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Non-destructive characterization of archaeological resins: seeking alteration criteria through vibrational signatures

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Abstract

Natural resins are prone, as all natural organic products, to ageing and degradation. Characterizing this alteration provides a better knowledge about their chemistry, and when they are involved in cultural heritage artefacts, it helps to define relevant conservation protocols. In this study, a set of archaeological African copals that present specific surface degradations and colors were analyzed by FT-Raman and ATR-IR spectroscopies. A methodology based on the modifications of the vibrational features between the bulk and the resins surface was define. A relation between the evolution of the molecular structure of the copal samples and some vibrational bands could be established; and possible ageing reactions occurring at the surface of the samples could be proposed. This specific surface aspect is actually related to an alteration, and the surface states and the colors variability are linked to different alteration degrees. This could refer to whether different conservation contexts (presence of air, water, etc), possible preparation or different origins: for example the collection of fresh or partly fossilized resins.

Keywords

FT-Raman, ATR-Infrared, archaeological resins, copal, ageing, spectral decomposition

A. Introduction

Natural resinous substances have been used, across time, for different purposes, and in different forms: in their raw form, such as frankincense or myrrh as incense ¹, or amber and copal for jewellery ^{2,3}; or different tree exudates for healing purposes or religious ceremonials

^{4,5}. They also have been used after some treatments (heating, mixtures): as adhesives ^{6,7} or waterproofing materials for ceramics ⁸ or ship building ^{1,9} and finally as binders for paint ¹⁰ or part of a varnish composition ^{11,12}.

Besides, as all natural substances, resinous materials are highly exposed to ageing and degradation, which constitute an issue when it comes to Cultural Heritage artefacts. It is thus important to characterize the alteration and degradation processes in order to have, on one hand, a better understanding of the past and present chemistry of these substances; and to be able, on the other hand, to make viable and accurate diagnoses about their conservation state.

The identification of such substances is usually done by separative techniques often coupled to mass spectrometry ^{13,14} which nevertheless require a destructive sampling and a reasoned choice of analytical and/or pre-treatment conditions. However, working on cultural heritage artefacts often requests non destructive techniques that perform rapid analyses with slight experimental constraints. Vibrational spectroscopies are increasingly employed for identification purposes by setting up reference databases, ^{15,16} or to give spectroscopic clues to differentiate between organic substances ^{17,18,19,20,21,22} with some specific studies on archaeological resins ^{23,24}. Indeed, when ancient organic materials are involved, the question of ageing and degradation is raised. The molecular modifications cause changes in the vibrational signatures, and it becomes difficult to define spectral databases of substances that evolve over time ²⁵.

Previous studies using Raman spectroscopy ^{4,26,27} tried to find ageing criteria for natural resins mostly based on two bands intensity ratio (I_{1650}/I_{1450}) that evolves from a fresh resin to an aged one. However they have based their work on a corpus of resins from different chemical families, origins, size and aspects. This large variety of parameters complicates the study; their respective influence is difficult to demonstrate.

This study focuses on artefacts with the same chemistry and origin, found in a same excavation site from the 13th century: copals from Africa and/or Madagascar found in Sharma (Yemen) ²⁸. Besides, the altered and unaltered analyzed materials are part of a same sample, since their surface seems degraded, and the core of the resins has a fresh transparent aspect. Furthermore, among all the copals found in this excavation site, three groups could be formed, based on their colors and aspects. This difference in the appearance might be related to different surface alteration states, and was the motivation for this work. We tried then to get

chemical information about the alteration processes with samples matching different stages of the copal ageing.

In this work, FT-Raman and IR-microATR analyses were performed on a set of copals, whether on the internal or external samplings. We applied the I_{1650}/I_{1450} ratio as an ageing criterion but the obtained trend was opposite to the one obtained by Winkler *et al.*²⁶. In order to understand this evolution and to get more precise degradation criteria, but also to propose some chemical interpretations to the spectral changes, spectral decomposition calculations were performed on different regions of the Raman and IR spectra. Finally, some hypotheses on the chemical evolution of the copals molecular structures are presented, and a progression of the ageing with the colors and surface aspects of the resins is highlighted with a proposition of new indexes.

