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► To cite this version:

Michel Sablier, C. Davron, M. Herbin. Characterization of the JAR Sealants in the Fluid Collections of the Muséum National D'histoire Naturelle. Collection Forum, 2020, 34 (1), pp.87-100. 10.14351/0831-4985-34.1.87 . hal-03375917

HAL Id: hal-03375917

<https://hal.science/hal-03375917>

Submitted on 23 Nov 2021

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**Characterization of the jar sealants in the fluid collections of the Muséum
National d'Histoire Naturelle**

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12 Abstract

13 Over the centuries, the composition of jar sealants in natural history museum fluid
14 collections has changed but has been little documented. Consequently, it is of
15 paramount interest to increase our knowledge of sealant composition as well as to
16 correlate this information to the date of manufacture and preparation. The proposed
17 approach is based on the development of an analytical protocol to characterize the
18 composition of sealants encountered in fluid collections of the MNHN. A method
19 based on FTIR spectroscopy and Pyrolysis-GC/MS was employed to investigate
20 sealant composition and was demonstrated to be efficient for the identification and
21 characterization of waxes and resin additives in sealing samples. First results are
22 very promising and should be continued on a large scale for an exhaustive analysis
23 of the fluid collections of the Muséum National d'Histoire Naturelle in Paris.

24

25

26 **Introduction**

27 Until the 17th century, most specimens in natural history collections were preserved
28 dry, consisting mainly of skeletons, taxidermy preparations, dehydrated specimens,
29 and casts. Many of the specimens which were kept in fluids were not well preserved
30 and degraded more or less quickly (but mostly inevitably). At that time, specimens
31 were collected and then preserved without undergoing any prior treatment or fixation;
32 for the most part they were simply immersed in a preservation solution (Herbin 2013).
33 The choice to preserve the appearance of specimens evolved with the development
34 of advanced research on better means of fixation of specimens. The aim was not
35 only to preserve the external appearance of organisms or organs, but also to fix the
36 tissues and their structures so that they could be studied later (Daubenton 1784).
37 Most of this research was intimately linked to advances in methods of teaching
38 anatomy and in the field of histology. The conservation of natural history specimens
39 has always posed a problem for people, including conservators and curators, who
40 are responsible for looking after their perpetuation.

41 An important concern perpetuated from the early days of fluid collections was how to
42 close a container hermetically to limit the evaporation of the preservative solution
43 (Daubenton 1749) and to limit the influx of oxygen. The study of the history of jar
44 sealing illustrates the clash of the theoretical methods of some with the
45 experimentation of others, and the contribution of practice to adjust established
46 approaches (Pequignot 2019). Jar sealing techniques applied to fluid collections
47 have evolved in close correlation with the evolution of conservation techniques in
48 fluid collections. Daubenton made an inventory of the techniques using metal sheets,
49 white lead, or pig's bladders in the middle of the 18th century (Daubenton 1749) and

developed a recipe for an amalgam based on mercury and lead. Air tight closure remained a concern for naturalists who, failing to find a suitable means of sealing containers, often found themselves powerless in the face of the evaporation of preservative fluids and the gradual degradation of specimens. In addition, given the growing preponderance of naturalist expeditions around the world, the need to find practical and effective solutions for sealing containers became urgent. Among the most important developments was the introduction of the *lithocolle* recipe by François Péron and Charles-Alexandre Lesueur (Péron & Lesueur 1810) which combined cork stoppers, turpentine oil, wax, resin, and red ocher to allow in situ jar sealing with a minimum of materials and best practical efficiency. Later, the introduction of the use of rubber (Maissiat 1847) led to the usage of this material in commercial seals applicable to natural history collections. Since the middle of the 20th century, the use of silicone sealants has increased.

As a consequence, considering both the chronology and the typology of jar sealants is the only reasonable angle allowing a thoughtful and rational approach to the conservation and management of fluid collections.

