



Application of Micro-Raman and FT - IR Spectroscopy in Forensic Analysis of Questioned Documents

Florin Mihai UDRI TIOIU¹, Andrei A. BUNACIU², Hassan Y. ABOUL-ENEIN³, I. Gh.
TANASE¹

¹*Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest,
92-96 Sos. Panduri, Bucharest - 5, 050663, Romania.*

²*SCIENT - Research Center for Instrumental Analysis, (S.C. CROMATEC_PLUS S.R.L.),
18 Sos. Cotroceni, Bucharest - 6, 060114, ROMANIA*

³*Pharmaceutical and Medicinal Chemistry Department, Pharmaceutical and Drug Industries Research
Division, Dokki, Cairo 12311, Egypt*

Received:23.09.2011 Accepted: 16.10.2011

ABSTRACT

The majority of questioned documents to be examined consist of handwritten, typed or printed information on paper, and therefore, a sizeable part of the document examiner's work should be the examination of the paper itself. There are two types of paper examination, destructive and non-destructive. The purpose of the non-destructive examination should be to find out as much as possible about the paper characteristics, which will enable the examiner to make a decision about its authenticity, or relationship with other documents, without affecting the document for any other type of examinations to follow. All Raman and infrared analysis is non-destructive. Raman and infrared spectroscopy are two complementary spectroscopic techniques that can produce fast and efficient analysis of paper of questioned documents. In this study the use of FTIR and Raman spectroscopy to differentiate paper samples was investigated.

Keywords: *Forensic analysis, questioned documents, Raman spectroscopy and infrared spectroscopy.*

1. INTRODUCTION

The evolution of papermaking from 12th century, in Europe, was characterized by continuous changes of fibrous and non-fibrous materials as cellulose, wood pulp, sizing agents, fillers and coatings. Over the years different fillers surface coatings or chemical additives have been added during the paper making process to improve the quality of the product. Other changes in the manufacturing processes have occurred for economic or environmental reasons. These innovations and modifications can establish the earliest date or period a particular sheet of paper was manufactured [1-4].

Many North American paper manufacturers stopped producing acidic paper in favour of alkaline or neutral process papers during the late 1980s and early 1990s. A simple pH test can indicate if a questioned document was produced before its purported date. This finding can be corroborated if certain chemicals that were introduced after the date on the document are present in the paper. For examples, when mills converted their operations to an alkaline process, many also began using calcium carbonate as a substitute for titanium dioxide in order to improve the brightness and opacity of papers. Caution should be exercised when interpreting such evidence and the paper manufacturer should be

consulted to confirm when the observed processes and material were introduced [5-8].

Infrared spectroscopy has proved an essential tool for studying paper structure and pulp chemistry [9]. Owing to the variety of their components of 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. Identification by infrared spectroscopy is accomplished by either assigning chemical groups to the peaks in a spectrum or inferring the chemical formula of the sample, or by comparing the spectrum to those of known compounds and making identification by the best match [10].

One of the researches has been focusing on some connection between the chemical composition of the papers obtained by Fourier transform infrared (FTIR) spectroscopy and the nature of the fillers, determined by energy dispersion X-ray fluorescence (EDXRF) spectroscopy. Doncea et al. [11] described the application of FTIR and EDXRF in the forensic analysis of some historical papers from books of the 19th and 20th centuries, from private collections. These analytical results allowed a first approximation of technological paper composition and of the age determination of the samples.

Raman spectroscopy is one such technique that provides fundamental knowledge on a molecular level and does not require chemical treatment of the sample (contrary to the case, for example, in fluorescence and electron microscopy). The technique is applicable to a variety of substances, but analytes of great forensic interest such as some natural and synthetic dyes found in textiles, inks, and paints display an excessive fluorescent background, which limits Raman efficiency in most situations, leading to poor analytical results [12-14].

Nevertheless, although the specificity of Raman spectroscopy is very high, its sensitivity is somewhat poor. Considering that only a small number of the incident laser photons are inelastically scattered, the detection of analytes present in very low concentrations is limited. To overcome this problem, special Raman signal-enhancing techniques can be applied. The two most prominent approaches are the resonance Raman effect and the surface-enhanced Raman scattering (SERS). Resonance Raman and SERS are only two of many special techniques in the field of Raman spectroscopy. Nonetheless, these two techniques open the possibility of investigating low-concentration samples. Moreover, resonance Raman and SERS spectra provide additional important information about the investigated system [15-18].

