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Characterizing amber and its imitations with dispersive Raman spectroscopy

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Introduction

Amber is a tree resin that has been fossilized over millions of years through polymerization, cross-linking of the long carbon chain organics, and expulsion of volatiles within the resin. Amber has a wide variety of applications, ranging from its traditional use in jewelry, art and craft objects, and folk medicine, to modern applications in skin care products, perfumes, and blood conservation devices. Authentic amber is a highly demanded commodity and its high value has fostered an extensive imitation market that abounds with both natural and synthetic resins. Copal is an example of one of the natural resins that is used as an amber imitation. It is a less mature tree resin product that has not gone through the entire fossilization process and, as a result, it is less expensive than amber.

Distinguishing authentic amber from its imitations is important for scientific, commercial and personal reasons. There are several simple chemical and physical tests that can be used to authenticate amber. These tests include solubility in organic solvents, floating in salt water for testing specific gravity, assessing melting points, and even evaluating hardness using scratch tests. The main limitation of those tests arises from the possible compromise in specimen integrity, which can be prohibitive when dealing with items of artistic, archeological or historical significance. To that end, Raman spectroscopy offers an attractive solution to the identification and characterization of amber, largely due to its non-destructive sample handling.

While FT-Raman spectroscopy, in the near-infrared (1064 nm) region, has been used successfully to analyze amber[1-3] because it minimizes the substantial florescence originating from the amber resin, dispersive Raman spectroscopy has important advantages over FT-Raman. The use of lasers of shorter wavelength (e.g., 780 nm), especially, in Raman microscopy allows for sample analysis on a sub-micrometer scale and results in significantly faster spectral acquisition, because of the high laser power density developed in the small focused laser spots coupled with more effective Raman scattering that is inversely proportional to the 4th power of the laser wavelength[4]. Furthermore, confocal Raman microscopy can provide useful information about the chemical composition of the relict biomaterials and inorganic inclusions[5].

In this note, the spectra of amber and some of its common imitations obtained using a dispersive Raman spectrometer are compared and discussed.

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Experimental

Samples of authentic and altered amber and its common imitations were used in this study, including: 1) Baltic amber from a contemporary bead necklace, 2) a metal- incrusted earring made of, supposedly, a synthetic resin, 3) a pipe bit made of melted and pressed Baltic amber; 4) West African copal, 5) Indonesian copal, 6) a sandarac from Australia, 7) a pine tar, 8) a mastic resin.

Raman spectra were acquired with a Thermo Scientific DXR™ Raman microscope using 780 nm laser excitation and 14 mW of power at sample. The typical exposure time was set to 5 minutes to maximize signal-to-noise ratio. The real-time autofluorescence correction was enabled to minimize fluorescence effects in the spectra. No further smoothing of spectral data was applied.

Results and discussion

Distinguishing amber from its synthetic forgeries by Raman spectroscopy is rather straightforward. Figure 1 shows the "fingerprint" region of the Raman spectra of an authentic Baltic amber and a synthetic resin, as well as a reference spectrum of bisphenol-A. The spectrum of the synthetic resin (Figure 1.2) bears little similarity with that of amber (Figure 1.1), but has features that can be unambiguously attributed to the bisphenol-A, the component of an epoxy resin. Thus, in the "fingerprint" spectral region, amber can be readily distinguished from synthetic plastics due to a significant difference in chemical composition and the identification of the synthetic plastics can be conducted using a search against extensive Raman spectral libraries of polymers.
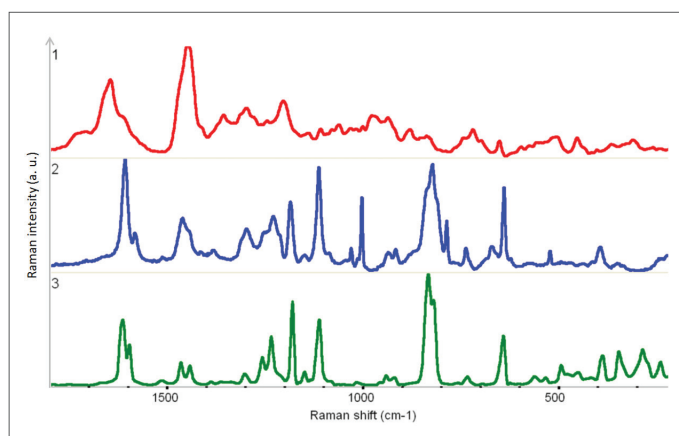

Figure 1. Raman spectra of: (1) authentic Baltic amber from a contemporary bead necklace; (2) synthetic resin from an ear-ring; and (3) bisphenol-A from the Nicolet Standard Collection of Raman Spectra. The spectra are normalized to the most intense spectral bands.

Discrimination between amber and copal is slightly more involved because of their chemical similarities. Figure 2 shows the Raman spectra of amber and two copal samples of different origins. The most conspicuous features in all spectra are the bands at 1646 cm^{-1} and 1450 cm^{-1}, resulting from the exomethylene stretching v(C=C), and the scissoring type deformation δ(CH$_2$) vibration in resin structure, respectively. It
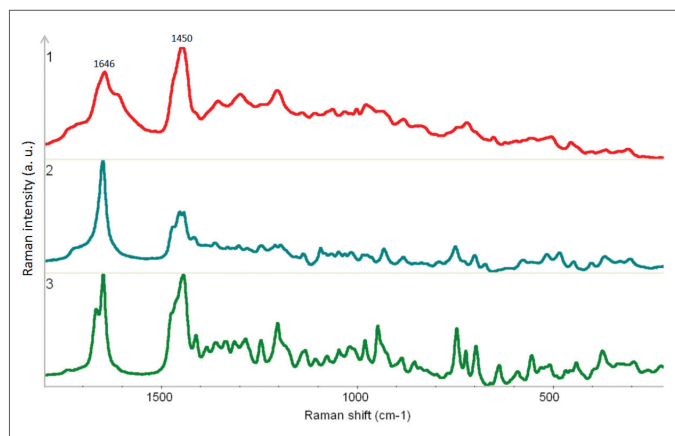