The quality of sealing systems in fluid collections is a key factor for their stability and long-term performance. The evaporation of preservatives, such as ethanol aerosols or formaldehyde gas, is a major problem in fluid collections that leads to a decrease in final concentration of the preservative in the solution, which is harmful to the specimen (Carter & Neumann 2016) and to airborne emissions that may accumulate in the storage area or the lab which can be harmful for staff members, researchers, and visitors (Burroughs et al. 2006; Defendini 2016). Another recurrent problem relates to the acidification of the storage medium resulting from the influx of oxygen

in the jar (e.g., oxidation of formaldehyde to formic acid, of ethanol to acetic acid, of lipids to fatty acids that opacify the fluid, and color fading caused by oxidation of pigments). These different aspects of fluids are largely dependent on the integrity of the closure, which can be compromised e.g. by microfissures in seals due to repeated expansions and contraction of sealants, on hardening of the sealants, and on the resistance of the seal to solvent vapors and oxygen. However, whether historical or current, their chemical nature, durability, and effectiveness remains largely unknown (van Dam 2000; Herbin 2017; Collins 2014).

A project designed to acquire a better knowledge of the composition and behavior of container seals used in the fluid collections of the Muséum National d'Histoire Naturelle (MNHN) was initiated. As sealing practices have evolved historically and this knowledge has often been abandoned or forgotten in favor of new techniques that were considered easier to implement or more efficient at the time. However, understanding these practices is important, not only for the history of the collections, but above all to also understand, from a conservation perspective, the materials that have proved to be the most effective and that could inspire new approaches.

According to some sources (Simmons 2014; Moore 2007; Herbin 2013) the hermetic seal of historic containers may consist of waxes, bitumen, vegetable resins (e.g. pine resin), paraffin, oils (linseed, turpentine) or a mixture of these components (plus pigments for aesthetic appearance). The naturalist François-Auguste Péron describes an effective luting called "lithocolle" as a mixture of "yellow wax", rosin, red ochre, and turpentine oil (Péron in Péron & Lesueur 1810). Sometimes, to complete the seal, a pig or sheep bladder was added, sometimes covered with a metal sheet made of lead or tin (personal observation). The possible impact on seals permeability

is unknown at this time. Today, contemporary sealing techniques employ different types of silicone which can be more efficient but are also more difficult to remove to access the specimen and are less flexible when environmental conditions (temperature, humidity) change in storage rooms or in galleries. It is therefore possible to classify the sealing techniques according to their composition by using the appropriate techniques for the analysis of these complex mixtures. Waxes, for example, have been widely studied (in other fields) since the advent of separation methods but their characterization remains an analytical challenge. The difficulty lies in the diversity of their components: alkanes, alkenes, acids, alcohols, long chain esters (unsaturated, saturated, or possibly hydroxylated) and polyesters. In addition, the physico-chemical properties of these components make their separation under conventional analytical conditions complex, particularly for mixtures. Their study therefore requires the use of analytical tools with increased potential for the elucidation of their composition.

Methods

Gas chromatography (GC) is one of the most widely applied separation techniques for the identification of organic samples, keeping in mind that these samples must be volatilized for analysis. Most studies of organic materials performed by means of gas chromatography (GC) used flame ionisation detectors (FID), which is a quantitative detector but lacks identification potential. In GC-FID, the compounds emerging from the column are recognized by their retention time so that standards and reference samples are required to positively identify the complex mixtures that compose the samples. The availability of appropriate standards is consequently a limiting step in

122 the application of GC-FID. The higher capacity of mass spectrometry (MS) detectors
123 coupled with the GC for identifying compounds, as well as their greater sensitivity,
124 are the main reasons for the extended use of GC/MS instruments in analytical
125 laboratories.

126 The analytical study of bulk samples (e.g., natural products, coatings) by means of
127 conventional chromatographic separation techniques (such as gas chromatography,
128 thin-layer chromatography and liquid chromatography) has been notably limited given
129 the high molecular weights of their components. This drawback can be overcome by
130 applying a high temperature heating process, commonly between 500 and 800°C
131 (significantly higher than room temperature) to obtain a sort of unspooling of the
132 polymeric structures of the sample, which enables the recovery of information
133 through the identification of building-blocks. This is the so-called analytical pyrolysis
134 which results in the decomposition of the architecture of the bulk sample into smaller
135 and volatile fragments.

