



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

SPECTRAL CHARACTERIZATION OF NATURAL RESINS USED IN CONSERVATION

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The weathering behavior of natural resin films has been examined using FT-IR and 2D IR correlation spectroscopy. The spectral changes observed after the irradiation regard the absorption bands assigned to the C=O and C–O stretching vibrations, which increase and enlarge progressively with increasing the exposure time. New information, which couldn't be acquired by using conventional IR and its derivative spectra were obtained by the 2D correlation IR spectroscopy.

The results evidenced chemical changes induced by exposure to weathering conditions, such as oxidation, ring disintegration, scissions and condensation of the original triterpenoid compounds.

INTRODUCTION

The identification and understanding of degradation processes of the materials from artworks is very important for conservation purposes. One of the most important challenges of analytical chemistry applied to the characterization of these materials consists in the recognition of the organic binding media and varnishes. Natural substances used by the Old Masters, *e.g.* siccative oils, animal glue, egg, waxes and resins, are complex and unstable mixtures. During ageing they undergo structural changes due to photo-oxidation and/or interaction with other materials.¹

Natural triterpenoid resins were once used as varnishes for wooden and painted artworks. A varnish is a protective coating uniformly spread on a surface in order to preserve its original aspect from a number of factors (temperature, humidity, light, biodeteriogens, dust, etc.) which can cause surface degradation.² The dammar resin contains

C30 isoprene derivatives with different basic skeletons, mostly tri- or pentacyclic. Monoric, oleononic, and dammararolic acids are some of the most important triterpenoid components of dammar resin.³

Many analytical techniques have been employed for the identification of resins and the characterization of their degradation pathway. Last decades, vibrational spectroscopic methods and particularly infrared spectroscopy have been widely used due to their versatility and ability to provide information on both organic and inorganic materials.⁴ As for resins, FT-IR techniques are important in recognizing their presence⁵ and in understanding their ageing.⁶

The present paper deals with the photo-oxidative stability of thin films of natural dammar resin. The chemical transformations appearing during artificial ageing have been monitored by FT-IR and 2D IR correlation spectroscopy.

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MATERIALS AND METHODS

Materials

The natural dammar resin was purchased from Kremer Pigmente (Germany) and was used without further purification. A 60% solution (weight/weight) of dammar resin in turpentine was prepared. The films were obtained depositing the solution on inert glass substrates. After drying, the samples were subjected to artificial light exposure (mercury lamp, $200 < \lambda < 700$ nm, incident light intensity 39 mW/cm^2) at a temperature of 40°C and 65% relative humidity in a commercial chamber (Angelantoni 250 Ind. Italy). The samples were removed from the chamber at regular time intervals ranging from 0 to 600 hours, were analyzed for chemical changes and compared with non-irradiated (reference) samples.

Methods

Powdered resin samples before and after treatment were used for analysis.

FT-IR spectra were recorded on solid samples in KBr pellets with a FT-IR DIGILAB ScimitarSeries spectrometer with a resolution of 4 cm^{-1} . The concentration of the sample in the tablets was constant, i.e. $5 \text{ mg}/500 \text{ mg KBr}$. The processing of the spectra was performed by using a Grams/32 program (Galactic Industry Corporation).

2D IR correlation intensities were calculated using the generalized 2D correlation method developed by Noda.⁷ In 2D correlation analysis, two types of correlation maps, synchronous and asynchronous, are generated from a set of dynamic spectra obtained from the modulation experiment. Synchronous 2D-correlation spectra represent the simultaneous or coincidental changes of spectral intensities measured at the ν_1 and ν_2 wavenumbers. The asynchronous 2D-correlation spectra represent sequential, or unsynchronized, changes of spectral intensities at the wavenumbers ν_1 and ν_2 . According to Noda⁷, the sign of asynchronous peaks provides very useful information about the temporal sequence of events taking place during the studied process.

RESULTS AND DISCUSSION

FT-IR spectroscopy was used to evaluate the compositional changes of the different hydrocarbon skeletal constituents and functional groups from the dammar resin. All FT-IR spectra were normalized at the C–H stretching band at 2950 cm^{-1} , which in triterpenoid resins is not affected by aging.^{8,9}

Figs. 1 and 2 show the FT-IR spectra and the second derivative of the IR spectra in the fingerprint region of the reference and artificially aged dammar films.

