Complex analytical investigations of old wax-sealed Romanian documents

NICOLAE-MIHAIL STIRBESCU[1], RODICA-MARIANA ION[2,3*], ADRIAN RADU[2], SOFIA TEODORESCU[1], IOAN ALIN BUCURICA[1], RALUCA-MARIA STIRBESCU[1], MARIA GEBA[4], IOANA DANIELA DULAMA[1]

[1] Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 13 Sinaia Alley, 130004 Targoviste, Romania

[2] The National Institute for Research & Development in Chemistry and Petrochemistry – ICECHIM, 202 Splaiul Independenţei, 060021 Bucharest, Romania.

[3] Valahia University of Targoviste, Faculty of Faculty of Materials Engineering and Mechanics, 13 Aleea Sinaia, 130004 Targoviste, Romania

[4] ”Moldova” National Complex of Museums, 1 “Stefan cel Mare si Sfant” Square, 700028 Iasi, Romania

**Corresponding author: rodica_ion2000@yahoo.co.uk.*

Waxes as a component of seals, are recognized in our history as adhesives, for surface coating purposes, modeling or casting materials and also in conservation practice. The waxes with mineral, vegetable and animal origin should be connected to modern methods of analysis, due to their complex composition: long chain hydrocarbons, acids, alcohols, esters. They support many mechanical damages in library and archive collections: cracking, pieces lost by an excessive handling of documents. In this paper the compositional analyses of some wax seals from 1852 have been achieved by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) - for molecular structural information of wax materials, by gas chromatography / mass spectrometry (GC/MS) - for evidence of some compounds with up to 27 carbon atoms, most of them resulted from degraded wax seal, and by optical microscopy and scanning electron microscopy – for visualization of the damaging effect of the wax seal. All these analytical investigations have been achieved for wax seals detached from the paper samples recovered from two disaffected pulp and paper factories - Letea and Busteni (Romania) belonging to Romanian industrial patrimony.

Keywords: waxes, FTIR, Raman spectroscopy, GC-MS, microscopy, old paper.

Waxes as translucent solid substances that melt easily, have various source: mineral, vegetable and animal. In general, they contain long chain hydrocarbons, acids, alcohols and esters or mixtures of these [1]. Waxes are known as adhesives, component of seals and as materials in conservation practice [2, 3]. Wax is a mixture of rosin, shellac, turpentine and mineral coloring agents which, because of their plastic properties when heated is used to seal letters, packages, the sealing of the vials [4]. Mountain wax or lignite wax, which is a mineral waxes obtained from brown coal, is a mixture of esters derived from lignite bituminous by solvent extraction. The untreated these products are hard and dark; after refining can be white. Mountain white waxes are used as insulating material, paper impregnation and the manufacture of special paints. Much of the archive seal's damage was caused due to brittleness over time, and excessive handling of documents, which provoke the materials to become opaque and friable [5, 6].

In order to identify the degradation sources, is important to use different concerted analytical techniques. In our research the analyses have been made by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, used to identify molecular structural information of waxes and for qualitative characterization of decomposition processes. FTIR can provide molecular structural information of wax materials. The paint cross sections were analyzed using Raman spectroscopy in order to identify pigments and additives. The composition of degraded wax seals was determined using gas chromatography/mass spectrometry (GC/MS). Some compounds with up to 27 carbon atoms are present in beeswax itself. Also, by different microscopic techniques, the degradation aspects are identified and the eventually impurities and damaging compounds generated during the degradation in time. The work outlined in this paper shows that small amounts of waxes and greases have been encountered in old paper conservation.

Materials and methods

Materials

Some paper samples with wax seals from two disaffected pulp and paper factories - Letea and Busteni (Romania) belonging to industrial patrimony, have been studied in this paper. The aspect of the wax seal is shown in Fig. 1.

