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Identification of treated Baltic amber by FTIR and FT-Raman (a feasibility study)

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Introduction

Baltic amber (succinite) is fossilised plant resin formed more than 40 million years ago (the late Eocene), in northern Europe: Fennoscandia (nowadays the area of the Baltic Sea). The Baltic amber exhibits a richness of varieties, colours and transparency range, which made it a very attractive and sought-after organic gemstone in the world. Advances in technology and increased demand for low-priced, more and more attractive gem materials, contributed to the development of treatment methods that aim to enhance the colour and transparency of gemstones. Amber, similar to some other gem materials, is frequently treated to improve its appearance.

The modification processes of amber consists of dying, coating, and heating. Nowadays the heat treatment, which is the most commonly observed technique in trade, includes clarifying, baking, and decrepitation of amber. Depending on the experimental parameters (temperature and pressure), different results, that affect the structure of the starting material to varying degrees, are obtained.

Materials & methods

Seven specimens of treated (Mod_1,3, ModOx_2 ModOx_4-5) and unmodified (Nat_6-7) Baltic amber (fig. 1) were analysed with macro- and microscopic observations supported by some gemmological tests (luminescence). Further, they were analysed using spectroscopic techniques [1].

Resin		No.	Photo	Weight [g]	Sample characteristics	Modification
Baltic amber	Modified	Mod_1		5,1	Brown (cognac-coloured) transparent amber with discoidal 'sun's sparkles' inclusions	Heated under high pressure (~3-5 MPa) with rapid decrease of temperature in an inert atmosphere
		Mod_Ox_2		0,3	Yellow 'Bee's wax' opaque amber in disc shape	Heated at low temperature (up to 60°C) in the atmospheric air
		Mod_3		0,9	Yellow (honey-coloured) translucent amber in oval-like shape	Heated under higher pressure (~2-3 MPa) in an inert atmosphere then slowly cooled
		Mod_Ox_4		5,6	Pink 'Dragon's Blood' amber in tear-drop shape set in a pendant	Heated under high pressure (~3-5 MPa) with an oxygen, then slowly cooled
		Mod_Ox_5		6,3	Red transparent amber in oval shape set in a pendant	Heated (even up to 210°C) under pressure (~3-5 MPa) with an oxygen and additional substances (manufacturer's secret), then slowly cooled
	Natural	Nat_6		1,0	White (milky) opaque amber with mosaic texture in tear-drop shape	-
		Nat_7		0,7	Orange 'Bees wax' opaque amber in oval cabochon	-

Figure 1. Samples of modified and natural Baltic amber.

The analysis of the 1737, 1703, 1642, 1012 and 993 and 888 cm^{-1} bands on FTIR spectra, as well as the nature of the band group referred to as the 'Baltic shoulder' allows for better identification of the method of interfering with natural Baltic amber [2].

FT-Raman spectroscopic method allows reading the bands invisible when using the FTIR method, e.g. originating from vibrations of stretching bonds in a group (C=C). These are complementary methods which when used simultaneously, give a full picture of the vibrations of functional groups [3].

Results

Macroscopic observations: The modified Baltic amber crumbs show weak Mod_1-4 or none-luminescence ModOx_5, while untreated Baltic amber Nat_6-7 exhibits a strong yellow-green luminescence under UVL light. The smell that the succinite gives off when rubbed, depends also on the nature of the sample. The samples Mod_3-4, which were modified under moderate conditions, and sample Nat_7 (natural weathered amber) show a weak smell characteristic of the pine-tree resins, while those samples modified in higher temperature and pressure conditions (Mod_1,2,5) do not emit any fragrance after rubbing. The sample of untreated Baltic amber with a fresh surface has the relatively strongest smell (Nat_6).

FTIR spectroscopy (fig. 2) The heat modification of succinite is manifested on FTIR spectra by characteristic features:

- The changes of the relative bands' intensities in the range of 1510–1830 cm^{-1}. The maxima of component bands caused by ν(C=O) bond are located at lower wavenumbers (about 1708 cm^{-1}) for modified samples than those in untreated amber found at 1735 cm^{-1}.
- The intensity reduction of 888 cm^{-1} band or its disappearance.
- The slight distortion of the "Baltic shoulder" shape. The maximum at 1260 cm^{-1} becomes less intense in the spectra of succinite modified under an oxygen atmosphere.
- The changes in the bands' proportion in the range of 900–1120 cm^{-1}. The doublet with maxima 1017 cm^{-1} and 975 cm^{-1} is far worse separated for treated than unmodified Baltic amber. It is especially well manifested in spectra of samples modified in the presence of oxygen, where one broad band with a maximum at about 1000 cm^{-1} is recorded.