In studies of wood and pulp fibers, Raman spectroscopy has become an important analytical technique because of the important technical developments with respect to both new instrumentation (especially instruments that successfully limit sample fluorescence) and new interpretive advances that have taken place within the past two decades. Such progress has made the macro- and micro level Raman investigations of wood and fibers much more valuable. For instance, in the area of micro investigations, chemical imaging of fiber cell

walls has become a reality and images of cellulose and lignin distributions in the plant cell wall have provided useful information on the compositional and organizational characteristics of woody tissues [19].

In this study, the composition of several paper documents is analysed by means of non-destructive Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy in order to identify the main components of paper and to evaluate the presence of other compounds. The most different features that could be measured by these techniques help us to do a primary discrimination between different sheets of paper of questioned document.

2. EXPERIMENTAL

Apparatus: FTIR micro-analysis was performed on a Nicolet 6700 infrared spectrometer coupled with a Nicolet Continuum Microscope (Thermo Electron Corporation, UK). The spectrometer has a KBr beam splitter and an EverGlo IR source. The microscope has a mercury cadmium telluride (MCT) detector refrigerated with liquid nitrogen and an attenuated total reflectance (ATR) objective of germanium. The FTIR spectra were recorded with the nominal resolution of 4 cm⁻¹ using ATR technique. Spectra were recorded over the range 650 ó 4000 cm⁻¹, five times for each sample and subsequently averaged. Each spectrum is the average of 64 individual scans.

The experimental spectra were mathematically evaluated using OMNIC (Thermo Nicolet Corp., UK).

Raman micro-analysis was performed on a DXR Raman microscope (Thermo Electron Corporation) equipped with the 780 nm laser. The Raman spectra were recorded with the spectral resolution of 5 cm⁻¹. Spectra were recorded over the range 30 ó 3500 cm⁻¹, five times for each sample and subsequently averaged. Each spectrum is the average of 10 individual scans.

Procedures: In order to realize an analytical characterization of papers, using IR spectroscopy, microscopic attenuated total reflectance (μ ATR) with a germanium internal reflection element (IRE). Attenuated total reflectance is applied to samples where the composition of the surface needs to be measured. This is especially useful when the sample is either too thick or cannot be destroyed, separated or manipulated and it is applied to soft samples, which can achieve good contact with the crystal of the ATR objective.

In order to carry out an analytical characterization of papers, using Raman spectroscopy, the samples were treated with colloidal silver (Merck, nanograde) and then analysed using Surface Enhanced Resonance Raman Scattering technique.

Materials: The paper chosen for analysis was the most commonly used office document paper, i.e., white, A4 (210/ 297 mm), 80 grams per square meter. Six different brands of paper:

- Paper 1 ó WINGS, office paper;
- Paper 2 ó XEROX, business paper;
- Paper 3 ó RTC, office paper;

- Paper 4 6 LUMISTAR, laser paper;
- Paper 5 6 ZWECKFORM, ink-jet paper;
- Paper 6 6 AUGUSTA PAPIER, office paper.

3. RESULTS AND DISCUSSION

Firstly, FTIR and Raman spectra of each paper sample were recorded from both sides, to exclude side-effect, described elsewhere. The side-differences are well observable in FTIR spectra, in the region of 3450 cm⁻¹

(O6H bond) and 110061000 cm⁻¹ (C6O bond). Characteristic is particularly the absorption around 1000 cm⁻¹. Only the spectra recorded from the same side were used for the evaluation of spectral changes in different paper samples.

Figure. 1-6 shows an example of the IR spectra that were obtained for papers.

