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FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FT-IR) AND X-RAY DIFFRACTOMETRY (XRD) AS METHODS FOR DISCRIMINATING AMBER AND AMBER-LIKE MATERIALS FROM THE ROMANIAN MARKET

Assoc.prof. PhD ANTONELA NEACŞU, Prof. PhD GHEORGHE C. POPESCU
University of Bucharest, Faculty of Geology and Geophysics

ABSTRACT. *Amber and amber-like material are often found our days in the Romanian gemstone exhibitions. Fake amber is more and more difficult to detect, because modern manufactured products made of natural resins and/or polymers are so perfect, that they can produce same esthetic effects of the transparent and colored–like amber pieces. Macroscopically, they can not be separated from amber without a good personal experience or only applying gemological classic tests. So, modern physico-chemical methods, as Fourier transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD) are applied, for discriminating amber and forgeries.*

Key words: *Baltic amber; romanite; copal; rosin; modern resins; Romanian gemstone market; Fourier Transform Infrared spectroscopy; X-ray diffraction; ageing study;*

1. Introduction

In Romania amber is treated as gemstone, including both commercial advantages and the risk of fake industry. Watching the gemstones events, shows and exhibitions organised in Romania especially after the 2000's, obviously raw amber and amber products are highly desirable.

A large number of European amber varities are exposed, both raw amber for the needs of manufacture or for the collectors, and amber objects: necklaces, pendants, pearls, islamic rosaries, earrings and finger rings with silver.

Amber art is installed for good on the Romanian market, most of the objects being jewellery and religious creations. A larger project started in 2010, with the aim of establish the amber varieties and amber-like materials found on the Romanian gems market applying analytical techniques (Fourier Transform Infrared spectroscopy and X-ray diffraction). Gems from the exhibitions organized by the Geological Institute of Romania (GIR) (2011-2013) (Fig. 5, 8), Museum of Mineralogy in Baia Mare (MMBM) (2013) (Fig. 1), Museum of Gold in Brad (MGB) (Fig. 2, 5), from a gift shop from Bucharest (2012) (Fig. 4, 6), and amber gems given by a popular mineralogical magazine (2012) (Fig. 3) were included in this study. In all investigated situations, amber-like material was sold or just exhibited as worldwide genuine amber varieties, e.g., Baltic Countries, Poland, Ukraine, Russia, Romania, Dominican Republic, Italy, Brazil, Myanmar, or as copal from Madagascar and Indonesia.

Some interesting data have already been published, regarding discrimination of amber from substitutes, or the characterization of modified amber due to natural processes or 'gemological' treatments [1], [2].

Other information is referring to the relationship between the environment where resins, subfossil resins and amber have lain during the geological ages and the gemological properties of material, adding to previous studies of Neacşu and Dumitraş [3].

Finally, there is a special concern over ageing studies, which might contribute to a better understanding of degradation mechanisms of amber and amber-like materials used in gemology. The circumstances of ageing experiment show that visible light, atmospheric oxygen and the increase of air temperature give spectroscopic changes after three months (April, May and June 2012) consequently of free external atmospheric exposure of amber and angiosperm resins in the temperate-continental climate of Bucharest, Romania [4].

2. Experimental procedures

Fourier Transform Infrared spectroscopy was performed in the Department of Mineralogy of the Faculty of Geology and Geophysics, University of Bucharest, using JASCO's FT-IR microscope system equipped with FT-IR 4100 spectrometer (DLATGS detector with Peltier temperature regulation, beam splitter substrate material Ge/KBr, resolution 0.9 cm-1, spectral range 7,800 to 350 cm^{-1}, Jasco software), and Irtronμ (IRT-1000) Microscope (objective mirror 8X cassegrain, manual exchange of objective with no alignment required, minimum measurement area 100 μm^2 DLATGS detector, sample observation area 1.2x0.9 mm; independent X and Y variable aperture; ATOS). FT-IR absorbance spectra (FT-IRA) were recorded for this study. Infrared spectra were also recorded in Geological Institute of Romania, using a Bruker Tensor 27 FT-IR spectrometer, using ATR accessory (DTGS detector, KBr beamsplitter, spectral range 7,500 to 370 cm^{-1}, resolution ±1 cm^{-1}, ±2 cm^{-1} OPUS software).