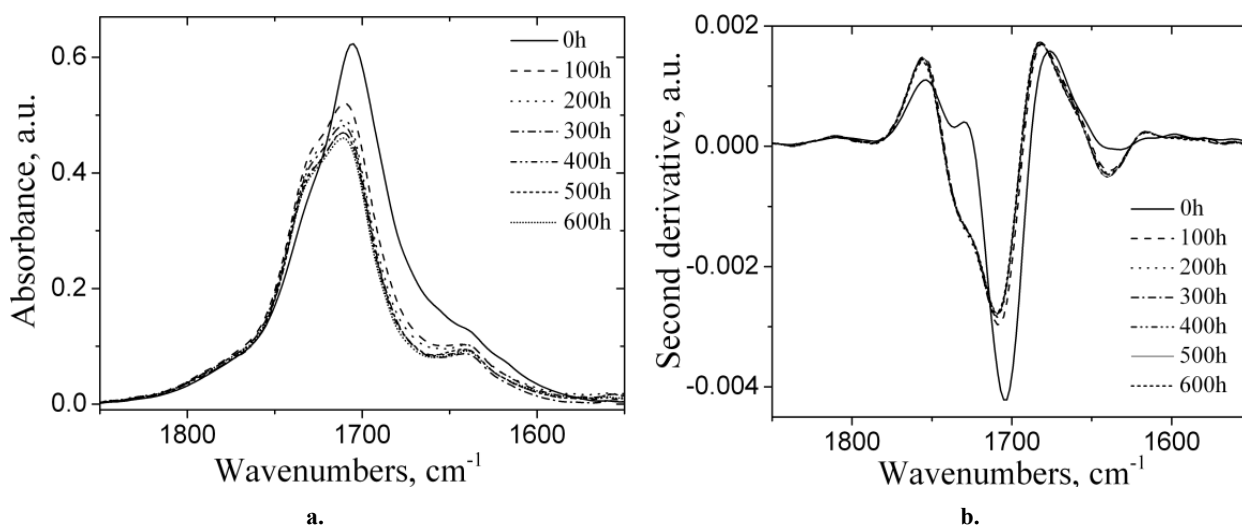


Fig. 1 – FT-IR spectra (a) and second derivative spectra (b) of the photodegraded dammar resin samples in the $1850\text{--}1550 \text{ cm}^{-1}$ region.

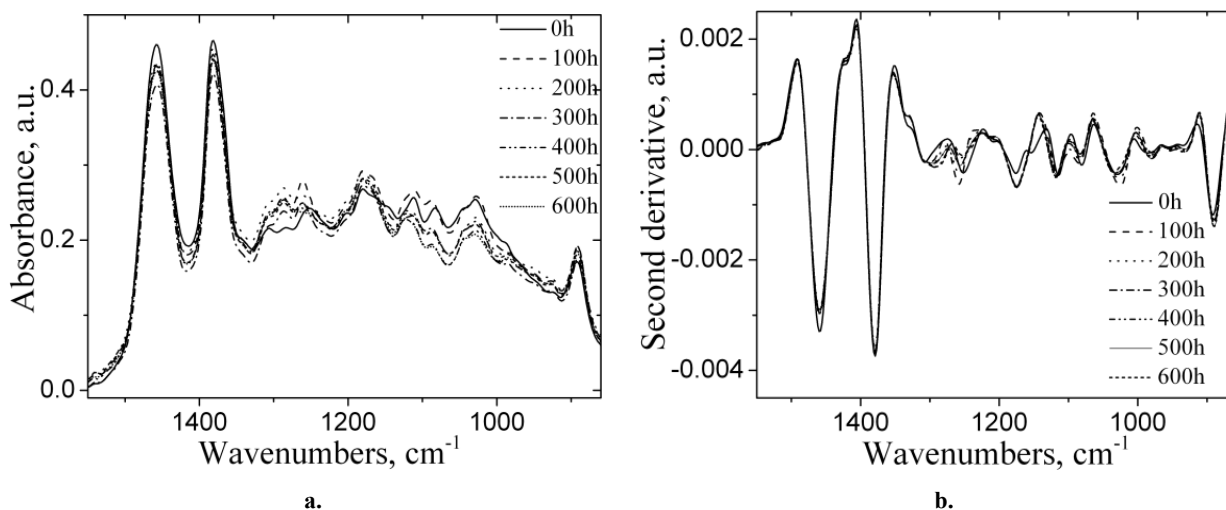


Fig. 2 – FT-IR spectra (a) and second derivative spectra (b) of photodegraded dammar resin samples in the 1550-860 cm^{-1} region.

