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Using Raman spectroscopy of counterfeit amber examinations

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Abstract
Background: Amber is a plant product. Amber is formed by fossilization of original tree resins. Resin is a complex substances produced by plants. Amber has a very rich history and has been used for different purposes. For thousands of years, amber is used as an ingredient in perfumes, as decorative artifacts, as a healing agent in folk medicine, and as jewelry. Due to the higheconomic value of amber, it is made especially easy to fake of the Baltic amber.
In this study we have aimed to investigate the potential of Raman spectroscopy in order to distinguish between the natural and fake amber. Ten different samples known as amber were investigated and selected center at 1300 cm^{-1} of Raman spectrum. Raman spectrums of samples were drawn with Matlab. While seven samples spectra were similar, three samples of them were different. The most characteristic peaks in the Raman spectrum of three samples (numbers of sample are 3, 7, 10) are fingerprint regions and strong features at 1204, 1446 and 1650 cm^{-1}, respectively. The most characteristic peaks in the Raman spectrum of seven samples (numbers of sample are 1, 2, 4, 5, 6, 8, 9) are fingerprint regions and strong features at 776, 846, 998, 1259, 1435 and 1608 cm^{-1}, respectively. Aman spectroscopy provided so quick analysis; non-destructive confirmatory identification and fake amber can be easily distinguished from the real amber. It is important in terms of take precedence against counterfeiting.

Keywords: Amber, Raman spectroscopy, Resin, Counterfeit

1. Introduction

Amber is a plant product. Amber was formed by fossilization of original tree resins and the resins were originated in an Early Cretaceous forest. Resin is a complex substances produced by plants. Amber obtained from similar locations may vary in molecular composition or resins of similar molecular composition can be produced by entirely different plants. The most commonly known type is the type extracted from the Baltic Sea. Amber can be in many different colors; it is most often pale to golden yellow or orange and can be fluorescent [1, 2, 3, 4].

Amber has a very rich history and has been used in different purposes. For thousands of years, amber is used as an ingredient in perfumes, as decorative artifacts, as a healing agent in folk medicine, and as jewelry. As, analgesic effect of succinic acid contained in the resin is believed has an analgesic effect. It is often used in the manufacture of goods which contact with the skin, such as necklace, ring and beads [5, 6].

Due to the high economic value of amber, it is made especially easy to fake of the Baltic amber but this may not contain succinic acid [1]. Fake amber has been produced for at least 600 years, but has no succinic acid content. Fresh resins, synthetic polystyrenes, bakelite, epoxy resins, celluloid, colored glass, plastics, and polyesters all have been used for imitation amber [2]. Great importance is the fact that only a limited number of ambers [7].

General formula of amber is generally known as $C_{10}H_{l6}0$ with variable C:H:O ratios. Amber is difficult to identify due to a polymerized resin with many components. The polymer fraction of the succinic acid is derived from polymers of communic acid, partially copolymerized with communal. Characteristics of amber change to the geological environment [7, 8].

Different several analytical techniques have been applied to identify components of amber such as infrared spectroscopy, ultraviolet-visible spectroscopy, and mass spectrometry [8, 1]. The more common way of applying infrared spectroscopy like a 'fingerprint' region method was shown by spectroscopic studies [7]. The infrared spectra of different ambers present similar features for ambers from different locations, refined differences in location and intensity of absorption peaks could be identified among them [9].

There are only a limited number of ambers and counterfeit of amber is widespread. So, in this study we have aimed to investigate the potential of Raman spectroscopy in order to distinguish between the natural and fake amber.

2. Experimental

2.1. Samples

Processed and unprocessed samples of amber were collected. Ten different samples known as amber were numbered (Figure 1). These samples were studied with Raman spectroscopy, respectively.

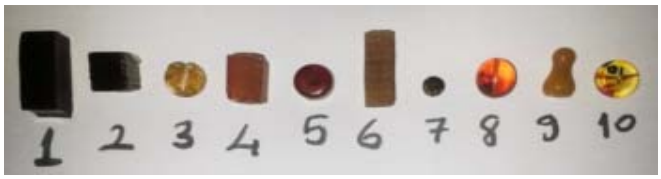

Fig 1: Numbered Samples

2.2. Raman spectroscopy

In this study, a RenishawinVia Raman Spectrometer with a 785 nm laser and Charge-Coupled Device (CCD) detector was used. The acquisition time, laser power and exposure time for all measurements were 20s, 10mW and 1s, respectively. The spectrums acquired by through 20x objective. The spectral resolution was 50 µm (Figure 2) and baseline correction was performed for all measurements.

