DETERMINATION OF BEESWAX AND SOME IMPURITIES BY IR SPECTROSCOPY

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IR spectroscopy has been used previously for studying a number of natural and synthetic waxes [1-3]. It has been shown that pure beeswax is readily identified from the presence in its spectrum of seven characteristic bands, while wax that has been boiled with sodium carbonate and is known as Punic wax can be distinguished from beeswax by the presence in its spectrum of an additional band in the 1550-1610 cm^{-1} region due to the stretching vibrations of ionized carboxy groups [1]. In the case of a mixture of wax with terpenoids (resins) the intensity of the bands in the region of absorption of un-ionized carboxy groups (~1710 cm^{-1}) rises [3]. In the present paper we consider the possibility of identifying beeswax and impurities in it in samples the ages of which amount to thousands of years, i.e., so old that they are stable to the action of natural conditions. We studied chloroform extracts of samples of the paintlayer taken from two icons — "Sergii i Vakkh" ["Sergius and Bacchus"] (~VIth century) and "Svyatye" ["Saints"] (~VIIth century) and a Fayum portrait of a woman, painted in encaustic, and also some fragments of antique murals of the period from the first centuries before our era to the first centuries of our era found in archaeological excavations in the cities of Rome and Kerch'.

Figure 1 shows IR spectra of extracts. The spectra show the bands characteristic for beeswax ([1] and Fig. 2a) at 3200-3450 cm^{-1} — the stretching vibrations of hydroxy groups of alcohol; doublet at 2850 and 2920 cm^{-1} — stretching vibrations of CH groups; 1740 and 1715 cm^{-1} — stretching vibrations of the carbonyls of esters and CO groups of un-ionized carboxyls of organic acids, respectively; doublet at 1465 and 1475 cm^{-1} — planar deformation vibrations of CH groups; 1175 cm^{-1} — stretching vibrations of C—O—C groups; and doublet in the 720-730 cm^{-1} region — nonplanar skeletal deformation vibrations of long-chain hydrocarbons. In the spectra of the compounds isolated, the ratio of the intensities of the high- and low-frequency components of the doublet in the 720-730 cm^{-} region is different from whtat it is in the spectra described by Kühn [1], which is apparently due to a different length of the chains of the components of the compound.

Some differences from the spectra of the pure wax ([1, 2], Fig. 2a) are observed in the IR spectra d-g, i. Thus, in spectra d and e there is a broad band at ~1600 cm^{-1}, and in spectrum g an additional hand appears at 1510 cm^{-1} with a shoulder at 1540 cm^{-1}. Spectrum i differs particularly strongly from the others: the shoulder at 1715 cm^{-1} is absent, a new band has appeared at 1380 cm^{-1}, and the band at 1465 cm^{-1} has broadened. Let us consider the possible causes of the differences observed.

Since the appearance of a narrow band in the 1570 cm^{-1} region can be explained by the vibrations of ionized carboxy groups (salts of fatty acids in Punic wax) [1], we have analyzed this region in more detail. The spectra of the samples investigated have a weak broad band in the 1600 cm^{-1} region (Fig. 1, d, e). Its appearance may be connected, in particular, with the presence in the substance of a nonsalt component, for example, with the presence of some resin as an impurity, as has been observed by other authors who have explained a band at 1612-1615 cm^{-1} by the presence in the sample of the aromatic groups of resin acids [1].

To check this hypothesis we prepared and investigated mixtures of wax with resins — dammar gum, mastic, sandarac, and rosin (it is known that resins might be added to beeswax in antiquity [1]) — and studied their IR spectra. As follows from Fig. 2b, the IR spectrum of the substance extracted after the fusion of beeswax with dammar gum in a ratio of 2 : 1 shows a new band at ~1600 cm^{-1} which was absent from the spectra of the pure beeswax and dammar gum (Fig. 2a; [4]). It is not seen, either, in the spectra of melts of the wax with other resins. In the case of spectrum d the appearance of this band is probably connected with the varnish coating this part of the icon. Dammar gum was most probably used for coating (spectrum of the varnish, Fig. 2c), but

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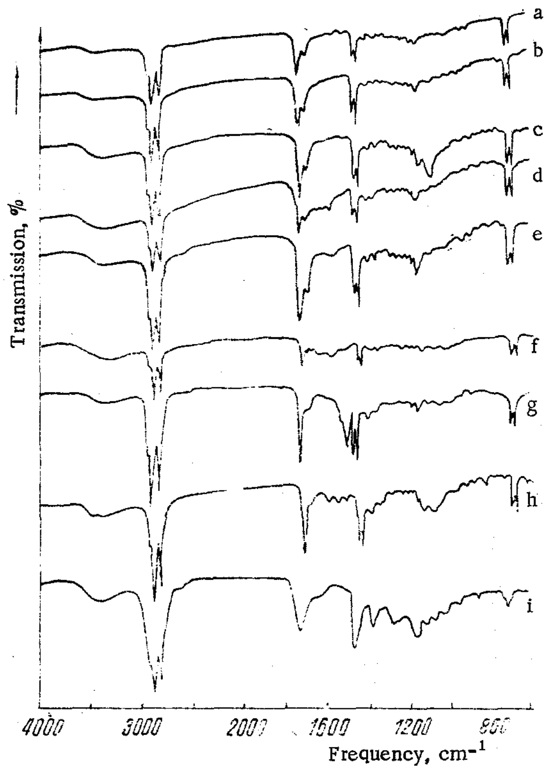

Fig. 1. IR spectra of extracts: a–e) from different parts of the icon "Svyatye," f) red fragment of a Fayum portrait, g) fragment of the green background of the icon "Sergii i Vakkh,"; h) red ornament from a Roman mural; i) yellow Panticapean painting (Kerch').

