Raman scattering spectra of amber

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Abstract. The Raman spectra of amber (succinite) of different transparency levels of the Palmniken Deposit of Kaliningrad of Russia were obtained using the Fourier Transform–Raman spectroscopy method, which allows obtaining real and elemental compositions. It was found that succinite (amber) is an organic unsaturated carbon - chain homopolymer with different valence oscillations of aliphatic CH₂ and CH₃ groups, containing heteroatoms C=C and CH in the main chain with valence in RNS=CH₂ and deformation in trans RHC=CHR' oscillations with chemical side chains of up to 8 subgroups. Three main connections were experimentally identified on the obtained Raman spectra, which can be used as characteristic features for identification and diagnostics of succinite of the Palmniken Deposit. Practical significance. The proposed method may be of interest for chemistry, materials science and research related to identification processes. The performed research can be used in the synthesis of high-molecular compounds, in issues related to the development and distribution of various applications of organic materials.

1 Introduction

In modern materials science, polymers are studied due to their wide use as materials with special optical, physical and mechanical properties [1-2]. For example, polymer materials are economically and technologically promising as optical communication components, since in the near future, modern thin and expensive optical fibers, as well as those made with glass or quartz, will be replaced with less expensive materials [3]. However, technologies for processing materials from polymer optical structures have not yet reached full development and are at the stage of searching for technologies for the development of polymer light-emitting diodes [4] or lasers, and even the possibility of light generation in polymers [5].

It is known that for optical materials and their structures, one of the most important properties is the surface quality, since the roughness of the waveguides leads to scattering of light streams and, consequently, losses during the interaction of transmitted modes in the boundaries of the waveguides themselves. Thus, the increase in optical losses in devices as a result of scattering is proportional to the third degree of the difference in refractive indices between the core and the shell [6-7].

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The next stage of studying polymer materials is to solve the problem of mechanical and chemical resistance and stability in the interaction of devices with the environment [8]. Thus, the choice of materials that have the above properties simultaneously allows you to adapt the optical or mechanical parameters in the process of polymer synthesis [9-10]. In this context, it is important to study and understand the structure of natural polymer materials, in particular amber, which shows very interesting characteristics in terms of optical properties, namely fluorescence, birefringence, transparency in UV radiation in combination with mechanical and chemical resistance [11-12].

Thus, the priority goal of the study is to study the optical properties of natural polymer materials on the example of succinite from the Palmniken Deposit (Kaliningrad, Russia).

Analysis of the development of scientific areas of processing, processing and application of amber has revealed that the main trends in this area are research on nanostructural properties, development of technologies for the production of composite (composite) materials and products in the art, electrical, paint, pharmaceutical and perfume industries, as well as research on the impact on biological objects and humans in medicine.

High interest in the raw materials of the amber industry and depletion of reserves on the one hand contribute to the development of macromolecular synthesized materials in the manufacture of products and parts with specified optical characteristics through synthesis, modification and processing, but on the other hand, high demand and high cost of natural materials, insufficient development of authentication tools contributes to the development of the amber imitation market.

Thus, the presented challenges determine the relevance of the present study. accordingly, the solution of this problem is the goal: obtaining IR- and Raman spectra of succinite from the Palmniken Deposit (Kaliningrad, Russia) and identifying the distinctive characteristics of optical properties.

The object of the study is selected polymer materials of organic origin, and the subject is succinite of the Palmniken Deposit (Kaliningrad, Russia).

The problem and purpose of the study determined the choice of the following tasks:

- obtaining the IR and Raman spectra of amber and install the characteristic;
- propose a method for identifying the Genesis of amber by Fourier Transform–Raman spectroscopy method.

The first results on the identification of amber were the work of professors C. W. Beck [13-14], E. K. Tratman [15], Dr. H. J. Plenderleith and Dr. M. H. Hey [16]. For the first time, spectra characterizing the structure of amber were identified using IR- spectroscopy. In the presented works, the amber material was dissolved in various organic solvents [17], and then the resulting solution and/or residual insoluble material were analyzed.

Also in the work in Alekseeva A.V., Samarina L. A. [18] the work on the study of IR absorption spectra of molecular and supramolecular structures of transparent, translucent, opaque and bony amber as fossil resins from Northern Eurasia was carried out. Based on the obtained data of IR spectroscopy of amber, types of fossil resins (succinite, rumanite, retinite, etc.) with a characteristic spectrum for the COOHA group in the range of 1720-1740 cm^{-1} and a band with clear boundaries at 1016 cm^{-1} , which can be attributed to C-O stretch fluctuations in acids, alcohols, esters and esters are identified. However, further study of the same samples, which are soluble in alcohol and petroleum ether, established the need for additional research of the IR spectra of amber, because the above-mentioned method is not sufficiently informative.

Currently, a number of papers are known about the studies of the Genesis of amber and copals on Raman spectra. Some characteristic features and features at various stages of amber maturation were determined [19] based on the structure of the labdanum triterpenoid matrix. Studies were conducted on different samples, but without a ratio by geographical location.

