

Potential of ATR-FTIR Spectroscopy for the Classification of Natural Resins

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ABSTRACT

This study reports evidence on the feasibility of a classification of natural resins by ATR-FTIR spectroscopy based on specific absorbance band positions. A set of twelve selected resins were used to assess band position variability and this vibrational data was put in relationship with the chemical composition of the resins. As a result, a classification of resins into the following four main families is proposed: 1) those correlated with communic acids (sandrac, black copal, pine pitch and amber); 2) those associated with abietic acid (rosin and mastic); 3) those with ketone groups (white copal, tragacanth and frankincense); and 4) those with ester groups (myrrh, shellac and propolis). This classification system may find application not only in facile quality control of natural products, but also for rapid characterization of cultural heritage materials.

Key words: Classification, FTIR, Resins, Vibrational characterization, *terpenes*.

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INTRODUCTION

Resins are lustrous, brittle, transparent and hard substances which are normally orange, yellow or brown in colour. They are amorphous and break with conchoidal fracture, and burn away completely, giving smoky flames and aromatic smells. They are water insoluble, but dissolve in organic solvents such as turpentine, oil or petroleum spirits. Natural resins are of vegetable origin, being obtained from tree exudation or from insects secretions.^{1,2}

The different types of resins

Notable examples of plant resins include black copal from the araucariaceae *Agathis dammara*, white copal (*Copalcuáuitl*) from *Bursera jorullensis* or *Bursera linanoe*, dammar gum from trees of the family *Dipterocarpaceae*, *Dragon's blood* from the dragon trees (*Dracaena* species), frankincense from *Boswellia sacra*, gum guaiacum from the *lignum vitae* trees of the genus *Guaiacum*, mastic (plant resin) from the mastic tree *Pistacia lentiscus*, myrrh from shrubs of *Commiphora* or sandrac resin from *Tetraclinis articulate*. Other well-known resins are pine rosin (from pines and conifers), produced from fresh liquid resin by vaporization of terpene components; shellac, secreted by the female lac bug (*Lacifer lacca*) on trees in the forests of India and Thailand; or propolis, consisting largely of resins collected from poplars and conifers and used by honey bees to seal gaps in their hives. Finally, ambers (also called *resinite*) from coniferous and other tree species³ and tragacanth, a polysaccharide gum extracted from several species

of leguminous plants of the genus *Astragalus* (which yields a sap-like material used in Medicine), can also be included in the resins category.

Composition

The resin produced by most plants is composed mainly of terpenes and their derivatives. The most common in resins are bicyclic terpenes (namely α -pinene, β -pinene, δ -3 carene and sabinene), followed by monocyclic terpenes (e.g., limonene and terpinolene) and –in smaller amounts– by tricyclic ones (such as sesquiterpenes, longifolene, caryophyllene and δ -cadinene).

Almost all resins also contain a high proportion of resin acids. These are closely related to the terpenes, if they derive from them through partial oxidation. Examples of resin acids are communic, abietic (sylvic acid) and boswellic acids (Figure 1).

Amber is heterogeneous in composition, but consists of a macromolecule formed by free radical polymerization of several precursors from the labdane family (e.g., communic acid, cummunol and biformene).^{4,5} These labdanes are diterpenes and trienes, equipping the organic skeleton with three alkene groups for polymerization. Amber also contains succinoabietic acid. Abietic acid can be extracted from rosin by means of hot alcohol and, upon oxidation, yields trimellitic, isophthalic and terebic acids. Boswellic acids are a series of pentacyclic triterpene molecules produced by plants in the genus *Boswellia*. An analogous terpenoid composition is also exhibited by com-

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mercial samples of Mexican *copal-lágrima* (*Bursera fagaroides*) due to the presence of boswellic acids.⁶ Other interesting white Mexican copals are those obtained from the *Bursera jorullensis* and *Bursera linanoe* trees.^{6,7}

Classifications of resins

Natural resins can be classified by genera. Thus, the *Bursereae* –which is further split into *Boswelliinae* and *Burserinae* subtribes– contains *Bursera* (copal), *Boswellia* (frankincense) and *Commiphora* (myrrh).