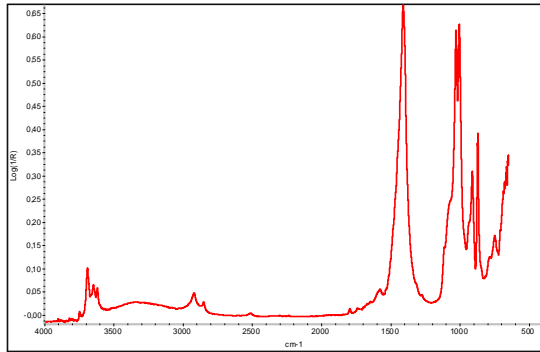


Figure 1 - IR spectra, Paper 1

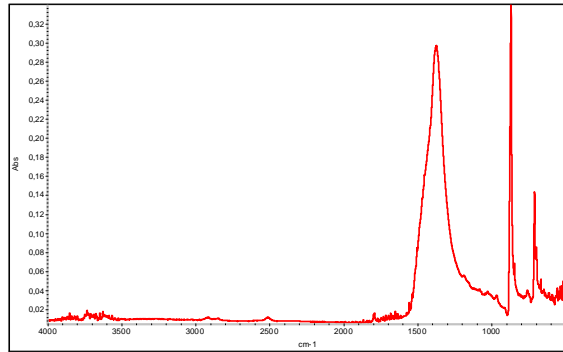


Figure 2 - IR spectra, Paper 2

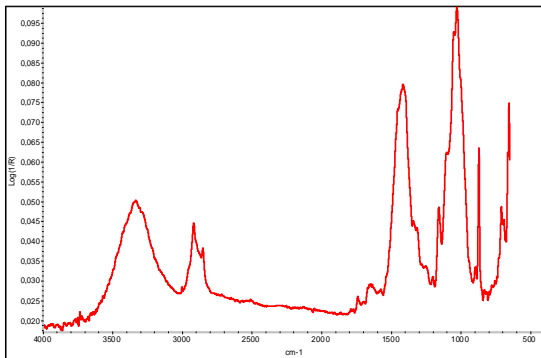


Figure 3 - IR spectra, Paper 3

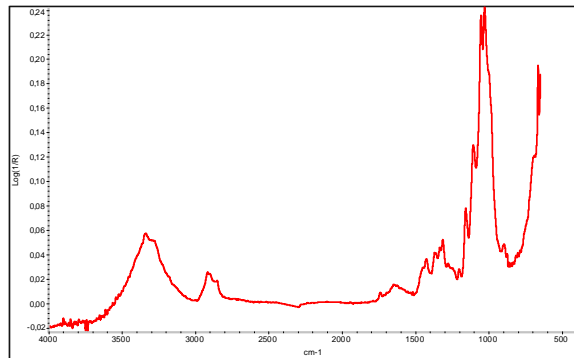


Figure 4 - IR spectra, Paper 4

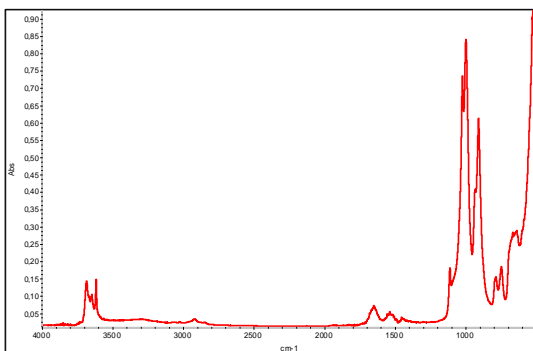


Figure 5 - IR spectra, Paper 5

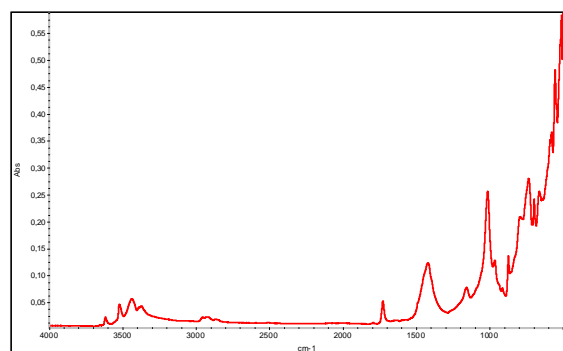


Figure 6 - IR spectra, Paper 6

These IR spectra are due to two main components: cellulose, which is the polymeric matrix which constitutes paper and inorganic filler added to confer good physical/mechanical properties.