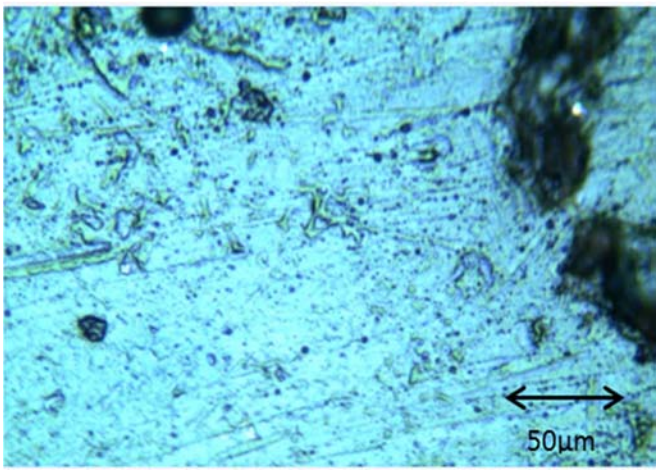

Fig 2: Sample views under laser power with Raman spectroscopy

2.3. Data analysis

All data were imported into MATLAB® (Matlab 7.13, The Mathworks, Natick, MA) for analysis.

3. Results and Discussion

Spectroscopy examinations based on Raman scattering and infrared absorption processes for detection of the vibration of molecules. These vibrations of molecules are used for identification of substances from characteristic spectral pattern known as "fingerprints". Spectral patterns or fingerprints provide information about the chemical composition and physical form of the materials and to determine the amount of a substance in a sample quantitatively or semi-quantitatively [10].

We investigated ten different samples known as amber and selected center at 1300 cm^{-1} of Raman spectrum. When we selected center at 1300 cm^{-1}, Raman spectrums of all samples were drawn between 720 and 1800 cm^{-1}. Raman spectrums of ten samples were drawn with Matlab (Figure 3). While seven samples spectra were similar, three samples of them were different. The most characteristic peaks in the Raman spectrum of three samples (numbers of sample are 3, 7, 10) are fingerprint regions and strong features at 1204, 1446 and 1650 cm^{-1}, respectively (Figure 4). The most characteristic peaks in the Raman spectrum of seven samples (numbers of sample are 1, 2, 4, 5, 6, 8, 9) are fingerprint regions and strong features at 776, 846, 998, 1259, 1435 and 1608 cm^{-1}, respectively (Figure 5).

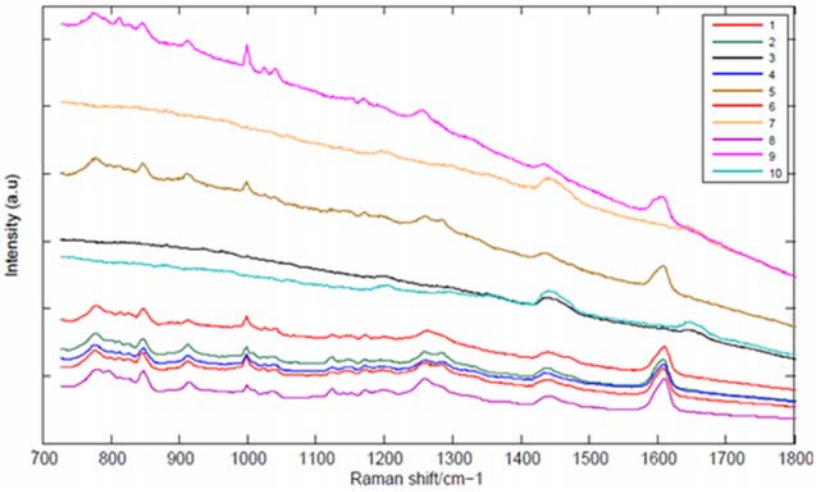

Fig 3: Raman spectra of ten samples

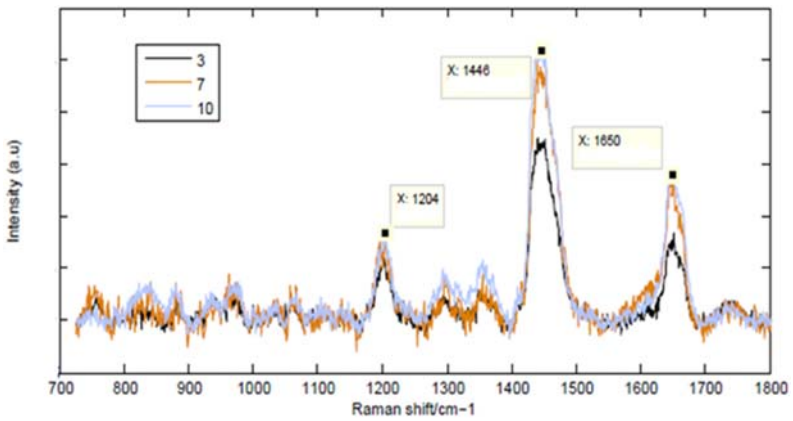

Fig 4: Raman spectra of three samples (numbers of sample are 3, 7, 10)