X-ray powder diffraction analyses were performed at the Geological Institute of Romania on a Bruker D8 Advanced

Fig. 1. Baltic amber beads (MMBM)

Fig. 2. Romanite samples (MGB)

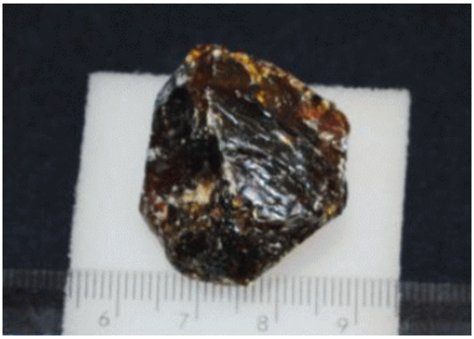

Fig. 3. Commercial “Indonesian copal” identified as rosin (scale in centimeters)

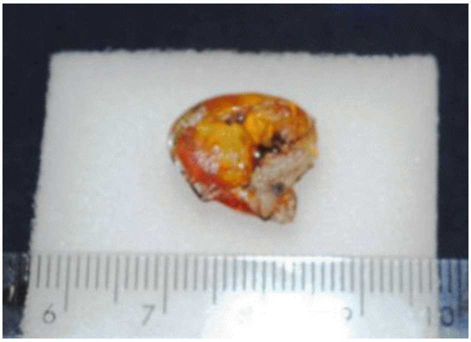

Fig. 4. Commercial amber identified as modern Angiosperm resin (scale in cm)

automated diffractometer equipped with a graphite-diffracted beam monochromator (Cu K radiation, = 1.54056 Å), at an operating voltage of 40 kV and a beam current of 40 mA.

3. Results and discussion

Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD) were employed on very small amounts of amber-like materials found as gemstone, art and religious objects, or different ornamental products, to look if they are natural or synthetic substitutes.

FT-IR absorbance spectra for amber-like samples are very similar to the previously reported by Beck et al. [5], Kucharska and Kwiatkowski [6], Kosmowska-Ceranowicz [7], Banerjee et al. [8], Pakutinskienne et al. [9], Kosmowska-Ceranowicz and & Wagner-Wysiecka [10], allowing the identification of Romanite (RO) and Baltic amber (Fig. 5). Kosmowska-Ceranowicz [7], Guiliano et al.[11], Abduriyim et al.[12] and Schollenbruch [13], give additional information for copal identification (Fig. 8), which is sometimes identified by mistake with amber [2].

Another unexpected surprise is the recent identification of burmite on the Romanian market (Fig. 7), based on spectral analysis of Kosmowska-Ceranowicz [7]. Modern resins are sometimes macroscopically identified as amber; consequently they could be sold as amber. After a comparison of their own spectral database and the atlas of Hummel and Scholl [14], Neacşu et al. [2], could identify Rosaceous resins as commercial ‘amber’ (Fig. 6). Based on the IR characterization of amber-like materials of Yoshihara [15], rosin was identified after it was sold as Indonesian copal together with a popular mineralogical magazine.

There are few interesting regions on the IR spectra considered characteristic for amber in literature, consequently they are investigated for identifying amber and substitutes: near 890 cm^{-1}, 995 ±15 cm^{-1}, 1250-1150 ± 15 cm^{-1}, 1375 ± 5 cm^{-1}, 1450 ± 20cm^{-1}, 1600-1650 cm^{-1}, 1735-1700 cm^{-1}, 2962-2853 ± 10 cm^{-1}, 3048, 3095 and 3100-3700 cm^{-1}. The 3700-3100 cm^{-1} region indicates a decrease of free water proportion to romanite in comparison with Baltic amber.

The fingerprints area of Baltic amber presented the characteristic Baltic ‘shoulder’ (1250-1150 cm^{-1}, -CO-O of succinate) [5, 16] IR analyses demonstrate that romanite has more carboxylic groups than Baltic amber (see the band of 1735-1700 cm^{-1}, >C=O stretching of esters and acids, which increases in intensity to romanite) (Fig. 5).

To distinguish amber from copal, the regions between 1700-800 cm^{-1} and 3100-2800 cm–1 are important (Fig. 8), where the vibrations of various C–O and C–H bonds, also C=C double bonds become visible [13]. Our data show that the band 1650-1600 cm^{-1} related to >C=C< (non-conjugated) is missing at romanite, probably consequently to its geological origin [17]. ‘Modified amber’ (ageing amber due to natural or artificial processes) and ‘modified copal’ (treated) could be identified among commercial amber objects, and described by Neacşu et al. [2], based on the comparison of IR spectral analysis with those of Pastorelli [16], Kosmowska-Ceranowicz and Wagner-Wysiecka [10] and Schollenbruch [13]. Also Dominican amber was identified, by confronting the FT-IRT spectra with those presented by Abduriyim et al. (2009), and Yoshihara et al. [12].

