Identification of succinite of infrared absorption spectra

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Abstract. The solution of the problem of identification of amber (succinite) on the example of natural polymer material of organic origin on the basis of its infrared absorption spectra is proposed. Taking into account the growing demand for the use of such composite materials on an industrial scale and the insufficiency of existing methods for determining their composition, the proposed method can become a new solution to the problem of identification. The basis of the proposed method for the study of succinite using infrared spectroscopy is translucent spectroscopy, with the measurement of mirror and diffuse reflection. The samples amber of the Palmniken Deposit obtained in the city of Kaliningrad of the Russian Federation were used as the objects studied. The data of infrared spectra of succinite obtained by the proposed method of infrared spectroscopy are obtained and presented in comparison. Five main links on the obtained infrared spectra have been experimentally determined, which can be used as characteristic features for identification and diagnostics of succinite by the material composition. The proposed method may be of interest in the theory of knowledge of material science, research related to the processes of identification, processing of production of amber.

1 Introduction

Currently, the growth of scientific interest in the physical, chemical, mechanical and technological properties of amber industry materials is caused by several factors:

– first, the high cost of amber and its constant growth both in raw and processed form;
– second, the limitedness of the natural resources of the amber and the exhaustion of its stocks with consistently high consumer demand;
– third, the wide practical application of amber not only in various branches of science and technology, but also in artistic, cultural and perfumery purposes, where the choice of materials and their quality is one of the most important criteria;
– fourth, the lack of study of amber as a composite material of heterogeneous structure and complex composition of components.

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Today a number of domestic well-known [1-3] and abroad [4-5] scientific works, devoted to the study of the optical properties of amber. They consider the methods of infrared (IR) spectroscopy on samples of both treated and untreated amber deposits in Bulgaria and Poland. However, in modern amber studies there are no samples not only of succinate the succinite of the Palmniken Deposit, but also the study of its structural transformations as a result of mechanical, thermal, physico-chemical treatment, including compression, pressure, as well as the use of paint and protective coatings.

This study allows us to obtain new scientific and methodological data for the analysis of optical properties of polymer materials of organic origin by IR spectroscopy on the example of amber (succinite).

To date, more than 100 types of fossil resins have been observed in the world, but their degree of study with the help of IR spectroscopy is insufficient. This is confirmed by a large number of works on the study of samples of materials from various fields presented only in a generalized form, without a detailed description of the obtained characteristics of IR spectra [6-13]. At the same time, spectral analysis in the infrared range is one of the universal methods of obtaining maximum complete information of the material and structural composition of the materials under study, which is necessary for scientifically based, complete and objective evaluation.

When carrying out the system and comparative analysis of information and scientific researches of existing classifications of amber materials [14-16] it is possible to allocate four basic their directions:

1. based on structural composition based on 30 types of fossil resins [14,16]: "amber-like" or "amorphous" polymer type (copalita, succinate, retinite, scuffy, pierrette) and "crystal";

2. on the structure of carbon skeleton of macromolecular structure of resin [17-18] and divided into 5 classes, the first of which includes Baltic (succinite) and Dominican amber with labdan lattice (skeleton);

3. by the degree of transparency that is associated with varying concentration of microscopic voids (cavities): "transparent" – no voids, highest quality, cloud – translucent, with the density of cavities 600/mm², "bastard" is opaque, with the density of cavities 2500/mm², the "bone" – opaque, reminiscent of the color of ivory, with the density of cavities 900 000/mm² and "frothy" – not-transparent, resembling externally sea foam, with a variety of cavities from the smallest to very large, of a few millimeters. There are also "overburden amber," featured a thick crust of weathering, found in later strata of occurrence than a typical support layer; "rotten amber" – variety, which is the transition from succinite to gedanite (hadano-succinite), sometimes erroneously called hedonic or "immature amber" – krantzite [19];

4. color, acquired by the presence of foreign substances in relation to the resin, mineral and formation conditions, which explains such a wide color range. However, this classification is based on visual, organoleptic or literary analysis of research works without the use of laboratory equipment colorimetric, spectral or other methods of analysis.

At the same time, there is a fairly large number of spectral collections of organic materials of varying degrees of informatively [20-22], presented as methodological guides for spectral analysis of elements and structures, but they all have a limited database on structural composition for use in fossil resins. In a number of other works there are restrictions on the set of studied elements and laboratory complex [23-29]. What is especially important-none of the above collections have maps and transcripts of the spectra of amber materials.