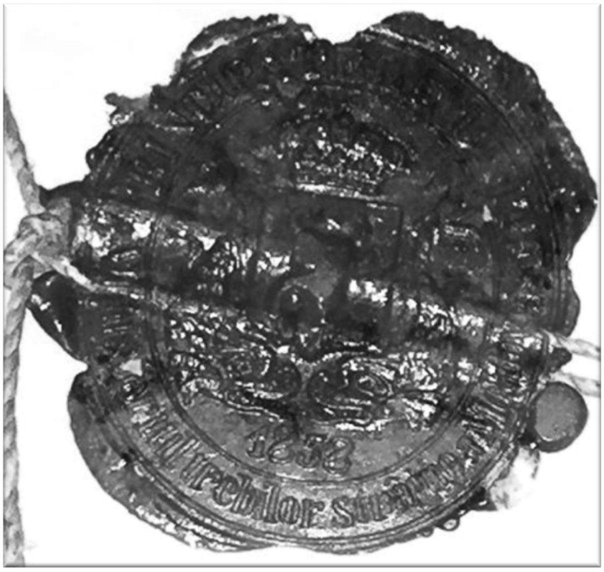


Figure 1. The aspect of the wax seal from 1852.

Stearin (Stearic acid 50, CAS Number 67701-03-5, tested according to European Pharmacopeia) and paraffin (CAS Number 8002-74-2, European Pharmacopoeia Reference Standard) reference materials were purchase from Sigma Aldrich Co. (Steinheim, Germany).

Bee wax sample was collected by beekeeper from apiaries and then, the samples were driven to laboratory and stored until the analysis at -20 °C. The wax sample was picked up after removing honey. The spruce and juniper resins were collected from the Bucegi Natural Park (Dambovita County), away from the road or other pollution sources.

Analytical investigations

The FTIR spectra have been recorded by Attenuated Total Reflectance (ATR) with a Perkin Elmer Spectrum GX spectrometer (PerkinElmer Ltd., UK), in the following conditions:

range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}. Also, some samples have been investigated using Vertex 80 spectrometer (Bruker), with the following parameters: range 8000-350 cm^{-1} and resolution 0.2 cm^{-1}.

Raman spectra have been obtained with a portable dual wavelength Raman analyzer IR - XANTUS 2 – RIGAKU, with the following parameters: Dual wavelength source 1064 nm & 785 nm, spectral range (cm^{-1}) 200 - 4000, spectral resolution (cm^{-1}) 7 - 10, LASER output power (mW) 400 - 490, LASER output power (mW) 30 - 490, cooled detectors: CCD and InGaAs. Spectra were acquired using 10 s of signal collection time and five accumulations.

Gas-chromatography with mass spectrometry (GC/MS) has been achieved with GC/MS Triple Quad Agilent Technology (for compounds identification we based on NIST Library). GC method: *Column DB-WAX* (L = 30m, D = 250 µm, d = 0.25 µm; oven program: 50 °C for 5 minutes, then 4 °C/min to 150 °C, then 10 °C/min to 320 °C; carrier gas: He, flow=1 ml/min; injector temperature: 250 °C; injection volume: 0.5 µl); *MS Method* QQQ Collision Cell: quench flow gas (He) = 2.2 ml/min; collision flow gas (N_2) = 1.5 ml/min; type of source: EI; electron energy: 70 eV; source temperature: 230 °C; auxiliary temperature 2: 280 °C; scan segment: 40-400; type of chromatogram: TIC.

The **SU-70 Field Emission - Scanning Electron Microscope (FE-SEM)** was used to produce enlarged images of a variety of specimens, achieving magnifications of over 800000X providing high resolution imaging in a digital format. The accelerating voltage (V_{acc}) of SU-70 may vary from 0.1 kV to 30 kV and the resolution is 1 nm (at V_{acc} = 15 kV).

For examination in transmitted light, it has been used a **direct microscope Primo Star**. It offers the possibility of examining evidence in transmitted light at a magnification of between 4X and 100X. Optional equipment can be attached to a digital video camera (Axiocam 105) which, through microscope software allows acquisition of information in real time, both static and moving and conversion from 2D to 3D.