In some cases, the records of amber-like materials exhibit the same XRD pattern as for Baltic amber, with a broad peak centered at 2θ ≈ 150, indicating an amorphous state [15], (Fig. 10). Some crystalline components of material e.g., quartz, or the substitution of organic matter by minerals give rise to diffraction patterns in all spectra (Fig. 9).

These assumptions are confirmed by the microscopic studies of romanite and succinite [1, 3, 18].

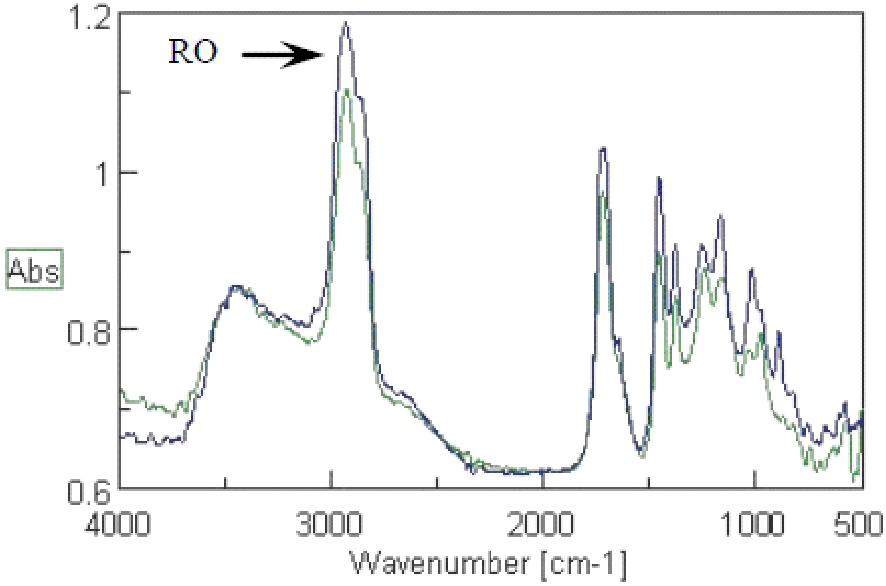

Fig. 5. The comparative FT-IRA spectra of amber identified as romanite (RO) and Baltic amber (GIR, MGB)

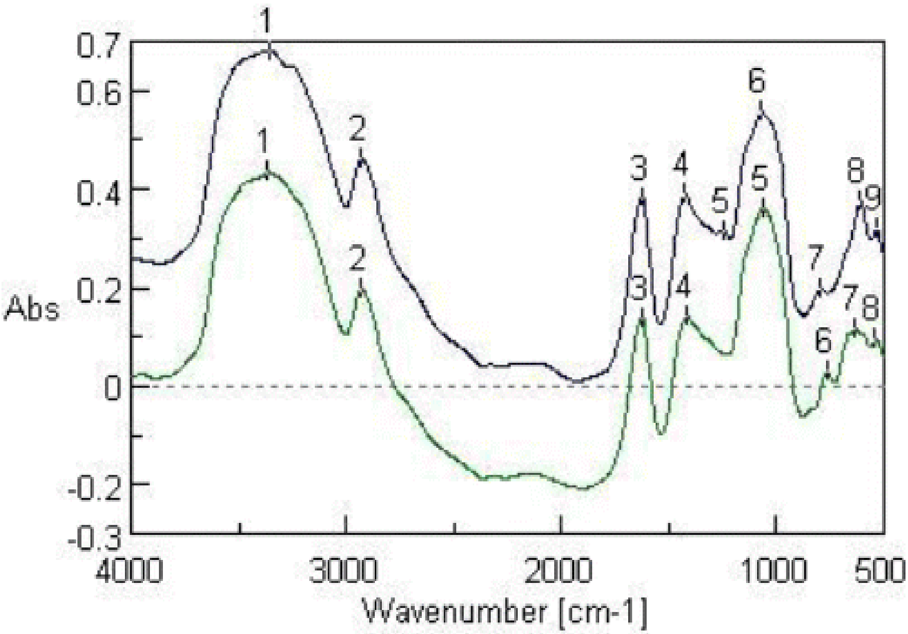

Fig. 6. FT-IRA spectra of commercial 'amber' identified as Rosaceous resins.