136 The process of analytical pyrolysis is commonly reported as being applied for the first
137 time in the second half of the 19th century to characterize natural rubber as a
138 polyisoprene compound (Greville Williams 1862). Thereafter, progress for its use was
139 slow until the advent of new analytical techniques such as organic mass
140 spectrometry (MS) and the development of modern gas chromatography (GC) in
141 about the middle of the 20th century. Firstly, linked directly with MS, pyrolysis was
142 latterly coupled to a gas chromatograph conducting the separation of the pyrolytic
143 products and their identification by means of their retention time. The first main
144 applications were in forensic science. In fact, the complexity of the thermal
145 degradation processes implicit in pyrolysis induces a noticeable difficulty in

accomplishing a satisfactory identification of materials from the recovered building blocks without the use of reference materials. The routine combination of pyrolysis-GC and MS (Py-GC/MS) has led to increasing applications of the characterization of synthetic and natural polymers since an MS analyzer allows more accurate identification of the pyrolysis products separated in the column (Sobeih et al. 2008).

As a consequence, Py-GC/MS offers several advantages compared to conventional GC/MS, namely (i) reduced and limited sample preparation, (ii) high sensitivity and limits of detection for sample sizes in or below the μg range, and (iii) the possibility of obtaining structural information from the pattern of fragmentation produced as a consequence of the pyrolysis process, the so-called fingerprint identification. In contrast to conventional GC/MS, the resulting chromatograms often are more complex than those obtained by conventional GC/MS due to the increased number of peaks corresponding to the pyrolytic fragmentation of the original molecular structure, and thus provide reliable identification of the sample through its characteristic "fingerprinting".

Three types of pyrolyzers are commercially available: Curie-point, furnace, and filament pyrolyzers. Curie-point instruments use the ferromagnetic properties of a conductor interacting with a high radio frequency to fix the pyrolysis temperature. A pyrolysis chamber indirectly heated by ceramics is commonly used in the furnace pyrolyzer. In the filament pyrolysis system, the required high temperatures are reached by applying an electric current to a platinum coil.

However, even if pyrolysis simplifies the direct analysis of samples, a chemical derivatization step can improve the performance of the separation in the chromatographic column, particularly if polar structures are present or assumed in

the bulk sample. The most common derivatization technique relies on methylation reactions associated with the pyrolytic process inside the pyrolyzer itself. This technique, called thermally assisted hydrolysis and methylation (THM), is commonly conducted with a liquid derivatization reagent added to the sample before pyrolysis.

In brief, since its first application in the 1960s, analytical pyrolysis linked to GC/MS has been successfully applied to the identification of natural oils and waxes as well as to terpenoid resins and binding media, including synthetic organic polymers such as acrylic and alkyd resins.

In the course of our work, reference samples of beeswax, paraffin and resin (these latter two samples coming from the reserves of the fluid collections in the MNHN), as well as three jar sealants selected for their ubiquity in fluid collections (fig. 1) have been analyzed by FT-IR spectroscopy and Py-GC/MS to evaluate the potentialities of this experimental approach for the characterization of unknown samples of jar sealants before a more systematic screening of the fluid collections in the museum is initiated.

<<Insert figure 1 here>>

Py-GC/MS analyses were performed using a vertical micro-furnace type pyrolyser PY-2020iD (Frontier Lab, Japan) directly connected to the injection port of a Shimadzu QP2010 gas chromatograph linked with a Shimadzu QP2010Plus quadrupole mass spectrometer (Shimadzu, Champs-sur-Marne, France). The sample was firstly diluted in chloroform (CHCl_3) to obtain low concentrations of materials in the low μg range when analyzed by pyrolysis (typically, the concentration was calculated to allow the deposition of ca. 1.5 μg of sample in the stainless-steel

sample cup). A derivatization reactant, tetramethyl ammonium hydroxide, was added to the previous sample solution to methylate the hydroxyl functional groups (of acids and alcohols) expected to be present within the jar sealant samples. Such in-situ derivatization is currently conducted during Py-GC/MS experiments to allow a better separation of polar compounds during the chromatographic separation (Challinor 2001). The sample cup was placed on top of the pyrolyser at near ambient temperature. For the analysis, the sample cup was introduced into the furnace at 600 °C, and then the temperature program of the gas chromatograph oven was started. The Py-GC interface was held at 320 °C. Chromatographic separation was carried out on an Agilent DB5-ms 5% phenyl–95% dimethyl polysiloxane fused silica capillary column (30 m long, 0.25 mm inner diameter, and coated with a 0.25 µm film thickness). The oven temperature was initially held at 40 °C for 8 min, and then ramped at 10 °C min⁻¹ to 340 °C, where it was held for 10 min. The total duration of GC analysis was 48 min. The helium carrier gas Alphagaz 1 (Air Liquide, France) was used in the linear velocity mode (1 mL min⁻¹). The injector was held at 280 °C and used in split mode (1:10 of the total flow). The mass spectrometer was operated at 10,000 mass unit per second (u s⁻¹), with a scan range from 40 to 800 u, using electron ionization (EI) at 70 eV. The interface was kept at 300 °C and the MS source at 200 °C. Identifications were achieved on the basis of EI mass spectra by interpretation of the main fragmentations and using the NIST MS library (NIST/NIH/EPA Mass Spectral Library 2011).