Results and discussion

The FTIR spectra achieved for the investigated samples put into evidence specific groups of the wax composition [7], as follows:

- The bands around 3500 cm^{-1} denote the presence of OH groups, more intense in the juniper sample. The C - H (methyl and methylene) stretching vibrations of saturated hydrocarbons are seen below 3000 cm^{-1}, and for the region of 2800-3200 cm^{-1}, especially.
- The bands from the region 2929-1456 cm^{-1} are attributed to CH_3 and CH_2 vibrations of hydrocarbonated structures, etheric and alcoholic groups. The same groups could be identified by the bands from 1242 to 1178 cm^{-1}, most probably for the acid resins.
- The main difference is the presence of a peak in region of 1700 cm^{-1} which corresponds to a carbonyl (C=O) stretching vibration from free carboxylic acid and from esters.
- The observed differences must be related to primarily the flavonoids and diterpenes and diterpene and triterpene compositions of the resins related to their sources.

In Fig. 2 it is presented the FTIR spectra of the unknown sample (wax seal compared with paraffin, stearin, and different resins collected from spruce, juniper and bee waxes). In the unknown sample, in the infrared spectrum can be detected bee wax and also the juniper resin.

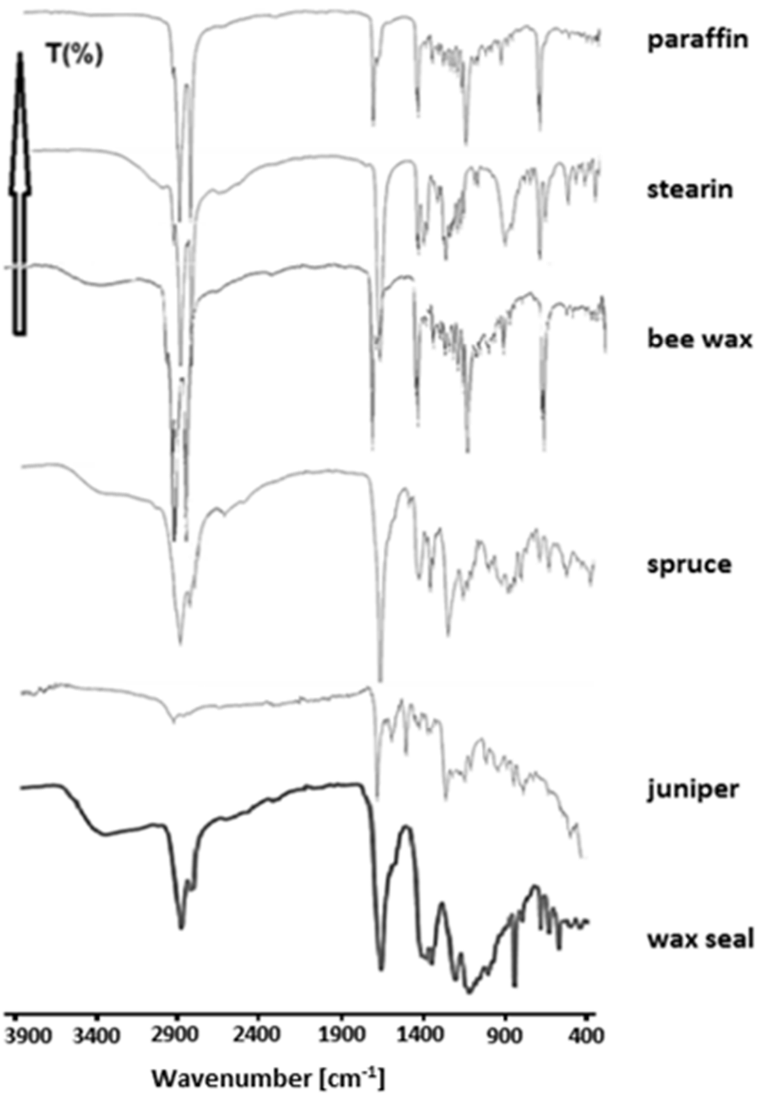


Figure 2. FTIR spectra of wax seal and the individual resin components

But, these compounds are easier to be identified by Raman spectroscopy (Fig. 3). Some extra peaks that don't belong to bee wax could be identified, belonging either to cellulose fiber from paper or to other ingredients present in wax seal, as paraffin, stearin and bee wax. As a partial conclusion, the wax seal contains in majority spruce resin, but also different ratios of juniper, bee wax, paraffin, stearin [7-9].