B. Analyzed material

B.1. Samples

Ten samples of archeological copal from a medieval site in Sharma (Yemen)^{28,29} have been analyzed. They have been previously identified as eastern African and/or Madagascar copals by their molecular markers thanks to GC/MS and py-GC/MS³⁰. This ensures, for the archaeological studied samples, a same biological origin and hence identical chemical characteristics. It is thus possible to attempt reliable statements about their degradation processes. These artefacts are raw fragments of copal which have a same hard and transparent bulk but different surface states and colors (Fig. 1): from yellow fragments with a thin dry surface, to orange fragments with a flaked-off surface and finally red fragments with a thick and very friable surface. Moreover, all the samples are wholly preserved, even sometimes with traces of sediments.

For these archaeological copals, a specific analyzing procedure was applied: small flakes from the internal and external parts of each artefact were sampled and separately analyzed to take into account this heterogeneity. Since the implemented analyses are non-destructive, each flake could be analyzed by FT-Raman then IR-microATR. For each fragments several points were analyzed and the very similar spectra were averaged in order to improve the signal-to-noise ratio.

B.2. Chemical composition

African and Madagascar copals are diterpenic resins that exude from trees of the *Leguminosae* family, and have as major components copalic and cis-ozic acids (Fig. 2) based on a labdane type skeleton³¹. Copals are known to be highly polymerized resins, and most of the time, a pyrolysis step is needed for the separative methods analyses^{32,33}.

C. Instrumentation

C.1. Raman spectroscopy

To overcome the high fluorescence of such organic samples which prevent the observation of Raman scattering, we favor a near infrared excitation at 1064 nm from an Nd-YAG laser diode. The FT-Raman spectrometer is a Bruker RFS 100/S based on a Michelson-type interferometer and equipped with a liquid nitrogen-cooled Ge detector.

The samples were analyzed using a microscope interface with a 40x IR objective, allowing a spot size of 30 μm approximately. In order to improve the collected Raman signal intensity, the samples were placed on a gold mirror. Laser power at the sample was adjusted at 250 mW (nominal power of 500 mW) and no damage or heating of the materials was observed. Spectra were recorded between 3500 and 50 cm^{-1} with a 4 cm^{-1} resolution and a low signal-to-noise ratio was achieved by accumulating 1500 scans.

C.2. Infrared spectroscopy

Non destructive micro-infrared spectroscopy analysis is carried out in micro Attenuated Total Reflectance mode (IR-microATR). Measurements by contact were performed with a 100 μm diameter Germanium crystal tip (mono-reflection) fixed on the 20x objective of an IRscope II microscope which also allows the visualization of the analyzed area. The microscope is linked to a Bruker Equinox 55 spectrometer equipped with a liquid nitrogen-cooled MCT detector. Spectra between 4000 and 600 cm^{-1} with a 4 cm^{-1} resolution were recorded with 200 scans accumulated.

D. Ageing characterization: methodology, results and discussion

D.1. The “vibrational features/molecular structures” relation

Spectra from internal and external fragments were first compared to underline their main differences and the effect of degradation on their molecular structure. Figure 3 presents the FT-Raman and IR-ATR spectra representative of an externally red archaeological copal. On the FT-Raman spectrum (Fig. 3 a)) of the external part of the copal grain, in addition to a light fluorescence background due to the intense color of the surface, the bands are less intense and broader than the internal part one. The most important differences are located in the 1650-1500 cm^{-1} region assigned to the stretching vibrations of the CC double bonds. Another region shows some decrease in the intensity, the CH stretching vibration massif, around 2900 cm^{-1} . For the IR spectra (Fig 3 b)), some bands decrease, for example the band at 887 cm^{-1} assigned to the bending vibration of the CH bonds in vinyl groups, others increase, especially a band around 1580 cm^{-1} , assigned to the C=C stretching vibration of aromatic groups. The alteration has also an impact on the CH stretching massif of the IR spectra, specifically the band at 3075 cm^{-1} assigned to CH bonds in vinyl groups.

The various observations made on the FT-Raman and IR spectra global profiles of a red copal underline the chemical transformations that occurred within the copal surface. These modifications can be considered as alteration, and can also be related to the color of the resin: more colored is the sample, more altered it will be. Moreover, it is correlated to the sample surface aspect, from dry in appearance to brittle, highlighting a mechanical de-cohesion derived from a chemical transformation. It is thus interesting to have an improved description and a better understanding of these spectral evolutions, and try to find specific alteration criteria that can be easily obtained.