The spectrum of the dammar resin film before artificial ageing shows an intense absorption band at 1713 cm^{-1} , assigned to stretching vibrations of C=O groups from aldehydes, ketones and carboxylic acids. During ageing, this band decreases in intensity and is shifted with 7 cm^{-1} to higher wavenumbers. A shoulder at about 1730 cm^{-1} can be also observed in the spectra of aged dammar films, shoulder which increases in intensity with increasing the ageing period, being overlapped with the 1720 cm^{-1} band. These observations are in agreement with the formation of new carbonyl compounds. In the same region, the band at 1647 cm^{-1} , assigned to stretching vibrations of C=C from *cis* -C=C- groups, in the reference sample spectrum appears as a shoulder, while in the spectra of aged resin samples becomes a prominent band.

Structural information on the hydrocarbon skeletons in the dammar resin are given by the bands at 1459 cm^{-1} , which includes information on the C-H bending vibration of methyl and methylene groups, 1379 cm^{-1} assigned to C-H bending of methyl groups, and 1307 cm^{-1} assigned to C-H bending vibration. In addition, the band at 1251 cm^{-1} is assigned to stretching vibrations of C=C groups, and the bands at 1180 and 1154 cm^{-1} are correlated with the saturated C-C stretching vibrations and also with the C-H bending of aromatic ring, and the bands at 1083 and 1032 cm^{-1} are assigned to C-O stretching vibrations in alcohols. The bands at 982 and 953 cm^{-1} indicate out-of-plane deformation vibrations of *trans* and *cis* C-H groups, respectively, while the bands at 932 and 892 cm^{-1} are assigned to out-of-plane deformation vibrations of a hydrogen attached to

aromatic ring and to C-H out-of-plane deformation of two hydrogen atoms in aromatic rings.

The structural degradation of dammar resin films was evidenced by the decrease of the bands from 1459 and 1379 cm^{-1} which in effect imply a reduction of the C-H bending vibration modes of methyl and methylene species. This observation indicates that artificial ageing of natural resin films induces ring disintegration and condensation of the original triterpenoid compounds. In parallel, the band at 1251 cm^{-1} decreases in intensity and is shifted with 15 cm^{-1} to higher wavenumbers indicating that oxidation of the C=C bonds occurs in the resin film. The two bands (1180 and 1154 cm^{-1}) assigned to saturated C-C stretching vibrations decrease in intensity, suggesting triterpenoid scissions during degradation.

For a better evaluation of the modifications taking place in the structure of the natural resin films during artificial ageing, an additional method was used to provide a deeper insight in the spectral features.

The 2D IR correlation spectroscopy can enhance the spectral resolution, gives new information, which cannot be acquired by using conventional IR and its derivative spectra. 2D correlation IR spectra offer unique advantages in identifying and distinguishing complex systems.

2D IR correlation spectra generated from the exposure time-dependent infrared spectra of the studied photodegraded dammar resin films were obtained. The correlation spectra clearly show the presence of synchronous and asynchronous correlation peaks among different modes of molecular vibrations. The contour maps were evaluated in the 1850 - 1550 and 1550 - 1080 cm^{-1} regions.