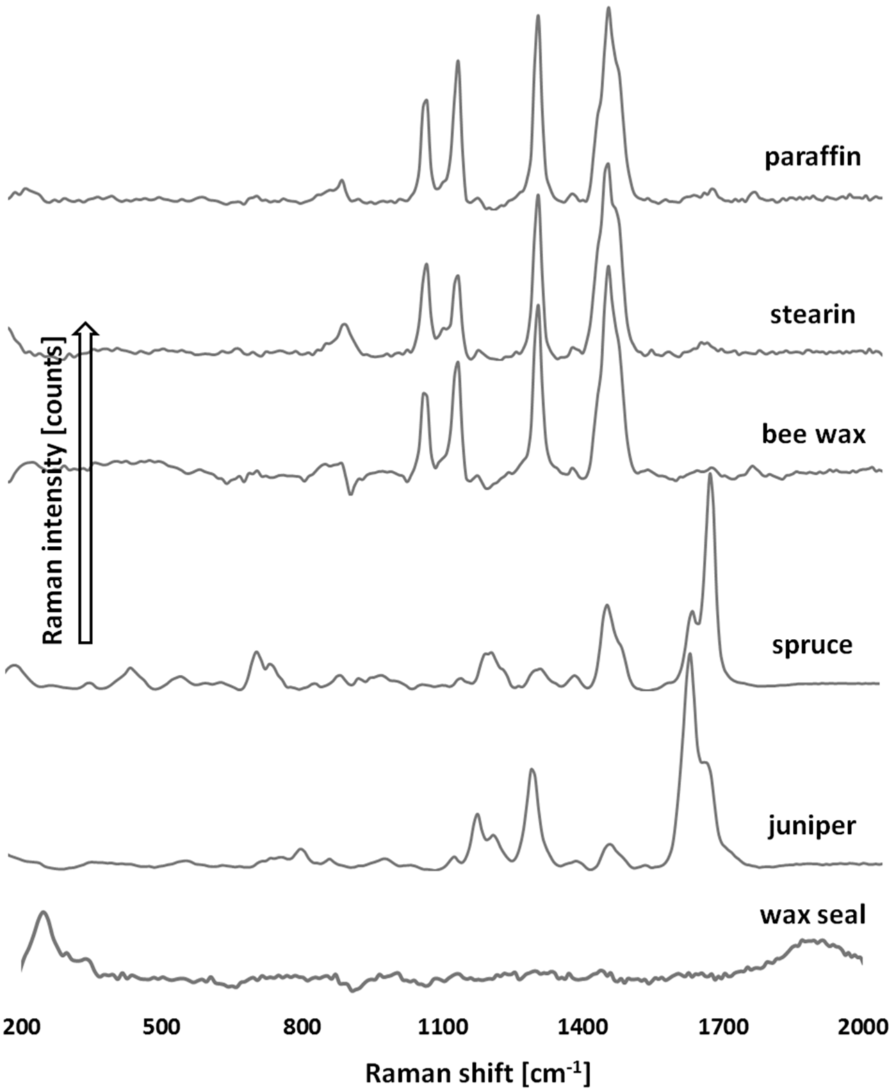
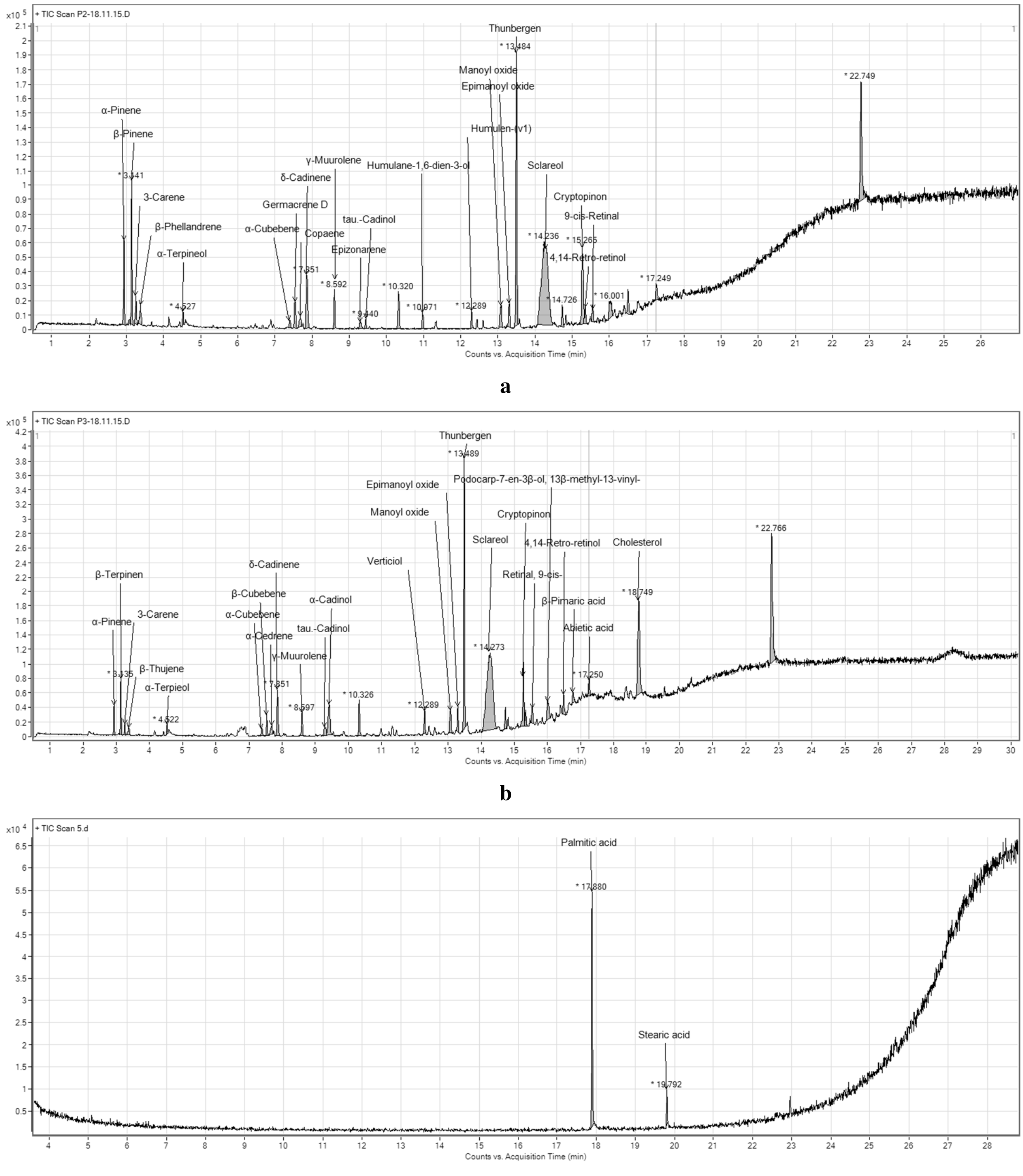


Figure 3. Raman spectra of wax seal and its individual components

The black colored seals is a sign of deteriorated due to the presence of the pigments added, which contain metal ions (e.g. lead, copper, iron, mercury). Several hypotheses for the decomposition and brownish coloration circulate, some based on the formation of black β-HgS or of metallic mercury as a deposit. The degraded wax seal may contain artificial cinnabar (α-HgS) which could be transformed into $HgCl_2$ as an extremely poisoning compound, able to sublimate [10,11]. The concentration of Hg detected in the wax seal is around % (determined by EDXRF and reported elsewhere [3]).