The Fourier transform infrared (FT-IR) data were acquired in the ATR mode using a Thermo Nicolet 6700 (Thermo Scientific, Courtaboeuf, France) within the range 500-4000 cm⁻¹. Each FT-IR spectrum was the result of four co-added scans at a nominal resolution of 4.0 cm⁻¹.

218

219 Results and Discussion

220 FT-IR analysis

221 As a first approach, screening of the samples was conducted by FT-IR spectroscopy.

222 Figure 2 shows the FT-IR absorbance spectra of the chosen reference samples: (2a)
223 commercial beeswax, (2b) paraffin, and (2c) resin of the MNHN collections.

224 Characteristic IR band vibrations of chemical functions present in these samples can
225 be observed (Derrick et al. 1999).

226 As generally noticed in FT-IR spectra, band assignment in the $4000\text{-}1500\text{ cm}^{-1}$ region
227 is quite straightforward. Wax samples are characterized by the stretching of their
228 numerous methylene groups at 2920 cm^{-1} and 2850 cm^{-1} , confirmed by the sharp
229 doublets at $1470\text{-}1460\text{ cm}^{-1}$ and $729\text{-}719\text{ cm}^{-1}$ (fig. 2a, commercial beeswax).

230 Bending of these methylene groups appeared around 1470 cm^{-1} . In beeswax, long-
231 chain hydrocarbons with CH_2 methylene groups and CH_3 terminal groups finally show
232 similarity to the spectra of paraffins (fig. 2b, paraffin). Specifically, aliphatic ester
233 groups of beeswax account for the stretching bands observed at 1710 cm^{-1} and 1170
234 cm^{-1} for C=O and C-O bonds, respectively.

235 For the reference resin sample (fig. 2 c), a broad band assigned to O-H stretch was
236 observed around $3000\text{-}3500\text{ cm}^{-1}$. The expected cyclic ring structures gave strong C-
237 H stretching vibrations found at 2930 and 2870 cm^{-1} . Due to a variety of molecular
238 environments for the methylene groups within the resin, and because there are
239 several methyl (CH_3) end groups, these C-H stretches are not as sharp and as well

separated as those seen in the beeswax and paraffin samples. A strong carbonyl band centered at 1690 cm^{-1} was observed for which enlarged band shape can be attributed to resin degradation and oxidation. Bands observed in the region $500\text{-}1500\text{ cm}^{-1}$, where bands at 1460 cm^{-1} , 1380 cm^{-1} are assigned to CH group bending, and other bands in the $1300\text{-}900\text{ cm}^{-1}$ region could be assigned to C-O stretching bands in accordance with the expected rosin origin of the sample.

<<Insert figure 2 here>>

Comparatively, considering the above assignments, if FT-IR spectra of the three selected jar sealants (fig. 3) showed some similarities to the reference samples, presence of additional bands revealed the possible presence of other components for two of them. Indeed, among these sealants, the jar sealant A8407 (fig. 3a) presented characteristic bands (2920 cm^{-1} and 2850 cm^{-1} , 1460 cm^{-1} , 719 cm^{-1}) of the methylene groups of beeswax as well as the stretching bands for C=O and C-O bonds at 1740 cm^{-1} and 1170 cm^{-1} , respectively. From these assignments, sample A8407 could be attributed to a beeswax-based composition. Only one additional band at 1380 cm^{-1} was observed that could not be definitely assigned to a reference. Sample 1974-66 (fig. 3b) showed mainly similarities with the previous A8407 sealant and beeswax, but showed discrepancies in the region $1240\text{-}820\text{ cm}^{-1}$, and a more intense doublet at $717\text{-}719\text{ cm}^{-1}$. The last sample, 1924-185, showed patterns in common with previous sealants but showed noticeable differences in the region $1260\text{-}500\text{ cm}^{-1}$, which indicates the presence of other components than those observed in beeswax.