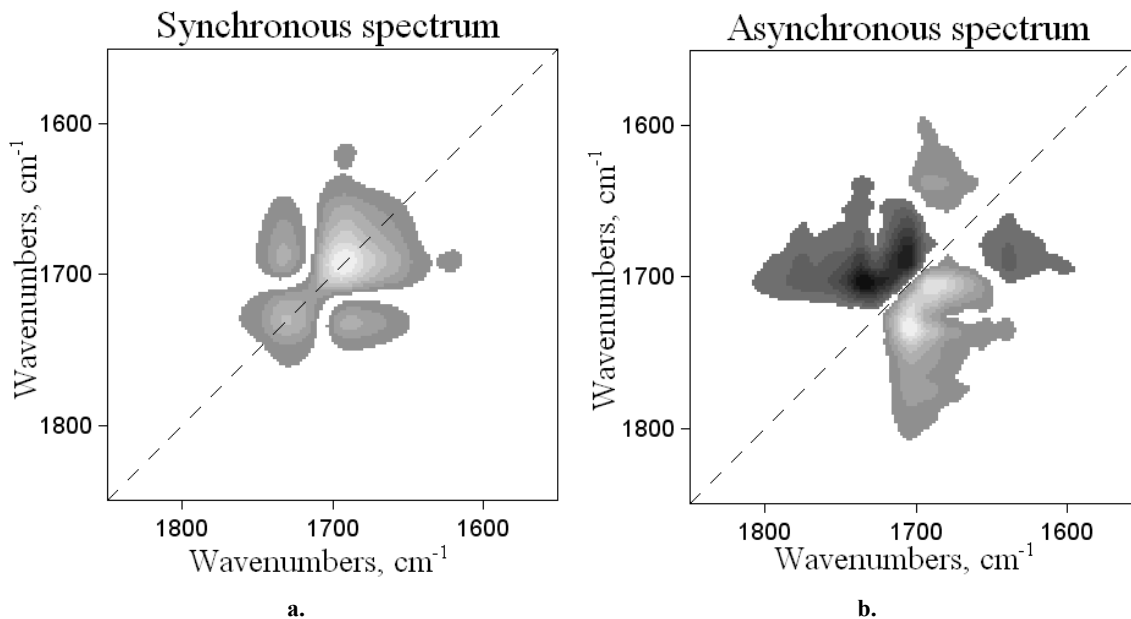


Fig. 3 – Synchronous (a) and asynchronous (b) 2D correlation spectra in the 1850-1550 cm^{-1} region constructed from the exposure time-dependent IR spectra.

In the synchronous 2D correlation spectrum (Fig. 3a), two auto-peaks at $\Phi(1732, 1732) > 0$ and $\Phi(1705, 1705) > 0$, and three cross-peaks at $\Phi(1732, 1705) > 0$, $\Phi(1732, 1688) > 0$ and $\Phi(1705, 1641) > 0$ are observed, implying that the bands at 1732, 1688 and 1641 cm^{-1} increase with increasing the exposure time.

In the asynchronous 2D correlation spectrum (Fig. 3b) four bands were identified at 1732, 1705, 1688 and 1640 cm^{-1} . These bands show five negative peaks at $\Psi(1732, 1705) < 0$, $\Psi(1732, 1688) < 0$, $\Psi(1732, 1640) < 0$, $\Psi(1705, 1688) < 0$ and $\Psi(1688, 1640) < 0$, and one positive peak at $\Psi(1705, 1640) > 0$. Based on the fundamental rule of an asynchronous spectrum, the following sequence of the spectral intensity changes was obtained during the exposure time: $1688 > 1640 > 1705 > 1732 \text{ cm}^{-1}$. This sequence indicates that the moment of C=O groups from α , β unsaturated aldehydes and ketones changes first, followed by the C=C from *cis* -C=C- groups, C=O groups from carboxylic acids and C=O groups from saturated aldehydes and ketones, respectively.

The second region is more complicated (Fig. 4). Here, in the synchronous spectrum (Fig. 4a), four auto-peaks at $\Phi(1456, 1456) > 0$, $\Phi(1379, 1379) > 0$, $\Phi(1284, 1284) > 0$, and $\Phi(1178, 1178) > 0$, and six pairs of positive cross-peaks at $\Phi(1456, 1379) > 0$, $\Phi(1456, 1284) > 0$, $\Phi(1456, 1178) > 0$, $\Phi(1379, 1284) > 0$, $\Phi(1379, 1178) > 0$, and $\Phi(1284, 1178) > 0$

are observed, implying that all bands around 1456, 1379, 1284, and 1178 cm^{-1} increase with increasing the exposure time. These bands are assigned to C-H bending vibration of methyl and methylene groups, stretching vibrations of C=C groups, C-C stretching vibrations and C-H bending of aromatic ring, respectively.

The asynchronous 2D correlation spectrum constructed from the exposure time-dependent IR spectral variations (Fig. 4b) shows seven bands at 1456, 1379, 1284, 1261, 1178, 1122, and 1097 cm^{-1} , respectively. Positive peaks at $\Psi(1284, 1178) > 0$, $\Psi(1284, 1122) > 0$, $\Psi(1261, 1178) > 0$, $\Psi(1261, 1122) > 0$, $\Psi(1178, 1122) > 0$, and negative peaks at $\Psi(1456, 1379) < 0$, $\Psi(1456, 1284) < 0$, $\Psi(1456, 1261) < 0$, $\Psi(1456, 1178) < 0$, $\Psi(1456, 1122) < 0$, $\Psi(1456, 1097) < 0$, $\Psi(1379, 1284) < 0$, $\Psi(1379, 1261) < 0$, $\Psi(1379, 1178) < 0$, $\Psi(1379, 1122) < 0$, $\Psi(1379, 1097) < 0$, $\Psi(1284, 1261) < 0$, $\Psi(1284, 1097) < 0$, $\Psi(1261, 1097) < 0$, $\Psi(1178, 1097) < 0$, and $\Psi(1122, 1097) < 0$ were identified.