In order to identify the presence of bee wax, a chromatographic technique has been used in this paper. Fig. 4 shows the comparative chromatograms obtained by GC-MS for a beeswax sample. Normal alkanes with odd carbon number (from C23 to C33, with C27 as the main alkane) and saturated free fatty acids (from C22 to C27) are identified in our cases. The fast GC analysis of the slightly more polar constituents of pine resin (Fig. 4 a, b) can be performed in less than 15 minutes with a good resolution for these kinds of diterpenoid isomers. Fig. 4c shows the GC/FID analysis of the sample, revealing the presence of common saturated acids. The results are similar with those reported by literature's publications [12].



a

b

c

Figure 4. GC-MS chromatogram of the wax seal extracts

This most important and widely used analytical tool for such studies is microscopy, which provides exceptional depth of the samples. By optical microscopy is possible a direct observation of the black degradation parts, most probably due to Hg presence (Fig. 5). The morphological structure of samples can be investigated through the images collected by SEM which allows the visualization of the fractures due to damages supported in time (Fig. 6).

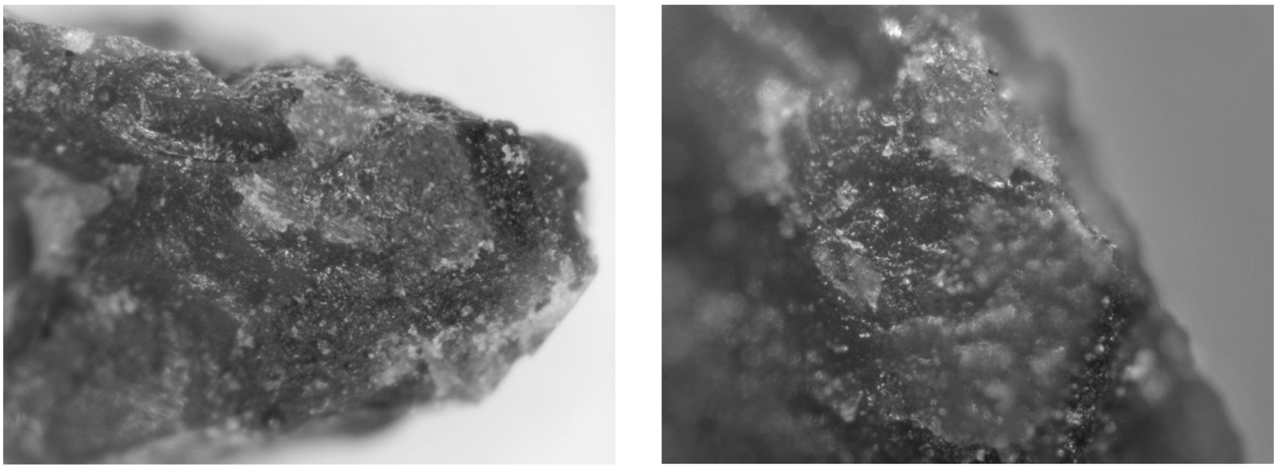


Figure 5. Optical Microscopy of the studied wax seal

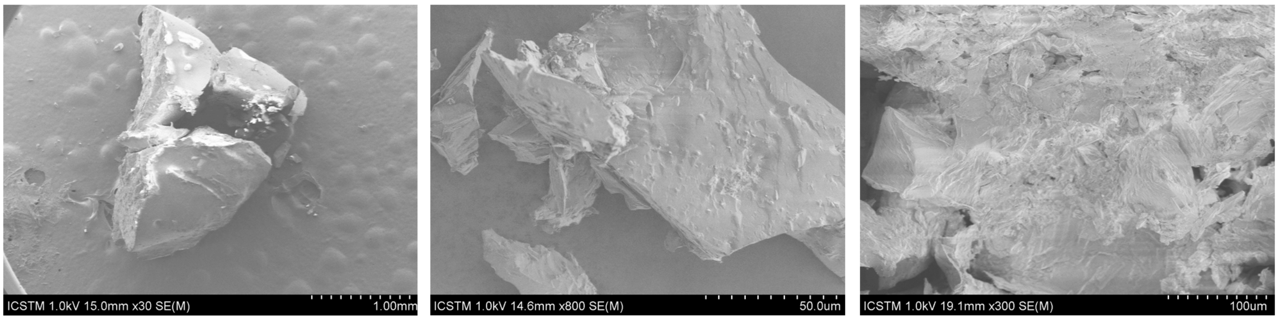


Figure 6. SEM of wax seal revealing the samples fractures

Conclusions

FTIR and Raman provide general characterization of the waxes containing different organic components and serve to identify coniferous resins, bee wax and organic molecular mixtures. These natural products are mixtures of diterpenoids, n-alkanes, long-chain alcohols and fatty acids. By optical microscopy and SEM is possible a direct observation of the black degradation parts, most probably based on Hg and their fractures due to damages supported in time.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI-UEFISCDI, projects number PNII 222/2012, PNII 261/2014 and PN 16.31.02.04.02.