The peaks at 2920 cm⁻¹ (CH₂ stretch), 1420 cm⁻¹ (CH₂ bending), 1372 cm⁻¹ (the last two generally used for the sample crystallinity determination and monitoring), 1160 and 1103 cm⁻¹ (C6O stretching and C6C

stretching) are the characteristic peaks of cellulose-containing sample. Band at 1510 cm⁻¹ originates from phenyls ring vibrations of lignins present in samples.

For paper 1, inorganic filler is kaolin in mixture with carbonate (Figure. 1). Kaolin's presence in the sample can be manifested by two spectral bands, at 3687 and 3620 cm⁻¹, Kaolin has also two strong bands in the region 11006900 cm⁻¹ (1025 and 1001 cm⁻¹). Calcium

carbonate produces a band at about 1410 cm^{-1} and two peaks at 871 and 712 cm^{-1} . These correspond to the asymmetric $\text{C}=\text{O}$ stretching mode, to the symmetric $\text{C}=\text{O}$ stretching mode and to the O-C-O bending (in-plane deformation) modes, respectively, of calcite, one of the polymorphs of CaCO_3 .

For paper 2 and 3, inorganic filler is calcium carbonate with band at 1380 cm^{-1} and two peaks at 870 and 710 cm^{-1} (Figure. 2 and 3). Because the papers contain the same filler we try to discriminate paper 2 and 3 with Raman spectroscopy.

For paper 4, inorganic filler is calcium sulfate with band at 1150 and 670 cm^{-1} (Figure. 4).

For paper 5, inorganic filler is only kaolin but it is different from paper 1 who contains both kaolin and calcium carbonate (Figure. 5).

For paper 6, inorganic filler is alumina trihydrate (Figure. 6), with two bands due to O-H vibrations at 3430 cm^{-1} (stretching vibrations) and 1015 cm^{-1} (bending vibrations).

Figures 7-12 show an example of the Raman spectra that were obtained for the tested papers. First, there are regions of the spectrum of wood where cellulose and the hemicelluloses do not contribute and the only features are due to lignin. For example in the 1600 cm^{-1} region only aromatic ring stretching vibrations and lignin's C=C and C=O stretching modes are observed. However, there are other regions of the Raman spectrum where all the components are represented and the interpretation is somewhat complex.

Cellulose has specific bands at 2897 , 1378 , 1183 and 434 cm^{-1} .