2 Materials and Methods
This gap in research dictates the purpose of this paper: the use of IR spectroscopy to study the optical properties of inhomogeneous polymer materials of organic origin with anisotropic physical and mechanical characteristics on the example of amber.

The objectives of the study include:

- obtaining IR spectra of amber absorption;
- systematization of the obtained data and extraction of essential features characterizing amber and amber resins from the obtained IR spectra, and their identification in the materials;
- determination of peculiarities of organization of structures of organic polymeric materials on the example of amber;
- comparative analysis of the obtained data of IR absorption spectra by type and intensity depending on the transparency and thermal treatment of amber.

The object of the study is the chemical and material composition, micro - and macromolecular structural formations of amber.

The subject of the study is the succinite of the Palmniken Deposit of Kaliningrad of the Russian Federation.

Thus, if we combine the work on the classification of amber materials, to enrich them with experimental data of IR spectra of structural and material composition, the basis for identification of nuclear materials based on infrared spectroscopy can be obtained.

Samples of amber (succinite) from the Palmniken Deposit of Kaliningrad of the Russian Federation were chosen as the material basis of the experimental study (table 1).

During the study of samples of succinite by IR spectroscopy, applied technology transmission spectroscopy, as well as mirror and diffuse reflection on the equipment IR Fourier spectrometer VERTEX 70 (BRUKER) on a pre-calibrated interferometer RockSolid with a microscope HYPERION 1000.

Infrared Fourier spectrometer VERTEX 70 (BRUKER) it is a stationary automated device, the basis of which is a two-beam interferometer, in which the change of the stroke difference between the interfering beams occurs when one of the mirrors is changed. To reduce the influence of external influences, the device is constructed according to the scheme with mirrors in the form of corner reflectors. The spectrum (in the wave number scale) is obtained after performing special mathematical calculations (inverse Fourier transform) of the interferogram. The movement of the mirror in the interferometer is carried out linearly by means of a precision mechanism. The exact position of the mirror (the travel distance in the interferometer) is determined using a reference channel with a laser. The zero value of the stroke difference (the main maximum of the interferogram) is determined by calculation. To eliminate the influence of external influences (the presence of water vapor in the atmosphere and carbon dioxide) there is a device for blowing dry air or nitrogen.

The measurement process is controlled by an internal controller and an external computer using the OPUS software designed to make the fullest use of all the capabilities of Fourier spectrometers.

With the help of a software configuration of the device, optimization of its parameters, its work, the Fourier transform of the interferogram, the processing of output information, including the construction of the calibration graphs, results printing and saving test results. The OPUS software package enables the use of measurement information by other programs for the preparation of documents with the results of measurements. Protection of software against unintentional and intentional changes corresponds to the average level according to P 50.2.077-2014. Measurements were carried out in the spectral range of 7500-370 cm\(^{-1}\) (1.3–25 microns), 25000-8500 cm\(^{-1}\) (400-1200 nm) with a spectral resolution of 0.4–32 cm\(^{-1}\) measurements. Scanning speed was 10 scans per second at a resolution of 8 cm\(^{-1}\). Photometric accuracy 0.1% T and signal-to-noise ratio (peak-to-peak).
At registration of absorption spectra the accumulation time was 5 s, (resolution 4 cm\(^{-1}\)), not less than 7000:1. Limits of permissible absolute error of measurement on a scale of wave numbers (in pairs of water in the atmosphere at a wavelength of 1554,353 cm\(^{-1}\)) ±0,5 cm\(^{-1}\).