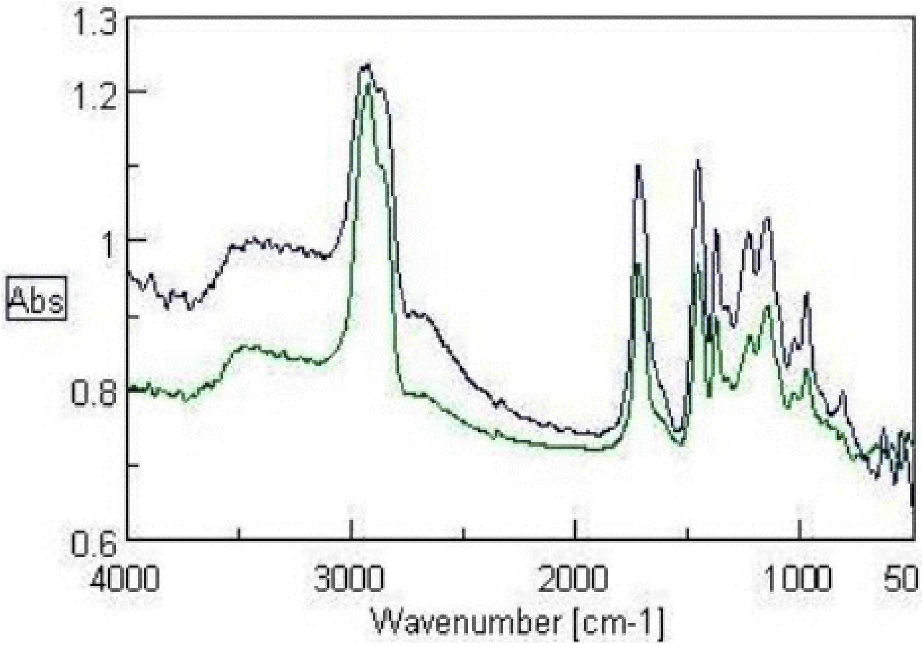

Fig. 7. FT-IRA spectra of amber identified as burmite (GIR)

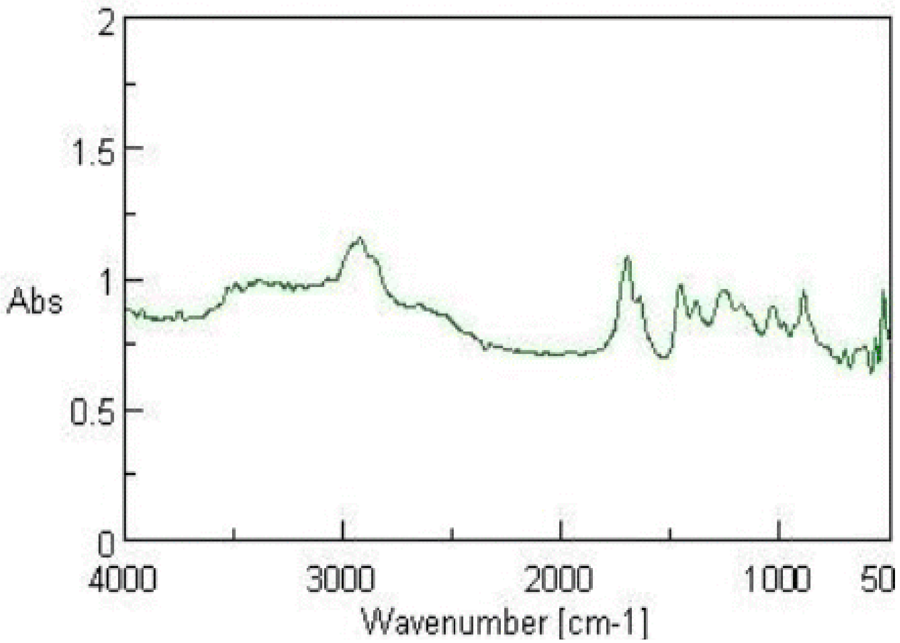

Fig. 8. FT-IRA spectrum of amber identified as Madagascar copal spectrum (Neacşu et al., 2013) (GIR)