263 <<Insert figure 3 here>>

264

265 Py-GC/MS

266 As stated above, Py-GC/MS analysis is based on pattern recognition of components
267 issued from thermal degradation of a given polymer, which results in a fingerprint
268 identification of this sample. Consequently, the reference samples investigated here
269 (fig. 1) were pyrolyzed under the experimental conditions described above to collect
270 characteristic fingerprints of materials likely present in historic recipes for jar sealants
271 in the MNHN collections. Figure 4 reports the chromatographic fingerprint of the
272 reference commercial beeswax in which a typical distribution pattern of the main
273 components of beeswax can be observed. These components are mainly long-chain
274 odd alkanes showing a peak distribution spanning from C23 (tricosane) to C35
275 (pentatriacontane) centered around the C27 congener (heptacosane), and
276 methylated long-chain acids showing a peak distribution with a maximum at C24:0
277 (tetracosanoic acid methyl ester). Additionnally, hexadecanoic acid methyl ester,
278 octadecenoic acid methyl ester, and octadecanoic acid methyl ester were detected
279 as first eluting compounds. These latter components were attributed to native side-
280 products in beeswax or products generated by the thermal decomposition of long-
281 chain palmitate esters present in beeswax but not eluted under the present
282 chromatographic conditions (Tulloch 1972). Details for the assignment of the
283 observed main products from beeswax pyrolysis are reported in Table 1.

284 <<Insert figure 4 here>>

285 <<Insert table 1 here>>

286

287 Comparatively, the reference paraffin presented a simpler fingerprint (fig. 5) with the
288 main distribution of long-chain alkanes of an even number of carbons centered
289 around the C24 (tetracosane). Details for the assignment of the observed main
290 products from beeswax pyrolysis are reported in table 2. Py-GC/MS of the reference
291 resin sample (not shown here) presented peaks assigned to hexadecanoic acid
292 methyl ester and octadecanoic acid methyl ester with numerous additional peaks,
293 corresponding to terpenic compounds, which led to assigning this resin sample to a
294 pine resin, likely rosin.

295 <<Insert figure 5 here>>

296 <<Insert table 2 here>>

297

298 Results from the Py-GC/MS analysis of the three investigated jar sealant samples:
299 A8407, 1924-185 and-1974-66 are visualized in figure 6. Sample A8407 (fig. 6a)
300 presents a distribution of peaks very similar to the reference beeswax sample (fig. 4),
301 in particular with a distribution of long-chain alkanes of odd-numbered carbon atoms
302 centered around the C27 congener and a distribution of methylated long-chain ester
303 centered around the C24 congener. In addition, hexadecanoic acid methyl ester and
304 octadecanoic acid methyl ester are also observed in high relative quantity. From
305 these observations, and at the present state of the investigation, sample A8407 can
306 be attributed to beeswax as a principal ingredient in its composition. In comparion,
307 sample 1974-66 (fig. 6c) shows a very divergent distribution of peaks in its
308 characteristic fingerprint with predominant long-chain alkanes of an even number of

carbons which led to assigning paraffin as a main component of this jar sealant. However, peaks corresponding to terpenic compounds are also detected in the chromatogram demonstrating the presence of at least one other component in this sample, likely a pine resin which showed similarities with the reference resin sample from the MNHN collections. The sample 1924-185 (fig. 6b) is characterized by a lower response under our pyrolysis conditions resulting in a lower signal-to-noise ratio for the peaks detected in the chromatogram. No satisfactory explanation can be drawn at this time from this observation: a mineral charge in the jar sealant sample, as suggested by the presence of numerous bands in the region 500-1400 cm^{-1} in the FT-IR spectrum (fig. 3c), can perturbate the pyrolysis process; on the other hand, a lower solubility of the sample could be proposed as a hypothesis. However, sample 1924-185 showed a distribution of peaks corresponding mainly to a series of long-chain alkanes centered around the C26 (hexacosane) congener attributing the composition of this jar sealant to a paraffin-like composition, even if minor methyl esters were also detected as additives.