Figure 2. Raman spectra of (1) melted and pressed Baltic amber from a pipe bit; (2) Indonesian copal; and (3) West African copal. The spectra are normalized to the most intense spectral bands.

has been shown [2-4] that the intensity ratio of the bands at 1646 cm^{-1} and 1450 cm^{-1} (I_{1646}/I_{1450}) is a good indicator of the maturity of fossilized resins. In general, the ratio is >1 for immature resins such as copal, and <1 for mature resins such as amber. Our experiment results conform to that criterion. In Figure 2, the peak height ratio I_{1646}/I_{1450} is about 0.8 for amber (1) and 2.5 and 1.1. for copal (2) and (3), respectively. In addition, there are noticeable differences between amber and copal in the spectral region below 1400 cm^{-1}, which is dominated by a series of less intensive peaks, especially, in the 800-500 cm^{-1} range. It was found that thermal and mechanical alteration of the amber leads to noticeable spectral changes in the region of 1800 - 1400 cm^{-1}, as shown in Figure 3.
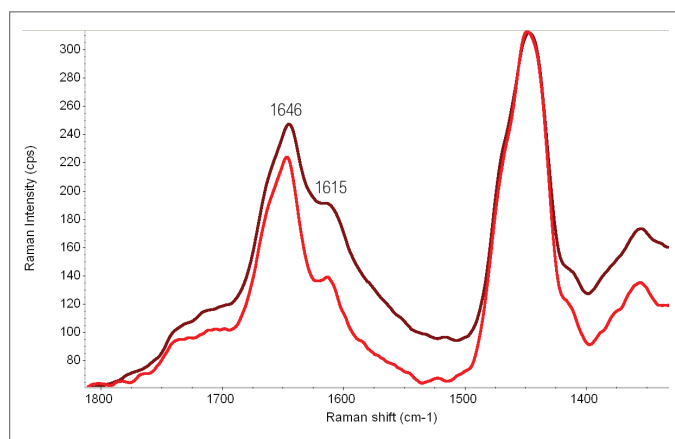

Figure 3. The Raman spectra of Baltic amber from bead necklace (red) and melted and pressed amber from a pipe bit (brown).

The band at 1646 cm^{-1} becomes broader, and the intensity of the shoulder at about 1615 cm^{-1} associated with the stretching of aromatic C=C increases in the spectrum of the processed amber. In [6], these changes have been observed and attributed to the increase of the aromaticity as the result of the thermal impact to the material.

Raman spectroscopy can be used to differentiate amber from other types of natural resins that look similar to amber. Figure 4 shows the Raman spectra of three different resins. In the spectrum of mastic resin (1), the ratio I_{1646}/I_{1450} is <1 indicating
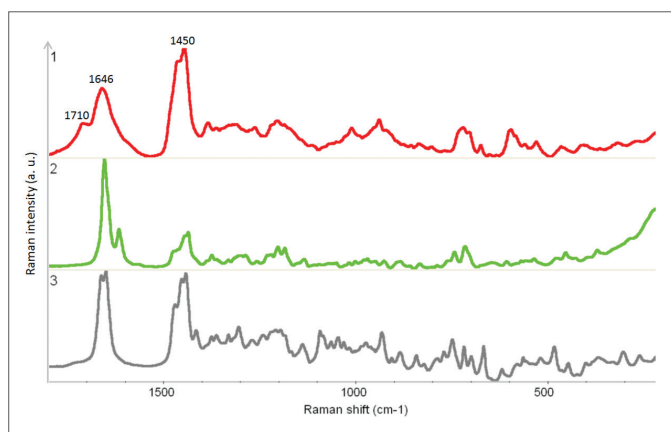
Figure 4. The Raman spectra of: (1) a mastic resin; (2) a pine tar; and (3) a sandarac from Australia. The spectra are normalized to the most intense spectral bands.

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its similarity to amber. However, the band at 1646 cm^{-1} in the spectrum of mastic resin exhibits a prominent shoulder at 1710 cm^{-1} less noticeable for amber (Figure 2.1) that is ascribed to the stretching mode v(C=O). For the pine tar (2) and sandarac from Australia (3), the ratio I_{1646}/I_{1450} is >1 and ≈1, respectively, typical for natural resins. In the spectrum of pine tar (2), there is also a salient side peak at about 1615 cm^{-1}.

All the collected spectra feature high signal-to-noise ratios and sufficient spectral resolution, allowing for the observation of fine spectral details for differentiation purpose.

Conclusions

Dispersive Raman spectroscopy is a practical tool for non-destructive identification and authentication of amber and its imitations made of natural and synthetic resins.

The spectral characteristics of amber are demonstrated to be vastly different from, for example, epoxy resin often used for amber imitation. The fluorescence typical for amber, copal and other natural resins are effectively suppressed by using a 780-nm excitation, or it can be removed with a real-time automated fluorescence correction procedure available in Thermo Scientific™ OMNIC™ software. The use of dispersive Raman instrumentation along with visible lasers enabled shorter sampling times in comparison with FT-Raman, where spectral acquisition times as long as hours are often required[5].

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