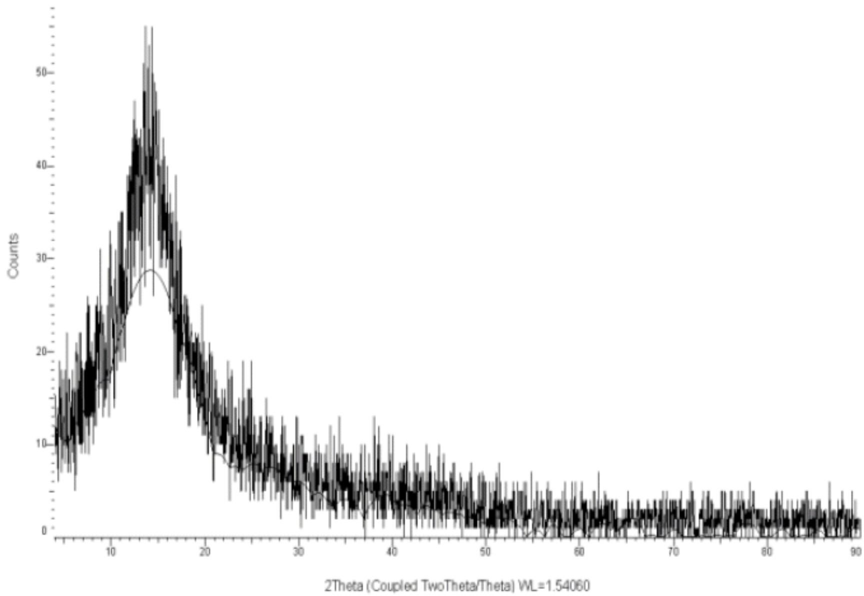

Fig. 9. X-ray diffraction of romanite (Neacşu et al., 2013)

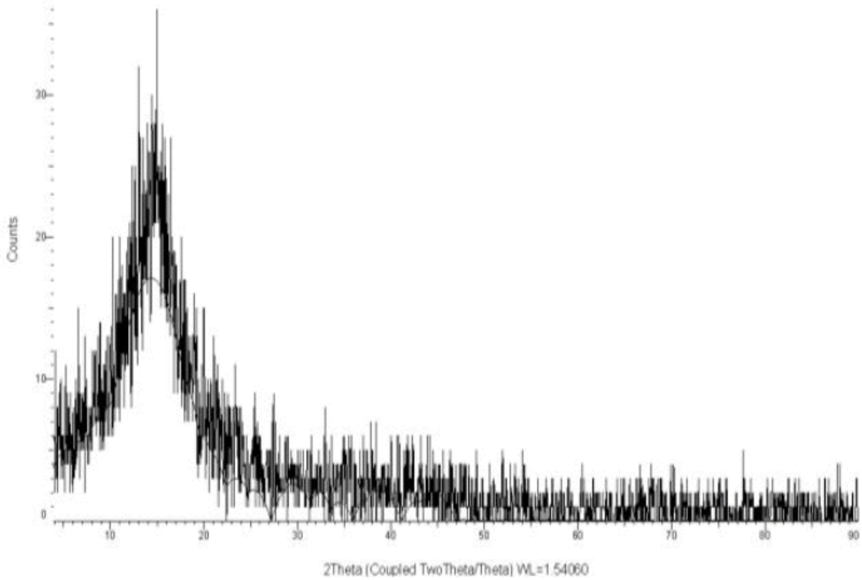

Fig.10. X-ray diffraction of Lithuanian amber (Neacşu et al., 2013)

4. Conclusions

None of the XRD records show any internal organizing tendency. These results contrast with previously published papers, where the XRD records indicate some internal organizing tendency for romanite, confirmed by the already mentioned microscopic studies. So, the possibility of using X-ray diffraction as a diagnostic method for romanite is not sustained for the moment.

All investigated materials presented FT-IR spectra that were compared with the already reported IR characteristic bands of amber and amber-like materials, confirming that this method is an excellent mean to detect fake amber. The IR analyses demonstrate that romanite has more carboxylic groups than Baltic amber, so romanite is strongly oxidized. The loss in C=C groups is an effect of maturation or ageing of amber (Shashoua et al., 2005). In sum, an older supposition that romanite could be 'aged' Baltic amber may be take into consideration.

XRD remains a valuable complementary method, for revealing an internal organizing tendency of material, or minerals trapped inside it.

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