In [20], as a result of the analysis of the infrared spectra of amber and Copal resins, a feature was identified – the presence of the "Baltic shoulder" in the range of 1250-1175 cm^{-1} . This fact has been suggested in determining deposits such as Sicily, Poland, and Lithuania, but the existence of this functional group in several North American amber limits the usefulness of this result for geographical diagnostics.

Thus, to summarize the data obtained and taking into account the works [21-22] it should be noted that the notion that amber is a fossil form of fossilization, the original organic compounds with terpenoid and labdanoids bars – is not true, because the process of fossils involves the replacement of the original organic material mineral compounds or water-soluble salts, but these elements are more likely to be present in the source material and saved in the future. The process of fossilization of amber resin implies diagenesis – rearrangement and transformation of chemical bonds in various compounds on the principle of a free-radical mechanism [23].

Thus, based on earlier studies, it can be concluded that amber is the result of the polymerization process of a resin with a macromolecular structure and includes an insoluble component, a macromolecular polymer network, and a soluble element with an aromatic unit-a ring-of low molecular weight [24].

It is worth noting that currently, no structural studies have been conducted on "bulk" amber samples on a submicrometric scale to get an idea of its macromolecular network, so it is necessary to develop a methodological complex for non-destructive research of amber materials.

2 Materials and methods

To date, there are more than 100 types of fossil resins in the world, but the degree of their study using IR and CR spectroscopy is insufficient.

The material base of the experimental study was selected samples of amber (succinite) from the Palmniken Deposit in Kaliningrad, Russian Federation.

During the study of amber samples by KR spectroscopy, Microspectroscopy technologies were used on Renishaw InVia Reflex equipment with a Leica DMLM microscope, in which inVia supports excitation wavelengths from the near-IR region to deep ultraviolet, with automatic switching of components, with the possibility of selecting the necessary laser, and the Leica research microscope installed on inVia supports a wide range of different types of samples and prefixes (low-and high-temperature, high-pressure prefixes, variable humidity, etc.).

The laboratory equipment is a complex consisting of a Renishaw InVia Reflex spectrometer and includes a Leica DMLM confocal microscope with a resolution of < 1 micron, which is used for illumination in reflected light with 5x, 20x, 50x and 100x lenses, 20x and 50x long-focus lenses, 15X and 40x UV lenses, as well as a trinocular tube with 2 eyepieces and a video camera. InVia Reflex spectrometer with a focal length of 250 mm, laser spot size from 1 to 300 microns, equipped with EDGE filter for shooting spectra starting from 100 cm^{-1} at each wavelength, NeXT filter for shooting spectra starting from 10 cm^{-1} for excitations of 514 and 633 nm diffraction monochromator 3600, 3000, 2400 and 1200 lines/mm, CCD detector 576x384 pixels with Peltier cooling (up to -70°C), CCD detector 1024x768 pixels with Peltier cooling (up to -70°C). The optical system is automated and includes a Changer with 16 ND filters for power control in the range of 0.00005-100%, and power adjustment of a set of lasers for excitation at wavelengths of 785, 633, 514 and 244 nm. Accompanying equipment includes an automated XYZ table that allows you to work in the "mapping" mode, a set of polarizers and analyzers for each wavelength and visible light, a line Focus system for working in the UV, visible and close ranges, a high-temperature object table (up to 1500°C), a MicrostatHe cryostat for working

with samples in the range of 2.2-500 K, and a system for direct display of the signal-Global Raman Imaging.

Table 1. The studied samples of succinite from the Palmniken Deposit of the Russian Federation

Morphology			
No.	Description	Color	Transparency, Shine
1.	Transparent unprocessed amber light yellow, surface polished, uniform transparency	yellow	Transparent, Shine on the crust is glass
2.	Opaque, cloud amber, surface polished, sometimes peel	Honey yellow	Cloudy, bastard, Shine on the rock is glass, on cork is missing
3.	Treated amber, bone, with elements of crust, fracture Matt, porous	White	Bastard, Shine on the rock is wax
4.	Partially treated amber, with peel, characteristic parallel directions, opaque with cloud texture	Honey yellow	Cloud, Shine on the rock is glass, on cork is wax
5.	Amber is not transparent, bone, light with elements of crust, surface polished	White	Bastard, bone, Shine on the rock is wax
6.	Opaque amber, light yellow, with diagonal deep crack	Light yellow	Bastard is bone, Shine on the rock is wax
7.	Opaque amber, uneven structure and color, with deep cracks, brittle, polished surface	White, light yellow	Bone, Shine on the rock is wax
8.	Opaque amber, light yellow honey color, with cloudy texture, peel elements	Honey yellow	Bastard, cloudy, Shine on the rock is glass, wax
9.	Transparent amber with characteristic crusts, sometimes polished	yellow	Transparent, Shine on the rock is glass
10.	Murky light brown, translucent in thin layer of amber ((heat treatment?) grinded surface	Light brown, caramel	Opaque, Shine on the rock is glass
11.	Light yellow opaque amber with white streaks, with crustal elements	Light yellow	Bastard, Shine on the rock is wax

Fig. 1. Optical scheme and lasers used in the Renishaw InVia Reflex spectrometer

Currently, the results of high - resolution characteristic Raman spectra of amber are obtained using the Renishaw InVia Reflex spectrometer when excited by a laser at a wavelength of 633 nm. However, when mapping the phonon spectra, intensity, and position of the bands using the fast sample mapping system in the 244-900 nm region, the

obtained spectra of amber and amber-like resins were compared with the existing database of organic compounds and polymers, but no matches were found with the existing databases of organic substances and materials.