<<Insert figure 6 here>>

Principal component analysis analysis

In order to improve the chosen approach based on a rapid screening by Py-GC/MS analysis, semi-quantitative experiments were conducted with the reference sample and the jar sealant samples. Quantification in Py-GC/MS experiments is difficult and necessitates careful analysis of experimental results, in particular because the pyrolysis process introduces possible sources of variability during the experiments. In

order to reduce the effects of the numerous factors that potentially influence the analytical results, heneicosanoic acid methyl ester ($C_{22}H_{44}O_2$) was added as an internal standard to each sample prior to analysis for the statistical treatment of data using a multivariate analysis (principal component analysis PCA). As the ionization response of acid methyl esters can be different from those of alkanes, a response factor for the integration of peak areas was applied for data treatment; this factor was calculated by comparing the peak area of the integrated peaks of the standard methyl ester (C22) to the tetracosane (C24) in an equimolar solution of both analyzed by GC/MS.

As a result, the PCA analysis of experimental data considering only the esters and alkanes present in the chromatograms provides a net distinction of the different samples (beeswax and the three jar sealant samples on the score plot are shown in fig. 7a). Contribution of samples to their PC1 and PC2 loading in principle component analysis are characteristic and dependent on their composition, and result in noticeable variations in peak areas of their main components.. Sample 1974-66, however, varies in its distribution among the three replicates. At the present state of the investigations, this was attributed with difficulties of correctly solubilizing paraffin samples homogeneously, which may amplify the variance in the principle component analysis.

The loading plot (fig. 7b) allowed the differentiation of nine main components for the discrimination of samples based on the analysis of their proportion of long-chain alkanes and long-chain methyl esters under Py-GC/MS analysis, identifying beeswax as a possible component of jar sealants. Besides characteristic methyl esters detected in beeswax, six long-chain alkanes of odd and even carbon numbers were

revealed as potential discriminants for the characterization of sample composition. This result is promising for a future screening of jar sealant samples on a larger scale.

<<Insert figure 7 here>>

Conclusions

This approach, which is based on the development of an analytical protocol using FT-IR spectroscopy and Py-GC/MS, allows characterization of sealant components commonly encountered in historic fluid collections. FT-IR spectroscopy is an efficient way to detect the main components of unknown jar sealants, which allows the classification of such unknown sealants into different groups according to their most likely composition. Py-GC/MS, using polymer fingerprints, allows a more precise identification of components of the jar sealant recipes. Both techniques are opened to multivariate data analysis that can amplify and enhance the results. In particular, the use of Py-GC/MS can be a very efficient way to simplify the analysis of experimental results as illustrated by the extraction of nine potential markers for the discrimination of jar sealant containing beeswax and paraffin samples.

Our knowledge of sealant composition in fluid collections as well as correlation of this information to their manufacture and date of preparation is essential for a conservation approach, and for the perpetuation of natural history fluid collections.

378 However, this knowledge is often limited because of various constraints inherited
379 from historical collections. Our new experimental approach to detect and identify the
380 composition of jar sealants is a promising tool to unlock past knowledge to better
381 understand the history and conservation of our fluid collections. Its application has
382 potential for other collections and hopefully will be applied more widely, and could be
383 promissingly enlarged to other collections.

384

385 Acknowledgments

386 The authors would like to thank the reviewers for their thoughtful comments and
387 efforts towards improving the manuscript.

388

389

Résumé

Au fil des siècles, la composition des lutages dans les collections en fluides des musées d'histoire naturelle a changé, malheureusement ces changements sont peu documentés. Par conséquent, il est primordial d'accroître nos connaissances sur l'évolution au cours des différentes époques de la composition des lutages des collections en fluide.

L'approche proposée repose sur le développement d'un protocole analytique basé sur l'utilisation de la spectroscopie FTIR et de la pyrolyse-GC / MS pour caractériser la composition des lutages rencontrés dans les collections en fluides du MNHN.

Cette approche s'est avérée efficace pour l'identification et la caractérisation de cires et de résines dans les échantillons de lutages étudiés. Ces premiers résultats sont très prometteurs et ces analyses doivent être poursuivies à plus grande échelle afin d'obtenir une analyse exhaustive des collections en fluides du MNHN.

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452 van Dam, A.J. 2000. The interactions of preservative fluid, specimen container and
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454

455 Table 1. Main products observed from the pyrolysis of reference beeswax with
 456 corresponding retention times, molecular weights, formulas, and assignments.