D.2. Seeking degradation criteria

Previous studies showed the possibility of characterizing the maturation of such resins using Raman spectroscopy, by a band intensity ratio: the stretching vibration of the C=C bonds band around 1650 cm^{-1} with the deformation vibration of the C-H bonds band around 1450 cm^{-1} ^{26,27}. We have already seen that the latter does not show an important intensity variation with degradation, but the former is highly influenced by the alteration process and significantly decreases. However this ratio has different meanings according to the different cited studies. Winkler *et al.*²⁶ underline that the resin is rather “fresh” or unaltered for higher intensity ratio ($I_{\text{vC=C}}/I_{\delta\text{C-H}}$) values, and that this ratio decreases with the sample age. Brody *et al.*²⁷ present the same ratio variation, but do not properly link it with the samples age. They

170 evoke the influence of environmental factors in the resins evolution, as well as the influence
171 of the different chemical compositions from a diterpenic resin to another (botanical origin).

172
173 The comparison between the internal and external parts of the studied copals shows an
174 inverse trend in this ratio (see Table 1 and Fig. 4). First, for the internal parts of the ten
175 samples, the ratio is located between 0.89 and 1.15 with a mean value at 1.05 for a standard
176 deviation of about 9%. According to Winkler *et al.*²⁶, all our copals have about the same age.
177 According to Brody *et al.*²⁷, this very similar index value underlines comparable chemical
178 states, which is consistent with the attested origin of our eastern Africa and/or Madagascar
179 copals. However, both papers^{26,27} do not specify the analyzed part of the samples (surface,
180 bulk, or possible heterogeneities), but since they are interested by representative samples, we
181 assume that only the “bulk” of their samples was considered. In our study, only one kind of
182 resinous material was selected: same chemistry³⁰ and thus same geological origin.
183 Furthermore, our aim is to compare the internal and external altered parts in order to follow
184 this degradation process. The expected results are therefore not related to the age, the
185 maturation or fossilization processes of the resin.

186
187 By comparing the index values for the external parts of the three groups of copals, it
188 can be noticed first that for the yellow samples, the ratios for the external samplings are
189 consistently lower than for internal ones. However, the ratio for the external samplings
190 increases significantly from yellow to red samples (from 1 to 1.76), according to the
191 established degradation progression. A deeper look at the Raman bands profile of the copals
192 external parts (Fig. 4) in the 1800-1400 cm⁻¹ region, highlights a stable shape the 1500-1400
193 cm⁻¹ area, while significant differences can be observed in the 1700-1500 cm⁻¹ region. For the
194 yellow copals, the C=C stretching band is less intense (Fig. 4 a) and b)), and seems slightly
195 larger than the internal part spectra. For the orange copals (Fig. 4 c)), the 1650 cm⁻¹ massif
196 increases; and finally get very intense and broad for the red copals (Fig. 4 d)) with a
197 maximum shifted to 1580 cm⁻¹. We can thus underline a clear global increase of the intensity
198 of the I₁₆₅₀/I₁₄₅₀ ratio related to the surface degradation state of these copals. This ratio index
199 is here considered as an alteration marker of the samples surface. Besides, the evolution of the
200 index all along the degradation process is not strictly linear, since a slight decrease is
201 observed between the external and internal parts of the less altered samples (yellow copal).

However, even if this index is easily calculated and appears to be related with the degradation state, more detailed information about the chemical processes that occur should be extracted thanks to a deeper analysis of the bands profile.

D.3. Spectral decomposition, finding a general pattern

D.3.1. Fingerprint spectral region

A specific methodology for the spectral decomposition process was adopted, with the aim of monitoring the bands evolution, and trying to define the bands, and thus the specific bonds, that are most affected by the ageing. It was first applied on the fingerprint region (1800-1400 cm^{-1}) since it seems to undergo several modifications, especially on the FT-Raman spectra. The spectra of all the internal and surface samples were truncated between 1925 and 1395 cm^{-1} , then a linear baseline was subtracted (set points: 1925, around 1515 and 1395 cm^{-1}) and finally the cut spectra were normalized on the 1450 cm^{-1} massif intensity, since it appears unchanged with the resin ageing (Opus software, Bruker).