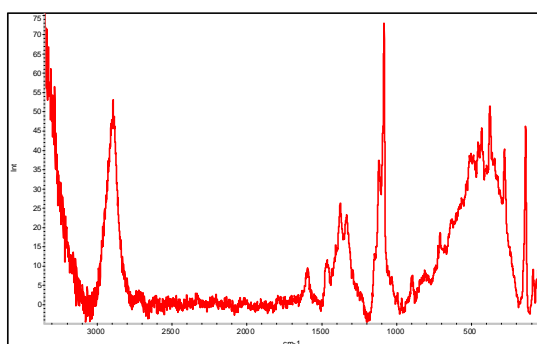


Figure 7 ó Raman spectra, Paper 1

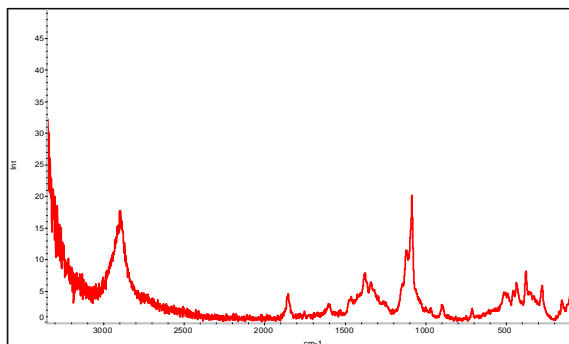


Figure 8 ó Raman spectra, Paper 2

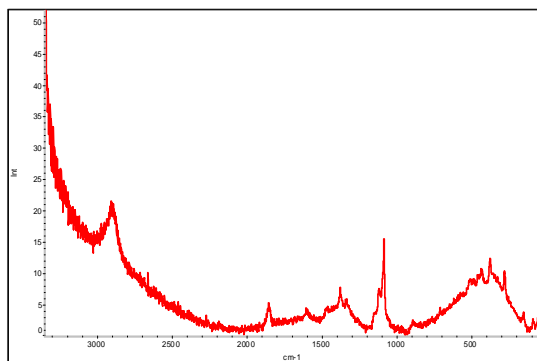


Figure 9 ó Raman spectra, Paper 3

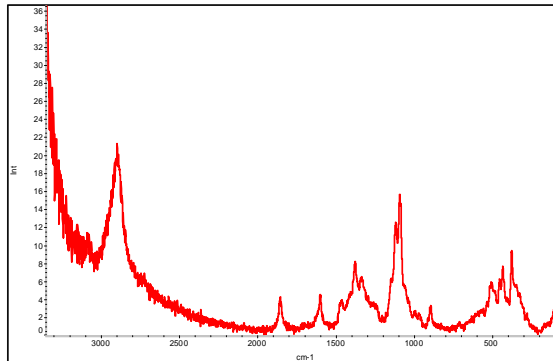


Figure 10 ó Raman spectra, Paper 4

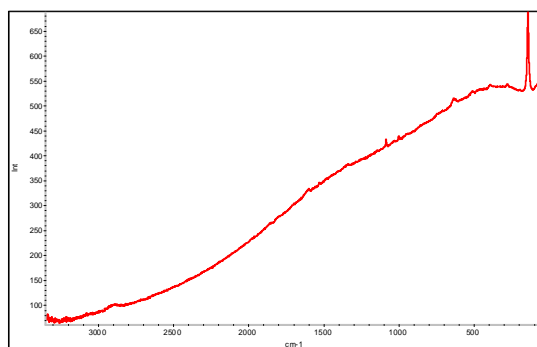


Figure 11 ó Raman spectra, Paper 5

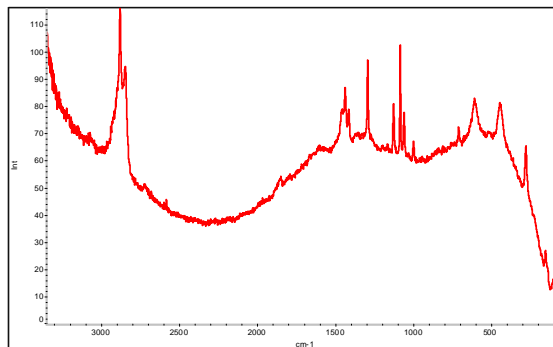


Figure 12 ó Raman spectra, Paper 6

Figure 7 shows the Raman spectra for paper 1. Kaolin has a band at 140 cm⁻¹. For calcium carbonate there are three major Raman bands in spectra at 1086 cm⁻¹, 712 cm⁻¹ and 282 cm⁻¹. The most intense band at 1086 cm⁻¹ band is assigned to the symmetric stretching vibration of carbonate group. Also, the band at 712 cm⁻¹ is the bending vibration the carbonate. The 282 cm⁻¹ is the rotatory lattice vibration of the CaCO₃ crystal.

Figure 8 and 9 show the Raman spectra for paper 2 and paper 3, which are not discriminated by FTIR spectroscopy. We observed in both spectra bands that are specific to calcium carbonate (1085, 712 and 281 cm⁻¹). Also we observed some differences at 901 cm⁻¹ and 160 cm⁻¹ due to, probably, different clay present in the paper 2 in comparison with paper 3.

Figure 10 shows the Raman spectra for paper 4. Calcium sulphate has specific bands at 1135, 978 and 454 cm⁻¹.

Figure 11 shows a great fluorescence for paper 5. This fluorescence masks out the weaker kaolin Raman bands shown in the spectrum with the expanded ordinate scale. Although the full-scale spectrum in Figure. 11 shows a band at 142 cm⁻¹, which is due to the trace TiO₂ from the kaolin.

Figure 12 shows the specific bands of alumina trihydrate at 1295 and 612 cm⁻¹ and it is specific for paper 6.