The following sequence of the spectral intensity changes was obtained: $1097 > 1261 > 1284 > 1178 > 1122 > 1379 > 1456 \text{ cm}^{-1}$. This sequence means that the moment of C-O groups in alcohols changes first, followed by C=C groups, C-C groups and C-H groups of aromatic ring, and C-H of methyl and methylene groups, respectively.

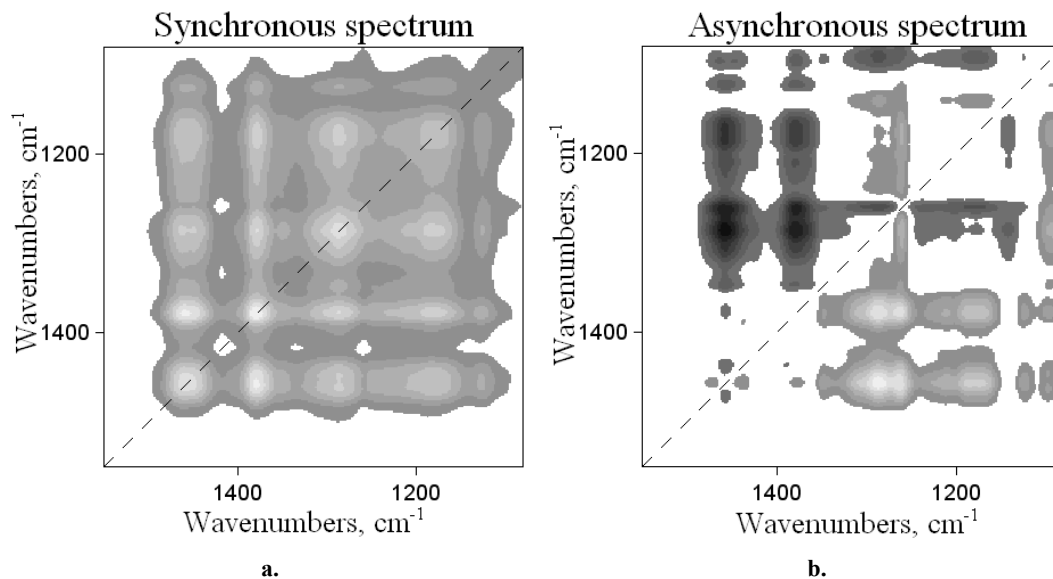


Fig. 4 – Synchronous (a) and asynchronous (b) 2D correlation spectra in the 1550-1080 cm^{-1} region constructed from the exposure time-dependent IR spectra.

The results presented in this paper suggest that during irradiation the photo-oxidative degradation of natural resin components takes place. According to experimental data, ketones are the main initiators of oxidation processes in the resin films following their exposure to light irradiation. The general pattern of oxidation consists in the incorporation of oxygen atoms accompanied by the elimination of hydrogen atoms. Cleavage reactions also lead to a broad distribution of compounds with smaller masses as compared to the initial compounds.¹⁰ Addition of the resulting fragments to another triterpenoid would lead to compounds in the appropriate mass range.

Dammar contains di-, tri- and tetramers of triterpenoids, but the regions between the oligomers are well filled in, indicating substantial cleavage of smaller units from the polymers. The incorporated oxygen is indicated by the increasing of the absorption bands assigned to different stretching vibrations of C=O and C–O groups and by the decreasing of the absorption bands assigned to different stretching vibrations of C=C and C–H groups.

CONCLUSIONS

The spectra of the natural resin films consist essentially in variations of the relative intensities of some significant bands. The spectral changes observed after the irradiation refer to the absorption bands assigned to the stretching and bending vibrations of the C=O, C–O, C=C, C–C

and C–H groups existing in the triterpenoid compounds.

During light irradiation, ketones act as the main initiators of oxidation and the photo-oxidative degradation of natural resin components takes place through the incorporation of oxygen atoms and elimination of hydrogen atoms. Cleavage reactions lead to a broad distribution of compounds with smaller masses than the initial compounds.

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