The decomposition procedure (Asrel2 homemade software, LADIR) was defined according to several parameters: the number of bands and their position (P), the area (A), the full width at half maximum (W) and the profile (K) of the band (which equals 0 if Gaussian, 1 if Lorentzian). The number and initial positions of the bands were determined by calculating the second derivative of the massif for each spectrum. Each minimum on the derivative indicates the position of a band. The same number of bands (11 bands) was defined for the internal and surface samples, 7 bands in the C=C vibration massif, and 4 bands in the C-H deformation massif. Concerning the adjustment procedure, it is based on a least squares method which adjusts the band parameters to fit the experimental spectrum.

Figure 5 illustrates the results of this procedure. For all the 10 internal samples, the decomposition result was the same, thus only one is presented (Fig. 5 a)). In general, for external samples same number of bands was obtained for all the fittings, but their position and profile differ from a sample group to another. Figure 6 shows a graph representing the evolution of the bands position between the surface sample fitting results and the internal sample ones, for the 3 groups of copals. For external samples (Fig. 5 b) to d)), it can be easily noticed that the positions of the 4 bands related to the C-H deformation massif are not really changing (bands 1 to 4), in contrast to the bands 5 to 11 that undergo important shifts

especially for the orange and red copals. Using this spectral region for the study of the resins ageing is therefore currently compromised by the difficulty of finding an objective generic fitting pattern for the Raman spectra of the internal and external parts. It is thus difficult to distinctly underline and follow the bands that evolve with the resin alteration, and even harder to link this evolution to specific vibrators in this spectral region.

D.3.2. CH massif region

It was therefore necessary to focus on another spectral area that show an evolution of its vibrational features with the resin alteration, in order to point out these bands and then correlate these changes to chemical modifications at the resins surface. As it was said before, the CH stretching vibration massif (centered at 2900 cm^{-1}) present several variations, whether on the IR or FT-Raman spectra. This region has been less studied, but can be very informative for substance discrimination^{34, 35}, or to assess if its features evolutions are characteristics of some organic binders alteration³⁶.

The previous spectral decomposition methodology was applied to this region: the spectra have been truncated, baseline subtracted, normalized, and finally fitted with 7 bands as observed on the second derivative for both Raman and IR spectra and all samples (see example on Fig. 7). It can be noticed that the minima observed on the second derivatives are in the same positions for the internal and external fragments spectra. These 7 bands (numbered from 12 to 18 to avoid any confusion with the $1800\text{-}1400\text{ cm}^{-1}$ region bands) are assigned to C-H bonds in different chemical groups or environments: band 12 is assigned to $\nu(\text{CH})_s$ in CH_2 groups; bands 13 and 14 to $\nu(\text{CH})_s$ in CH_3 or CH groups; band 15 to $\nu(\text{CH})_{as}$ in CH_2 groups; band 16 to $\nu(\text{CH})_{as}$ in CH_3 groups; band 17 to $\nu(\text{CH})$ in aromatic groups; and finally band 18 to $\nu(\text{CH})$ in vinyl groups.

Comparing internal and external samplings signatures, the bands that generally vary the most are bands 12 and 18, at respectively 2849 and 3081 cm^{-1} for Raman and IR data (Fig. 7 c), colored bands). These two bands decrease significantly: indeed the 2849 cm^{-1} band that appears thin and relatively intense on the internal fragment spectrum, is more like a shoulder on the external sample spectrum; and the 3081 cm^{-1} band seems to decrease and gets broad, and tends to disappear. In order to quantify and characterize the spectral modifications, the fitting parameters (A, W and K) of the internal and external samples have been taken into account. Since the bands positions (P) are the same for the internal and external samples

spectra, it was not taken into account for these calculations. Figure 8 represents the calculated differences for the areas (A) and the width at half maximum (W). Globally, the parameters do not show the same progress for all the bands. For Raman and IR data, the A and W parameters of bands 14 and 15 present an about 10% variation between the surface and the core of the resins: these two bands are in the middle of the CH stretching massif, and are not strongly affected by the resin ageing. Bands 12 and 18 are the most affected by the surface alteration: the areas are highly decreasing (up to 80% for band 18 on the IR spectra), and the widths at half maximum are increasing (up to 100% for band 18). These remarks are directly related to previous qualitative observation on the spectra fittings: if a band decrease and gets broader, its intensity necessarily decreases. Finally, A and W for bands 13 and 17 are slightly increasing: it is probably due to the fitting procedure during which the bands fulfill the massif ends to optimize the spectral adjustment. Finally, figure 8 shows that the extreme values for the relative differences are for the red copals, which are the most altered resins of the corpus. The last parameter, K the band profile, tends to decrease for all the bands and all the samples, evolving towards a Gaussian profile.

