected by FTIR.

1800-1960 (*ca.*) A.D. samples. In the XIX century paper was made principally by mechanical wood pulp and sized with rosin and alum. While rosin and alum escape the FTIR analysis, wood pulp is characterized (Fig 1d) by the lignin absorption at about 1730 (oxidized groups), 1590 (generally attributed to carboxylates), 1505 (lignin marker), 1237 (broad absorbance due to C-O of syringyl or guaiacyl ring) and 808 cm^{-1} (typical of hemicelluloses). The 1237 cm^{-1} absorption band allows the identification of hard and softwood pulp[4], while the height of lignin band at about 1505

cm^{-1} generally decrease with ageing. The removal of lignin by the Kraft process eliminates all these features but the 808 cm^{-1} band still allows the identification of wood pulp.

1960- today A.D. In these years the acid rosin-alum sizing has been substituted by the alkaline sizes alkylketene dimers (AKD) and alkenylsuccinic anhydrides (ASA) with $CaCO_3$ as filler. Both AKD and ASA cannot be easily be detected while calcium carbonate shows strong absorption bands at about 1415 and 874 cm^{-1} (Fig 1e). Owing to modern papermaking technology these paper materials may show strong differences in their composition between the *recto* and *verso* sides.

Coated paper. In the XIX and XX centuries several method of surface coating have been adopted, characterized by inorganic materials and polymeric binders. Although the FTIR technique is not specific for inorganic fillers, some can be detected through their infrared absorbance. Clay materials (Fig 2b) are characterized by the small doublet at 3690 and 3620 cm^{-1} together with other sharp peaks at 1000 and 910 cm^{-1}, while talc can be detected only with the matrix algorithm[2]. The features of $CaCO_3$ have been already depicted while gypsum ($CaSO_4*2H_2O$) shows (Fig 2c) a typical wavy pattern in the OH region (3700-3000 cm^{-1}) together with a small but sharp peak at 1620 cm-1 and an increase of the cellulose band at 1110 cm^{-1}. Infusorial earth (diatomite) and TiO_2 generally escape the FTIR analysis. Most of the organic binders can be identified in FTIR-ATR mode which probes mainly the surface of paper. Waxes as calcium stearate (Fig 2d) show a typical doublet at 1577 and 1541 cm^{-1}.

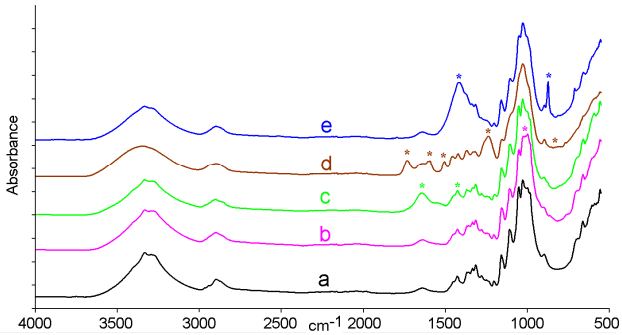

Fig 1; FTIR spectra (Absorbance vs. wavenumbers) of (a) cellulose, (b) starch- and (c) gelatin-sized papers; (d) wood pulp and (e) AKD-sized paper

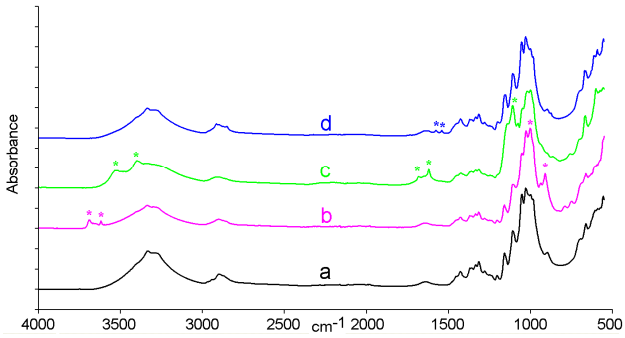

Fig 2; FTIR spectra (Absorbance vs. wavenumbers) of (a) cellulose, (b) clay-, (c) gypsum- and (d) calcium stearate-coated papers

Conclusions

FTIR-ATR analysis allows a rough classification of paper materials by examining the infrared bands not masked by cellulosic components. Although FTIR data processing (deconvolution and matrix based methods) allows a deeper insight, some inorganic and organic compounds require other techniques, such as XRD, SEM and pyrolysis chromatography. Once obtained, these data can be usefully subjected to multivariate analysis and chemometric methods for a better classification of ancient paper materials.

References

1) P. Calvini, A. Gorassini, FTIR-deconvolution spectra of paper documents, Restaurator, ISSN 0034-5806, 23(1) (2002), 48-66

2) P. Calvini, S. Vassallo, Computer-assisted infrared analysis of heterogeneous works of art, E-Preservation Science, ISSN: 1854-3928, 4, (2007), 13-17

3) S. Kokot, B. Czarnik-Matusewicz, Y. Ozaki, Two-dimensional correlation spectroscopy and principal component analysis studies of temperature-dependent IR spectra of cotton–cellulose, Biopolymers, 67(6), (2002), 456-469

4) K. K. Pandey, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, J. Appl. Polym. Sci., 71(12), (1999), 1969-1975