References

1. TOMLINSON, C., Tomlinson's Cyclopaedia of Useful Arts, **II**, Virtue & Co., London, 1866, p. 495.
2. GIEDRAITIENE, B., Synthesis of art and science in conservation: trends and achievements, Proceedings of 9th Baltic States Triennial Restorers Meeting, 2011, p. 243.
3. ION, R.M., FIERASCU, R.C., FIERASCU, I., ION, M.L., TEODORESCU, S., GEBA, M., Spectral and microscopic characterization of manuscripts with wax seal, Proceedings of The 4th Advanced Research in Scientific Areas Advanced Research in Scientific Areas, 2015, p. 178.
4. MILLS, J.S., WHITE, R., The Organic Chemistry of Museum Objects, Butterworth, Boston, 1987, p. 41.
5. MASSCHELEIN-KLEINER, L., Ancient Binding Media, Varnishes and Adhesives, Proceedings of ICCROM, 1995, p. 33.
6. PUREWAL, V.J., An Investigation into the Composition of Botanical Wax Models with a View to Their Conservation, Proceedings of SSCR Conference of Resins, 1995, p.42.
7. ION, R.M., DONCEA, S.M., ION, M.L., Nanomaterials for Chemical and Biological Restoration of Old Books, in New Approaches to Book and Paper Conservation and Restoration, Verlag Berger, Wien/Horn, 2011, p. 389.
8. POLOVKA, M., POLOVKOVA, J., VIZAROVA, K., KIRSCHNEROVA, S., BIELIKOVA, L., VRSKA, M., Vibrational Spectroscopy, 41, 2006, p. 112.
9. GARDINER, D.J., Practical Raman spectroscopy, Springer-Verlag, Berlin, 1989, p. 90.

10. HAVERMANS J., HIJMAN W., VAN RENESSE A., SPORTEL, R., DEKKER, R., The Emission Of Mercury From Mercuric Chloride Treated, Herbariums, Proceedings of 11th International Conference Indoor Air Quality in Heritage and Historic Environments, 2014, p. 38.

11. GETTENS, R.J., FELLER, R.L., CHASE, W.T., Vermilion and Cinnabar, in Artists' Pigments. A Handbook of Their History and Characteristics, **2**, Oxford University Press, 1993, p. 159.

12. TULLOCH, A.P., HOFFMAN, L.L., J. Am. Oil Chem. Soc., 49, 1972, p. 696.