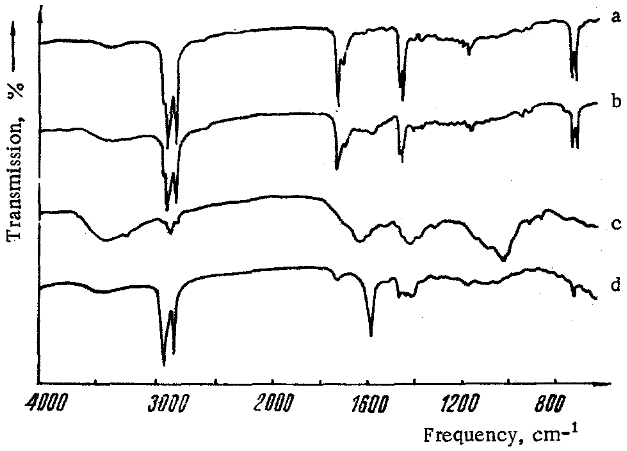

Fig. 2. IR spectra: a) pure beeswax; b) extract from a melt of the wax with dammar gum; c) coating varnish; d) green pigment from the icon "Svyatye."

an accurate identification of the substance is difficult because of the similarity of the IR spectra of resins [4,5], although individual resin acids have fairly characteristic IR spectra [6-8]. It may be assumed that in the process of coating the surface of the icon with varnish the wax was partially dissolved and mixed with the dammar gum. It is not excluded that painters deliberately added some resin to the wax.

The appearance of a broad band at 1600 cm^{-1} in spectrum e must also apparently be connected with the presence of resins in the sample. Thus, the spectrum of the green substance remaining after the extraction of the wax from the paint (Fig. 2d) is most probably the spectrum of a resinate. It is true that this spectrum differs from the IR spectra of copper resinates prepared by the usual method from copper acetate and rosin or other compounds [5, 9, 10]. At the same time, since copper was found in this substance by emission spectral analysis, the 1590 cm^{-1} band must be assigned to the vibrations of ionized carboxy groups present in the pigment. On the basis of these facts it may be concluded that the pigment was a salt of a resin acid. The possibility also cannot be excluded that the compound studied is not a true pigment but a product, formed in natural aging, of the interaction of the original substance, for example, copper acetate, with organic acids and, in particular, with the free fatty acids of the wax.

Judging from the presence in the IR spectrum of the substance isolated from the Fayum portrait of a broad band at ~ 1600 cm^{-1} (Fig. 1f), resin was also added to the wax in this case.

The IR spectrum g is most similar to the spectrum of Punic wax; since it contains a band at 1500 cm^{-1} with a shoulder at 1540 cm^{-1}, it may be assumed that the substance isolated contains as impurities salts of fatty acids with metal cations [1, 8].

IR spectrum h has weak bands at 3540, 3400, 1680, 1620, 1110-1140, and 662 cm^{-1} – in regions characteristic for the absorption of gypsum [11]. Apparently, minute particles of the mineral component of the pigment could not be completely eliminated from the wax.

Spectrum i differs somewhat from the IR spectra described above. The presence of characteristic bands shows that it relates to beeswax. The decrease in the intensity of the unresolved band at 720-730 cm^{-1} and the absence of a doublet in this region, and also the absence of resolution in the 1470 cm^{-1} region must be explained by the partial destruction of the long-chain hydrocarbon components of the wax. This shows either a natural aging of the molecules or, more probably, that in this case the wax was subjected to some kind of treatment before use.

Thus, we have shown that beeswax is preserved without appreciable changes for an extremely long time under very diverse condition and can be identified by IR spectroscopy even in archaeological samples that have been buried for about 2000 years. The chemical stability of the wax has been reported previously by certain authors [1]. It has been established that paraffin waxes [12], and even many lipids which, in a number of cases, are found in the bones of fossil animals [13, 14], possess the same property.

EXPERIMENTAL

Small pieces of the layer of paints from the paintings or details of murals were extracted with chloroform. The resulting solution was filtered through a glass filter and deposited in drops on a plate of KBr. The IR spectra were recorded in a Perkin–Elmer 257 instrument, which was calibrated from the spectrum of polystyrene. The accuracy of the measurements was ± 2 cm^{-1}. Quantitative emission spectral analysis was carried out on an SP instrument.

SUMMARY

Analysis of the IR spectra of waxes isolated from samples of paints from paintings dating from the Ist to VIIth centuries of our era and fragments of archaeological antique murals has shown that in some cases the wax isolated is pure beeswax and in others it contains as impurities what are presumably resin acids, and also salts of fatty acids. The IR spectrum of pure beeswax extracted from a fragment buried for 2000 yr is absolutely identical with the spectrum of modern beeswax, which shows the extreme chemical stability of the wax.

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