Natural resins may also be categorized according to their age: recent resins from growing or standing trees (e.g., rosin); recent fossil resins (e.g., copal); and fossil resins (amber).¹

Hardness has been used as a grouping criterion too: soft resins (dammar, mastic, sandarac) and hard resins (Madagascar and Zanzibar copals).^{8,9}

Alternatively, the cataloguing can be conducted according to their solubility in specific solvents: spirit soluble (shellac, rosin, sandarac); turpentine soluble (dammar and mastic); and oil soluble (copal from Congo).¹

On the other hand, natural resins may also be organized according to their terpene composition: abietane diterpenoids (rosin); labdane diterpenoids (sandarac and copal); and triterpenoids (dammar and almáciga).¹⁰

Nevertheless, in spite of aforementioned suggested classifications, the identification of natural resins is still an open problem, not only because of their large number (when the resin comes from tropical countries this number may run into hundreds), complexity and variety of their compositions (many of which are unknown), but also because they frequently change with ageing due to oxidation or polymerization processes.¹¹

ATR-FTIR spectroscopy as a classification tool

Infrared spectroscopy is a valuable method for the classification of organic materials. Complex natural materials produce overlapping spectral bands resulting in a blended, yet representative, plot which may be used to identify a material. Pure synthetic resins produce vibrational bands which are readily identifiable by Fourier Transform Infrared spectroscopy (FTIR), a fact that led to a first classification attempt by Derrick *et al.*^{12,13} Nevertheless, traditional transmission-based FTIR involves the use of KBr pellets and liquid cells, which has some drawbacks. These disadvantages can be overcome by resorting to ATR (Attenuated Total Reflection), which enables all sort of samples (e.g., solids, liquids, powders, pastes, pellets, slurries, fibres, etc.) to be examined without further preparation in a fast, reliable and cost-effective way.¹⁴ This technique is based on the attenuation effect of light when it is internally reflected at an interface between a high refractive index material (an internal reflection element) and an infrared absorbing low refractive index material (the sample). The light extends into the latter as an evanescent wave with a depth of penetration typically between 0.5 and 2 μm , and the beam –after one or several reflections– is then collected by a detector as it exits the crystal.¹⁵ The accessibility of ATR-FTIR and its high reproducibility has led to a substantial use by the scientific community.

MATERIALS AND METHODS

In this study, four resins were characterized: *copal blanco* from Chiapas, Mexico; myrrh from the region south of the Gulf of Aden (where it is named *mur* or *mulmul*); tragacanth from Turkey; and shellac from India. All samples were acquired *in situ* at local dealers. Their infrared spectra were recorded with a Thermo Scientific (Waltham, MA, USA) Nicolet iS50 FT-IR spectrometer, equipped with an in-built diamond ATR system, with a 1 cm^{-1} spectral resolution and 64 scans.

The other natural resins spectra were obtained from a bibliographical survey or from IRUG (Infrared and Raman Users Group) spectral database (www.irug.org).

RESULTS

The ATR-FTIR spectra of white copal, tragacanth, myrrh and shellac resins are shown in Figure 2. Their bands have been put in relation with those of other resins reported in the literature (see Table 1). Band assignments are summarized in Table 2.

The various types of natural resins exhibit several important spectral features in the infrared region. Resins can be distinguished from carbohydrates, waxes and oils by the presence of two bands: one between 1650 cm^{-1} and 1633 cm^{-1} and the other between 1260 cm^{-1} and 1238 cm^{-1} . The first is due to $\nu(\text{C}=\text{C})$ vibrations and the second is associated to $\delta(\text{C}-\text{H})$ vibrations. Another distinguishing band that all resins share is a strong carbonyl ($\text{C}=\text{O}$) stretch at 1738–1694 cm^{-1} . This band broadens with resin degradation and oxidation, but the band maximum remains within this wavenumber region. Bands in the fingerprint region are characteristic for each particular resin and may be used to distinguish them (e.g., 879 cm^{-1} for true copal¹⁶ or 725 cm^{-1} for myrrh).