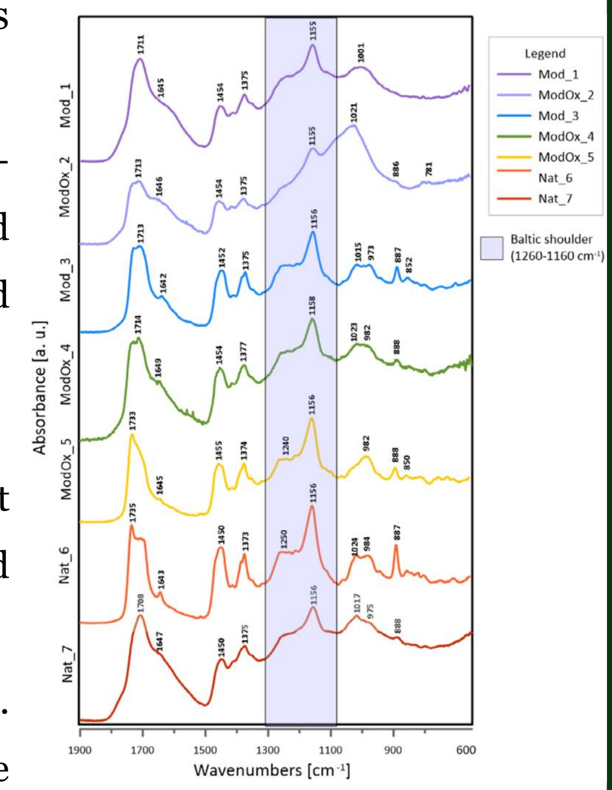

Figure 2. FTIR spectra of modified and natural samples of Baltic amber.

Raman spectroscopy (fig. 3) Some heat modification of Baltic amber noticed on Raman spectra are marked by:

- The change of relative band intensities – modified samples are characterized by the higher relative intensity of high frequency bands (2800–3200 cm^{-1}) of symmetric and asymmetric vibrations of CH and CH groups compared to bands at 1650 cm^{-1} due to C=C. This difference is also visible for bands typical of the same functional groups at the lower Raman shift.
- The change in the relative intensity of the bands assigned to scissoring vibrations of CH and CH groups at 1445 cm^{-1} relative to those originating from C=C and found at 1650 cm^{-1}. It is well documented by higher values of the intensity ratio (I1650/1445) for the modified amber than untreated Baltic amber samples.

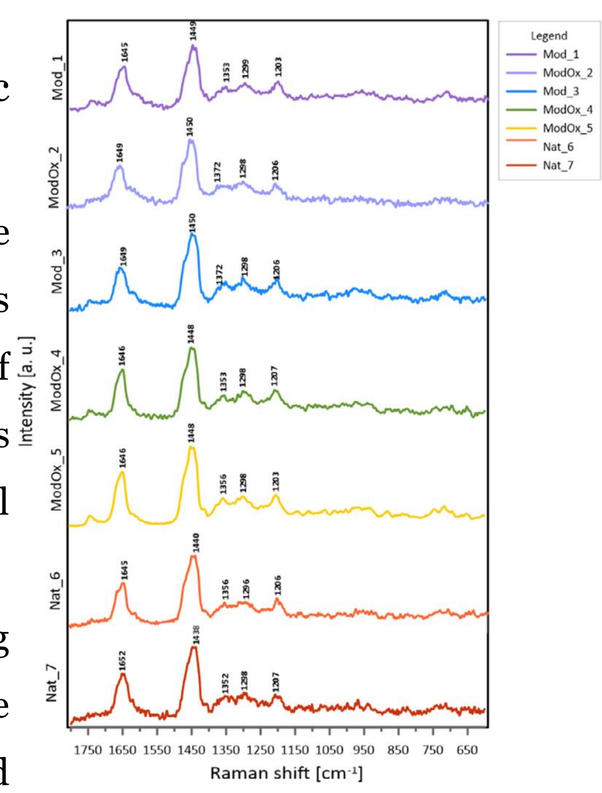

Figure 3. FT-Raman spectra of modified and natural samples of Baltic amber.

Conclusions

- The modifications of fossil resins aimed to change the colour and degree of transparency, also affect their other physical and chemical properties. In the case of the studied samples, some of the amber enhancements are easily recognized even with the naked eye (sample Mod_1 showing characteristic discoidal 'sun sparkles' diagnostic for high-temperature heating followed by the rapid cooling) and others need analytical method to recognize a nature of amber.
- Infrared spectra still provide the best way to evaluate natural samples of Baltic amber and to distinguish spectral features that appear due to the heat modification.
- The FT-Raman remains a complementary technique to FTIR to trace changes caused by heat modification of Baltic amber. RS spectra are much more difficult for interpretation due to the presence of less abundant bands and their lower relative intensities of the bands

References

[1] Drąg, Karolina, Maja Mroczkowska-Szerszeń, Magdalena Dumańska-Słowik, and Grażyna Żukowska. 2022. 'Identification of Treated Baltic Amber by FTIR and FT-Raman – A Feasibility Study'. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 279: 1386–1425
[2] Wagner-Wysiecka, Ewa. 2018. 'Mid-Infrared Spectroscopy for Characterization of Baltic Amber (Succinite)'. Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy 196 (May): 418–31.
[3] Brody, Rachel H, Howell G M Edwards, and A Mark Pollard. 2001. 'A Study of Amber and Copal Samples Using FT-Raman Spectroscopy'. Spectrochimica Acta Part A. Vol. 57