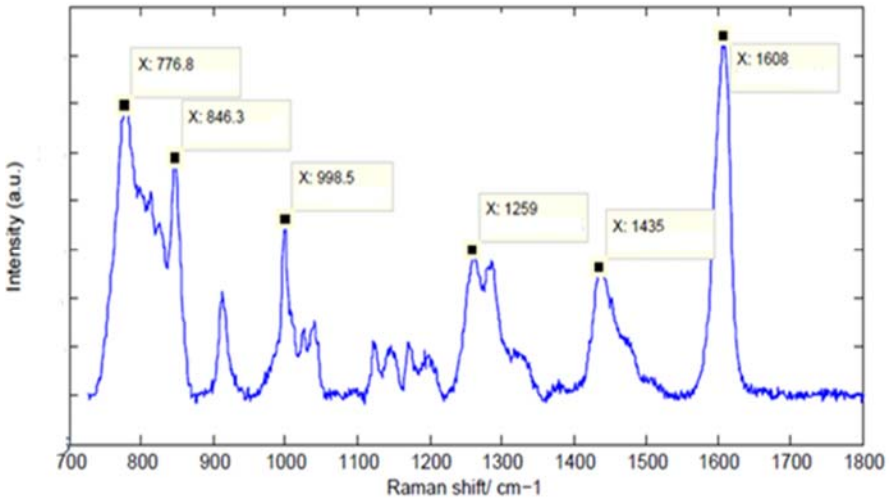

Fig 5: Raman spectrum of numbered sample 4

Amber has many components, so identify of amber is difficult. Different tests and methods have been developed for identify of amber [11]. *Sonibare et al.* investigated to the geochemical characterization and biochemical classification different fossilized plant resins, so they used Infrared (IR) Spectroscopy and Gas Chromatography (GC) with Mass Spectrometry (MS) [12]. There are also several studies to examine amber with Raman spectrum in literature. Thomas *et al.* [13] found at 1193, 1436, 1452 and 1647 cm^{-1}, Edwards *et al.* (8) found at 1646 and 1450 cm^{-1} and they concluded that 1646 cm^{-1} assigned to ν(C=C) stretching and 1450 cm^{-1} assigned to $\delta(CH_2)$ deformation modes. Brody *et al.* [14] differentiated amber samples and found in all the Baltic amber spectra centered between 1652 and 1645 cm^{-1}, North Germany amber spectra at 1659 cm^{-1} and bands at 1205 and 1143 cm^{-1} were assigned to δ (CCH) and ν (CC) ring breathing modes. Also, wavenumber region at 1250–1175 cm^{-1} is associated with the presence of succinic acid and its esters within the amber samples from the Baltic region. Rao *et al.* [6] studied on natural amber, copal resin and colophony and they found position of natural amber at 1417, 1630 cm^{-1} and calculated density.

Raman peaks of 3, 7 and 10 were different from Raman peaks of 1, 2, 4, 5, 6, 8, 9. Only spectra of the fourth and the ninth examples of the samples were drawn separately (Figure 5 and Figure 6). Raman peaks of the fourth and the ninth samples are almost the same as shown in Figures 5 and 6.

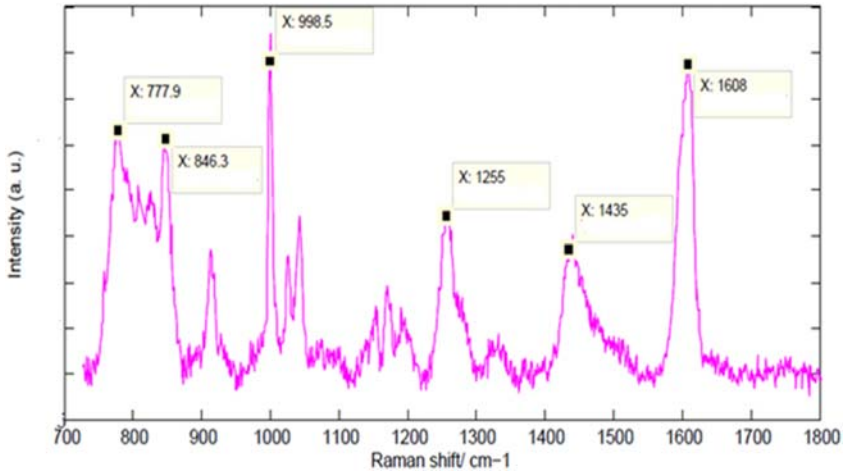

Fig 6: Raman spectrum of numbered sample 9

In this spectroscopic study, we investigated neither chemical nor physical characteristics of amber. Only fingerprint region were investigated for amber and it was shown that different samples could be distinguish with Raman spectroscopy. Raman spectrums are useful to identify differences in the maturing processes of amber, but not for determine its geographical origin [12, 15].

Raman spectroscopy provided so quick analysis; non-destructive confirmatory identification and fake amber can be easily distinguished from the real amber. It is important in terms of take precedence against counterfeiting.

4. Conclusion

When samples were analyzed by Raman spectroscopic technique, prominent peaks have a significant role in the investigation of different materials. In our opinion, we can identity to counterfeit amber with these peaks.

Raman spectroscopic technique is a non-destructive way to analyze of amber. It could be concluded that Raman

spectroscopy proved its efficiency in evaluation of the different amber samples and its structure for different aspects. Raman methods used in this study can definitively and non-destructively identify amber or materials like amber.

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