In agreement with the literature,^{12,17} the frequencies at around 1700 cm^{-1} were chosen as a criterion for ordering and grouping the different resins into three main families: those which absorb at lower wavenumbers, between 1690 and 1710 cm^{-1} , due to the presence of carboxylic acids (juniper, sandarac, black copal, Madagascar copal, dammar, rosin, pitch, mastic and Baltic amber); those with bands at wavenumbers between 1713 and 1727 cm^{-1} , associated with phenol group (spinifex and mopamopa) or ketone group (white copal, tragacanth and frankincense); and

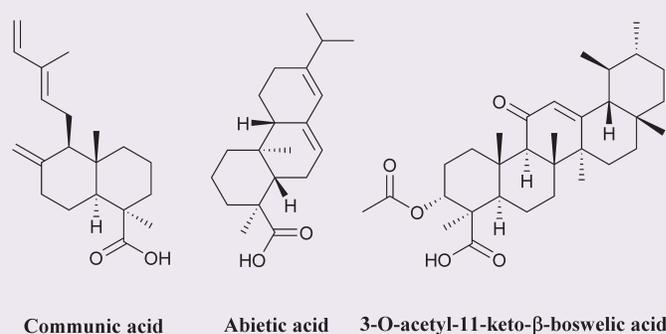


Figure 1. Examples of resin acids.

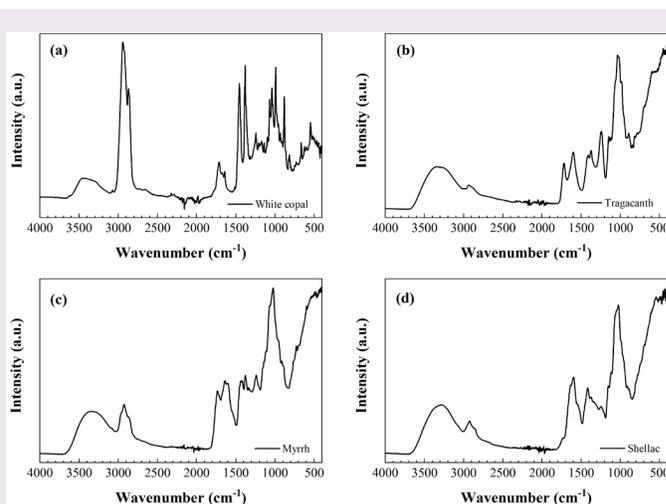


Figure 2. ATR-FTIR spectra of (a) white copal, (b) tragacanth, (c) myrrh and (d) shellac resins.

Table 1: Main band wavenumbers in the infrared spectra of various resins (in cm⁻¹).

	Sandarac ¹²	Black copal ¹²	Pine pitch ¹⁹	Amber ⁴	Rosin ¹²	Mastic ¹³	White copal	Tragacanth	Frank incense ²⁰	Myrrh	Shellac	Propolis ²¹
1	3079	3079	3070	3076			3477	3335	3423	3348	3277	
2	2933	2933	2931	2927	2936	2949	2943	2932	2929	2925	2921	2930
3	2873	2873	2869	2867	2870	2874	2868				2854	2873
4	1694	1694	1694	1696	1697	1707	1713	1716	1718	1732	1738	1740*
5	1643	1643		1643	1650	1650	1641		1658	1635	1633	1640
6			1607		1612			1600			1597	1598
7	1497		1515		1496							
8	1449	1449	1453	1454		1459	1453	1410	1456	1435	1417	
9	1329	1329	1379	1384	1365		1379	1371	1377	1378	1373	1377
10	1236	1228	1243		1239	1245	1242	1242	1242	1238	1247	1228
11	1153	1149	1125	1159	1130	1161	1137	1145			1150	1136
12			1114		1107	1115	1095	1120			1112	
13							1067		1078			1078
14			1033	1024		1046	1036	1034	1045	1023	1023	1038
15	972			975	980	1008	989					989
16	909		909		910						909	920
17	856	889		887			879	892				
18	823				823	837	819	846				836
19				744						725		
20						580		595		597	599	
21				540			547	521			542	
22							500	499		494	495	
23							473			475	483	
24							455	455			454	
25							438	440		440	446	
26								429		422	421	

* Band not always present: it depends on the origin of the propolis. Its presence has been associated to 3,7-dihydroxy-5-methoxyflavone²² or a chemical interaction with hemicellulose from wood.²³