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

| No. | Description                                                                 | Color       | Transparency, Shine                                                                 | Sample size, mm |
|-----|-----------------------------------------------------------------------------|-------------|--------------------------------------------------------------------------------------|-----------------|
| 1.  | Transparent unprocessed amber light yellow, surface polished, uniform transparency | yellow      | Transparent, Shine on the crust is glass                                             | 7×10            |
| 2.  | Opaque, cloud amber, surface polished, sometimes peel                        | Honey yellow| Cloudy, bastard, Shine on the rock is glass, on cork is missing                      | 43×37 mm        |
| 3.  | Treated amber, bone, with elements of crust, fracture Matt, porous           | White       | Bastard, Shine on the rock is wax                                                    | 19×27 mm        |
| 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                                    | 37×42 mm        |
| 5.  | Amber is not transparent, bone, light with elements of crust, surface polished | White       | Bastard, bone, Shine on the rock is wax                                              | 13×21 mm        |
| 6.  | Opaque amber, light yellow, with diagonal deep crack                          | Light yellow| Bastard is bone, Shine on the rock is wax                                            | 19×27 mm        |
| 7.  | Opaque amber, uneven structure and color, with deep cracks, brittle, polished surface | White, light yellow | Bone, Shine on the rock is wax                                                       | 18×54 mm        |
| 8.  | Opaque amber, light yellow honey color, with cloudy texture, peel elements   | Honey yellow| Bastard, cloudy, Shine on the rock is glass, wax                                     | 18×58 mm        |
| 9.  | Transparent amber with characteristic crusts, sometimes polished             | yellow      | Transparent, Shine on the rock is glass                                             | 38×56 mm        |
| 10. | Murky light brown, translucent in thin layer of amber ((heat treatment?) grinded surface) | Light brown, caramel | Opaque, Shine on the rock is glass                                                  | 37×38 mm        |
| 11. | Light yellow opaque amber with white streaks, with crustal elements          | Light yellow| Bastard, Shine on the rock is wax                                                    | 18×54 mm        |

In the study of absorption coefficients, a special preparation of samples was carried out, namely, "sample preparation" was used for the study of the first – order absorption-abrasion of the sample and pressing of the tablet based on KBr. This "sample preparation" allows to obtain a thin (first microns) layer of the material and to average the spectra in all possible orientations, compensating for anisotropy.

**3 Results**

As a result of the experiment, IR spectra of absorption of succinite from the Palmniken Deposit of Kaliningrad of the Russian Federation were obtained (Fig. 1) and identified the main characteristics for this type of material (Fig. 2).
Fig. 1. IR absorption spectra of samples of succinite (amber) Palmniken Deposit

Fig. 2. Characteristic areas of IR absorption spectra of samples of succinite (amber) Palmniken Deposit. Place of birth: IR spectra at the site 1000-1300 cm⁻¹ (a); IR spectra at the site 1000-4000 cm⁻¹ (b)

4 Discussion

The analysis of the obtained data allows to draw the following conclusions that the study of succinite of the Palmniken Deposit has the following features and characteristics:

1. There are distinctive characteristics in the four main groups of spectra 1700-1735 cm⁻¹, 1640 cm⁻¹, 2800-3000 cm⁻¹, 3400-3480 cm⁻¹, regardless of the characteristics of the transparency of the materials, which leads to the conclusion that the number of bubbles in the composition can only be a characteristic for the classification of the physical properties of amber.
2. The marked distinctive characteristics and their components in the four main groups of 1700-1735 cm\(^{-1}\), 1640 cm\(^{-1}\), 2800-3000 cm\(^{-1}\), 3400-3480 cm\(^{-1}\), complicate the differentiation between mixtures and compounds, therefore, as essential features of IR spectra, the compounds of carboxylic and oxygen-containing C=O groups (1700-1735 cm\(^{-1}\)), unsaturated C=C bonds (1640 cm\(^{-1}\)), CH\(_2\) and CH\(_3\) groups are accepted 2800-3000 cm\(^{-1}\)), hydroxyl groups on (3400-3480 cm\(^{-1}\)).

3. Five main links on the obtained IR spectra are experimentally determined, which can be used as characteristic features for identification and diagnostics of Palmniken Deposit field succinite by the material composition.

4. The influence of thermal treatment of amber on the differentiation of its structure is shown, in particular, the reconstruction of the C–O group – this complicates the identification in heat-treated materials, and requires further study of this phenomenon.

5 Conclusions

The results of the research are of high interest both in theoretical application-obtaining data of the infrared spectra of the amber of the Palmniken Deposit using samples of different transparency and heat treatment, and in practical application – in the development of scientific and methodological guidance of the processes of processing, processing and manufacturing of amber products, cataloguing of amber materials, methods and ways of their storage, identification of articles This study may be of particular interest in the development of new directions of use of composite materials of organic origin, which, respectively, open and new opportunities for the use of macromolecular materials in the manufacture of products and parts for wider areas of use. For example, in jewelry and arts and crafts, where artistic expressiveness of amber products due to optical properties of materials can be of decisive importance.

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

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