Measurements were performed in the spectral range of $7500\text{--}370\text{ cm}^{-1}$ (1.3–25 microns), $25000\text{--}8500\text{ cm}^{-1}$ (400 – 1200 nm) with a spectral measurement resolution of $0.4\text{--}32\text{ cm}^{-1}$. The scanning speed was 10 scans per second at a resolution of 8 cm^{-1} . Photometric accuracy is 0.1% T, and the signal-to-noise ratio (peak to peak). When recording absorption spectra, the accumulation time was 5 seconds (4 cm^{-1} resolution), not less than 7000:1. Limits of the allowed basic absolute error of measurements on the wave number scale (for water vapor in the atmosphere at a wavelength of $1554,353\text{ cm}^{-1}$) $\pm 0.5\text{ cm}^{-1}$.

Processing of the obtained empirical data was carried out using statistical and regression mathematical analysis in the Matlab environment.

3 Results

The resulting Raman spectra succinite from the Palmniken Deposit of Kaliningrad of the Russian Federation (Fig.2) and highlights the main characteristics for the material under study.

Fig. 2. Raman spectra of succinite (amber) samples from the Palmniken Deposit, Russian Federation

4 Discussion

The analysis of the obtained data allowed us to draw the following conclusions that the study of succinite has the following features and characteristics:

Succinite (amber) is an organic unsaturated carbon - chain homopolymers (saturated hydrocarbons) with valence asymmetric ($2920\text{--}2935\text{ cm}^{-1}$), symmetric ($2840\text{--}2860\text{ cm}^{-1}$), deformation ($1450\text{--}1470\text{ cm}^{-1}$) oscillations of aliphatic CH_2 groups, as well as valence symmetric ($2860\text{--}2880\text{ cm}^{-1}$), deformation ($1450\text{--}1470\text{ cm}^{-1}$, $\sim 1380\text{ cm}^{-1}$) oscillations of aliphatic CH_3 groups containing heteroatoms $\text{C}=\text{C}$ and CH in the main chain with valence

in $\text{RNS}=\text{CH}_2$ ($1640\text{--}1648\text{ cm}^{-1}$) and deformation in $\text{TRANS RHC}=\text{CHR}'$ ($968\text{--}972\text{ cm}^{-1}$) oscillations. Also in chemical side chains up to 8 subgroups.

It is worth noting that in the areas of $\sim 3400\text{ cm}^{-1}$, $\sim 1650\text{ cm}^{-1}$ – O-H valence fluctuations, deformation fluctuations in vinyl alcohol; $\sim 1735\text{ cm}^{-1}$, $\sim 1380\text{ cm}^{-1}$ – C=O valence fluctuations, CH_3 deformation fluctuations in $\text{CH}_3\text{C}(\text{O})\text{O}-\text{R}$; $\sim 1020\text{ cm}^{-1}$ C-O valence fluctuations in $\text{S CH}_3\text{C}(\text{O})\text{O}-\text{R}$; $830\text{--}940\text{ cm}^{-1}$, $1080\text{--}1150\text{ cm}^{-1}$ – symmetrical and asymmetric C-O-C valence oscillations in aliphatic esters; $800\text{--}900\text{ cm}^{-1}$ predominantly Valence oscillations C-C; $1735\text{--}1770\text{ cm}^{-1}$ C=O valence oscillations in aliphatic esters.

Thus, the data obtained allow us to identify significant characteristic features of the Baltic amber spectra in the range of $2929.72\text{--}2924.91\text{ cm}^{-1}$, $1737.77\text{--}1643.91\text{ cm}^{-1}$, $1448.02\text{--}1456.18\text{ cm}^{-1}$.

It is also worth noting that the most significant features– the "Baltic shoulder" -in the spectra, in the range of $1250\text{--}1175\text{ cm}^{-1}$, are also highlighted.

Experimentally, three main bonds were identified on the obtained Raman spectra, which can be used as characteristic features for identifying and diagnosing succinate.

5 Conclusion

The results of the study can be of high interest both in theoretical application-obtaining data of the Raman spectra of amber from the Palmniken Deposit, and in practical application - in the development of scientific and methodological guidelines for the processing, processing and manufacturing of amber products, cataloging of amber materials, methods and methods of their storage, and identification of succinite products.

This research may be of particular interest in the development of new directions for the use of organic optical materials, which, accordingly, open up new possibilities for the use of macromolecular materials in the manufacture of products and parts for wider areas of use.

The presented data indicate the complexity of polymer organic compounds and the need for further research in this area.

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