D.4. Ageing and degradation: chemical interpretation

Band 18 is the most changing band and is assigned to CH vibrations in exocyclic CC double bonds which are highly present in the copal major components molecular structure (see Fig. 2). The important decrease of this band could be explained by an oxidation of the C=C bonds, and a cyclization reaction. These phenomena can occur more or less moderate, depending on the conservation environments: a resin exposed to the air is more prone to oxidation than a buried resin in a dry and close climate. Such reactions can explain the broadening of the 1630 cm^{-1} band on the Raman spectra and, on the IR spectra, the presence of a band around 1580 cm^{-1} , and also the decrease of the 887 cm^{-1} band, assigned to the bending vibration of olefinic CH. The two former observations can point out the formation of conjugated C=C aromatic bonds, which also explain the shift of the 1650 cm^{-1} band to lower wavenumbers; and the coloration of the samples surface as well.

Band 12 is assigned to the symmetric vibration of CH bonds in aliphatic CH_2 groups, and shows a relatively significant variation which can be related to cyclization reactions leading to the loss of CH_2 aliphatic chains; or, if the surface is highly altered, to chain breaking, explaining the brittleness of the surface for some samples.

Finally, the decrease of the K parameter, describing the evolution to a Gaussian profile of most of the bands, illustrates the emergence of disorder within the altered material. Indeed, a vibrator has normally a Lorentzian shape, but when a kind of disorder appears (for example random chain breakings) the vibrators are no longer identical because of the new different structural environments. Their characteristics are then randomly dispersed around a mean value, introducing a Gaussian feature in the band profile.

Alteration indexes can also be calculated or drawn based on the CH massif decomposition parameters. Figure 9 shows two plots of different fitting parameters of the external samplings spectra, involving the full width at half maximum of various bands. As said before, bands 12 and 18 are the two bands that evolve the most within the CH massif, and band 15 is the central and most intense one, and is the less influenced by the alteration. Nevertheless, it evolves sufficiently to inform about the degradation state. We can notice, on these two plots, that the samples are sorted along the diagonal according to their colors, with an internal sample at the very beginning of the graphs, as a reference point. These parameters (or ratios) can thus be considered as new degradation indexes involving the CH massif features. It is thereby possible to monitor the copals alteration by considering the external parts of the samples. With this new approach, it appears that sampling is not necessary to characterize a sample degradation state; the analyses can be performed directly on the samples surface in a totally non destructive way.

E. Conclusion

The study of a collection of ancient copal artefacts from the same family tree and preserved in the same archaeological site allowed the observation of molecular scale alterations thanks to non destructive FT-Raman and IR-microATR spectroscopies. These artefacts, first classified by their apparent color (from yellow to red) and surface aspect (from dry to pulverulent, respectively), were sampled at their surface and in their bulk, enabling a direct comparison, and a characterization of their surface degradation. The restriction of the study to this samples set has prevented the introduction of additional parameters (variability of the chemical nature and uncertain origins) that can complicate the interpretations.

General observations of the vibrational signatures have underlined more important modifications of the molecular structure for the red copals than for the orange and yellow ones. The degradation state was first evaluated by FT-Raman using a previously proposed I_{1650}/I_{1450} ratio^{26,27}. However, in our study, this ratio has a reverse evolution; lower values are obtained for less altered samples, and the index increases with the degradation state. This questions the chemical processes documented by this index. Is it related to long term fossilization processes affecting the whole sample, or some alterations starting from the surface? To meet some further detailed studies are required in order to specify the role of each parameter (chemistry, environment, time, etc) and their possible interactions.

Then, a relation between the copals molecular structures and the evolution of some vibrational features were investigated focusing of the spectral regions presenting the larger variations. Spectral decomposition was then implemented to identify and monitor the evolution of the bands assigned to specific structural features. A too important bands shift in the fingerprint region ($1800\text{-}1400\text{ cm}^{-1}$) has hampered the built up of a unique decomposition model according to the resins degradation; and therefore the precise identification of the concerned bands and chemical bonds. However, the treatment of the CH stretching region ($3100\text{-}2800\text{ cm}^{-1}$) has underlined bands variations that follow the resins degradation state. Hypotheses on the chemical evolution of copal with ageing were then proposed, as well as other indexes involving the CH massif.