Table 2: Infrared band assignments

Band	Assignment	Band	Assignment
1	$\nu(\text{O-H})$	12	O-H group, $\nu(\text{C-O-C})$
2	$\nu(\text{C-H})$ from CH_3 and CH_2	13	$\nu(\text{C-O-C})$
3	$\nu(\text{C-H})$ from CH_3	14	$\nu(\text{C-O})$
4	Ketone, ester	15	C-O bonds
5	$\nu(\text{C=C})$ / exocyclic methylene groups. Typical of resins	16	$\delta(\text{C=CH}_2)$
6	$\nu(\text{C=C})$ aromatic ring / $\nu(\text{C=O})$ amide	17	Exocyclic methylene groups.
7	$\nu(\text{C=C})$. Typical of phenolic resins	18	Typical of phenolic resins (after heating)
8	$\delta(\text{CH}_2)$, $\delta(\text{CH}_3)$	19	1,2-cis-disubstituted olefin. Typical of myrrh
9	$\delta(\text{CH}_3)$	20	$\delta(\text{C-H})$ in the furan ring
10	$\delta(\text{C-H})$, $\nu(\text{C-O-H})$. Typical of resins	21	Unsaturated bonds
11	$\nu(\text{C-O-C})$, esters		

those with bands located at higher wavenumbers, between 1731-1738 cm⁻¹, because of ester group (myrrh and shellac).

When –for the first of aforementioned families– the comparison of that single band is extended to the whole spectrum, a close correspondence for rosin and mastic was readily found (revealed by a high correlation

value, see Table 3), which would allow their differentiation from the other two resins (sandarac and black copal).

This finding opened the possibility of splitting the first family into two sub-families: those with communic acids (sandarac, copal and ambers) and those with abietic acid (rosin and mastic).

Table 3: Correlation matrix

	Rosin	Pitch	Sandarac	Black copal	Mastic	White copal	Frankincense	Myrrh	Shellac
Rosin	1.000	0.895	0.900	0.903	0.906	0.903	0.885	0.885	0.899

DISCUSSION

The proposed classification of the resins into families is based on the frequencies of their infrared spectra, and such spectra can be obtained either by FTIR or by ATR-FTIR, which is known to lead to small shifts in peak positions.¹⁸ Four spectra were obtained by ATR-FTIR and compared against analogous IRUG database spectra (obtained by KBr method). Good correlation was observed, with shifts below 3 cm⁻¹ in all cases and was comparable to those found amongst samples from different laboratories in the IRUG database. Special attention was paid to the differences that may arise in the wavenumbers of the band(s) around 1700 cm⁻¹, which were taken as a classification key: for fresh samples, the maximum difference was 2 cm⁻¹. Another was the case for aged or heated samples, but the incidence of such interferences can be easily anticipated by checking the disappearance upon aging of the bands at 1643 and 1607 cm⁻¹, attributed to $\nu(\text{C}=\text{C})$ vibrations, and the increased absorption upon heating of $\nu(\text{C}-\text{O}-\text{C})$ and $\nu(\text{C}-\text{O}-\text{H})$ bands at 1153 and 1240 cm⁻¹, respectively.

The purity degree would also have a remarkable impact on the resins' absorption bands. For instance, seedlac (which contains 3–5% impurities) would absorb at 1714 cm⁻¹, whereas when it is purified by thermal treatment or by solvent extraction (resulting in the so-called shellac) it absorbs at 1731 cm⁻¹ and even at 1738 cm⁻¹ (if it is very pure).

CONCLUSION

ATR-FTIR spectroscopy can provide a useful approach to allow the categorization of resins into families based on a set of band positions (in particular the bands located at around 1700 cm⁻¹). The vibrational features suggest the differentiation of at least four main families: (I) those with communic acids (including sandarac, black copal, pine pitch and ambers), which absorb between 1690 and 1696 cm⁻¹; (II) those with abietic acid (consisting of rosin and mastic), with absorption bands between 1697 and 1710 cm⁻¹; (III) those with ketone group (encompassing white copal, tragacanth and frankincense), which absorbs between 1713 and 1727 cm⁻¹; and (IV) those with ester group (comprising myrrh, shellac, and propolis), which absorbs between 1731–1738 cm⁻¹.

ABBREVIATION USED

FTIR: Fourier Transform Infrared spectroscopy; **ATR:** Attenuated Total Reflection.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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