4. CONCLUSIONS

Paper analysis by infrared spectroscopy is complicated by a number of factors that are not generally a problem with visible range spectroscopy. Among these are cellulose interference and surface inhomogeneities. FTIR-ATR analysis allows a rough classification of paper materials by examining the infrared bands not masked by cellulosic components. However, infrared absorbance spectra are not definitive and therefore Raman spectroscopy can provide complementary information.

Raman and FTIR both offer non-destructive, complementary information. FTIR provides greater sensitivity and is not impeded by fluorescence of the sample. Raman often provides a weak signal and may be masked by sample fluorescence. The Raman effect may be enhanced by a factor up to 14 orders of magnitude if the molecules of the samples are attached to or within a few Angstroms of metal particles (SERS or Surface Enhanced Raman Spectroscopy).

REFERENCES

[1] Calvini P, Gorassini A., FTIR - deconvolution spectra of paper documents, *Restaurator*, 23 : 48-66 (2002).
 [2] Calvini P., Vassallo S., Computer-assisted infrared analysis of heterogeneous work of art, *E-Preservation Science*, 4 : 13-17 (2007).
 [3] Biermann CJ., Handbook of Pulp and Papermaking, *Academic Press.*, New York, 2nd Edition, 40-42 (1996).

[4] Conners TE.; Banerjee S., Surface Analysis of Paper, *CRC Press*, New York, 25-32 (1995).
 [5] Jixing P., Ten Kinds of Modified Paper of Ancient China: A Summary, *Institute of Paper Historians Information*, 17 : 151-155(1983).
 [6] Baker M., von Endt D, Hopwood W., Erhardt D. FTIR-microspectrometry: A Powerful Conservation Analysis Tool, American Institute for Conservation of Historic and Artistic Works, *The Sixteenth Annual Meeting*, New Orleans, LA, June 1-5, 1-13, (1988).
 [7] Tsang, J.-S., and R. H. Cunningham, "Some Improvements in the Study of Cross-Sections," *The American Institute for Conservation of Historic and Artistic Works, the Seventeenth Annual Meeting*, Cincinnati OH, May 31-June 4, 20-21(1989).
 [8] Pandey KK, A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy, *J. Appl. Polym. Sci.*, 71 : 1969-1975 (1999).
 [9] T nase I.Gh., Techniques and methods in spectrometric analysis, *Ed. Ars Docendi Bucharest*, 125-127 (2001).
 [10] Causin V, Marega C, Marigo A., Casamassima R, Peluso G, Ripani L., Forensic differentiation of paper by X-ray diffraction and infrared spectroscopy, *Forensic Science International* 197 : 70674 (2010).
 [11] Doncea SM, Ion RM, Fierascui RC, Bacalum E, Bunaciu AA., Aboul-Enein H Y., Spectral methods for historical paper analysis: composition and age approximation, *Instrumentation Science & Technology*; 38: 96-106 (2010).
 [12] Schmitt M, Popp J. Raman Spectroscopy at the Beginning of the Twenty-First Century, *J. Raman Spectrosc.*; 37: 20628 (2006).
 [13] Ferraro JR, Nakamoto K, Ferraro J. Introductory Raman Spectroscopy, 2nd Edition; *Academic Press*, New York, (2003).
 [14] Long DA, Raman Spectroscopy; *McGraw Hill*, New York, Chapter 7(1977).
 [15] Champion, A.; Kambhampati, P., Surface-Enhanced Raman Scattering, *Chem. Soc. Rev.*; 27 : 2416250 (1998).
 [16] Moskovits, M., Surface-Enhanced Raman Spectroscopy: A Brief Retrospective, *J. Raman Spectrosc.* 36: 4856496 (2005).
 [17] Lewis IR, Edwards HG. Handbook of Raman Spectroscopy, *Marcel Dekker Inc*, New York, 116 40 (2002).
 [18] Vikman, K, Sipi K. Applicability of FTIR and Raman spectroscopic methods to the study of paper-ink interactions in digital prints, *Journal of Imaging Science and Technology*, 47: 139-141 (2003).
 [19] Agarwal UP, Reiner RS; Ralph SA. Dependable Cellulose I Crystallinity Determination using Near-IR FT-Raman, *CELL Division*, Abstract 95, 233rd ACS National Meeting; Chicago, IL, March 25-29, (2007).