Moreover, knowing that these copals found in Yemen are from eastern Africa and/or Madagascar, they are a testimony of the ancient commercial routes during the 13th century, and their aspects and their conservation states might then be related to specific collection and exploitation modalities. Are the resins freshly collected or gathered from partly fossilized deposits, or have they undergone some possible treatments? The conservation state could underline here if one or several geographical or technical origins are involved for these copals. Further studies with direct dating of the artefacts should bring further information.

Non destructive analytical approaches, with Raman and/or IR spectroscopies, could contribute to the study of resins degradation mechanisms, and propose ageing characterization and monitoring for conservation purposes. As resins are involved in various cultural heritage objects (in raw form, or in preparations as varnishes) such diagnostic tools could be easily implemented by respecting the conservation constraints.

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		I_{v(C=C)} / I_{δ(C-H)}	
Sample		Internal	External
Yellow copals Dry surface	MR1210	0.94	0.83
	MR1212	0.89	0.85
	MR1211	1.09	0.94
	MR1213	1.13	1.07
Orange copals	MS5673	1.11	1.21
	MS5676	1.07	1.25
Red copals Pulverulent surface	MR1225	1.10	1.29
	MR1226	1.15	1.31
	MR1214	0.91	1.33
	MR1234	1.07	1.76

Table 1: Intensity ratio of the 1650 cm⁻¹ / 1450 cm⁻¹ massifs (I_{v(C=C)} / I_{δ(C-H)}) calculated for internal and external parts of 10 copals samples with different external aspects. The intensities were measured at the most intense point of each whole massif, and not at a specific wavenumber.

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473 Fig. 1: Representative samples of the studied copals illustrating the external aspect variability
474 (Samples refs: MR1211, MS5673, MR1234).
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478 Fig. 2: Molecular structure of the majors components of Africa and Madagascar copals. See
479 text (part D.4) for a detailed description of the functions affected by alteration and monitored
480 by vibrational spectroscopy.

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485 Fig. 3: a) FT-Raman and b) ATR-IR spectra from internal (gray line) and external (black line)

486 parts of an externally red sample (Ref: MR1214).

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491 Fig. 4: Representative FT-Raman spectra of 3 copals samples, one from each group: a) yellow
 492 (MR1211) – internal sampling, b) yellow (MR1211) – external sampling, c) orange (MS5673)
 493 – external sampling, and d) red (MR1234) – external sampling. The spectra have all been
 494 normalized on the 1450 cm^{-1} band intensity in order to monitor the 1650 cm^{-1} band evolution.

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498 Fig. 5: Representative band decomposition of FT-Raman spectra for: a) yellow (MR1211) -
 499 internal sampling, b) yellow (MR1211) - external sampling, c) orange (MS5673) - external
 500 sampling and d) red (MR1234) - external sampling (same samples as Fig. 4). Decomposition
 501 bands are numbered from 1 to 11 according to their increasing positions.

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507 Fig. 6: Difference between the external and internal sample bands positions (Δv) of the 11
 508 decomposition bands of the 1900-1400 cm^{-1} region. These are mean values for each group.

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Fig. 7: ATR-IR and FT-Raman CH massifs for internal and external parts of a red sample (MR1214). a) Spectra and their second derivative, b) Decomposition of Raman and IR spectra of its internal part. c) Decomposition of Raman and IR spectra of its external part (colored bands are the most modified during ageing).

Fig. 8: Evolution of some bands parameters (the area A, and the width at half maximum W) between internal and external samplings, mean values for the 3 groups of copals. These normalized relative differences were calculated by the following equation (for each parameter i): $(i_{\text{int.}} - i_{\text{ext.}}) \times 100 / i_{\text{int.}}$

Fig. 9: Plots of parameters extracted from the CH massif band decomposition. A progression in the colors can be observed on the diagonal of each graph which could define new alteration indexes. a) Full width at half maximum of band 12 (W12) versus W15, and b) W18 versus W15.

Graphical TOC

New insights about copal degradation mechanisms are introduced and relevant analytical strategies for resinous substances through non destructive approaches by FT-Raman and ATR-IR are presented.