Retention time (min)	Molecular mass (g/mol)	Formula	Assignment
26.71	270	C ₁₇ H ₃₄ O ₂	Hexadecanoic acid methyl ester
28.41	296	C ₁₉ H ₃₆ O ₂	Octadecenoic acid methyl ester
28.65	298	C ₁₉ H ₃₈ O ₂	Octadecanoic acid methyl ester
30.14	324	C ₂₃ H ₄₈	Tricosane
30.98	338	C ₂₄ H ₅₀	Tetracosane
31.78	352	C ₂₅ H ₅₂	Pentacosane
32.06	354	C ₂₃ H ₄₆ O ₂	Docosanoic acid methyl ester
32.55	366	C ₂₆ H ₅₄	Hexacosane
33.29	380	C ₂₇ H ₅₆	Heptacosane
33.55	382	C ₂₅ H ₅₀ O ₂	Tetracosanoic acid methyl ester
34.01	394	C ₂₈ H ₅₈	Octacosane
34.72	408	C ₂₉ H ₆₀	Nonacosane
34.97	410	C ₂₇ H ₅₄ O ₂	Hexacosanoic acid methyl ester
35.38	422	C ₃₀ H ₆₂	triacontane
36.04	436	C ₃₁ H ₆₄	Hentriacontane
36.30	438	C ₂₉ H ₅₈ O ₂	Octacosanoic acid methyl ester
36.67	450	C ₃₂ H ₆₆	Dotriacontane
37.17	464	C ₃₃ H ₆₈	Tritriacontane
37.55	466	C ₃₁ H ₆₂ O ₂	triacontanoic acid methyl ester
38.66	492	C ₃₅ H ₇₂	Pentatriacontane
38.76	494	C ₃₃ H ₆₆ O ₂	Dotriacontanoic acid methyl ester
40.11	522	C ₃₅ H ₇₀ O ₂	Tetratriacontanoic acid methyl ester

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459 Table 2. Main products observed from the pyrolysis of reference paraffin with
 460 corresponding retention times, molecular weights, formula and assignments.

461

Retention time (min)	Molecular mass (g/mol)	Formula	Assignment
26.817	270	C ₁₇ H ₃₄ O ₂	Hexadecanoic methyl ester
28.369	296	C ₂₁ H ₄₄	Heicosane
28.660	298	C ₁₉ H ₃₈ O ₂	Octadecanoic acid methyl ester
29.253	310	C ₂₂ H ₄₆	Docosane
30.120	324	C ₂₃ H ₄₈	Tricosane
30.959	338	C ₂₄ H ₅₀	Tetracosane
31.769	352	C ₂₅ H ₅₂	Pentacosane
32.554	366	C ₂₆ H ₅₄	Hexacosane
33.317	380	C ₂₇ H ₅₆	Heptacosane
34.057	394	C ₂₈ H ₅₈	Octacosane
34.773	408	C ₂₉ H ₆₀	Nonacosane
35.474	422	C ₃₀ H ₆₂	triacontane
36.153	436	C ₃₁ H ₆₄	Hentriacontane
36.807	450	C ₃₂ H ₆₆	Dotriacontane

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466 Figure captions

467 Figure 1. (a) Commercial beeswax, (b) reference paraffin from the MNHN collections,
468 (c) reference resin from the MNHN collections, (d) sample A8407 - a waxy red-violet
469 sealant covered with a metal sheet dating from 1893, (e) sample 1924-185 - a waxy
470 brown sealant dating from 1924, (f) sample 1974-66 - a waxy yellowish sealant
471 dating from 1924.

472 Figure 2. FT-IR spectra of reference samples of commercial beeswax (blue), paraffin
473 (orange), resin (green) from the MNHN collections.

474 Figure 3. FT-IR spectra of jar sealant samples: A8407 (blue), 1974-66 (red), 1924-
475 185 (green).

476 Figure 4. Chromatogram obtained from the Py-GC/MS analysis of reference beeswax
477 at 600°C with characteristic distributions of long-chain esters (orange squares) and
478 odd alkanes (orange plain circles).

479 Figure 5. Chromatogram obtained from the Py-GC/MS analysis of reference paraffin
480 at 600°C with a characteristic distribution of long-chain alkanes (orange plain circles).

481 Figure 6. comparison of the chromatograms obtained from the Py-GC/MS analysis of
482 the investigated jar sealant samples: (a) sample A8407 (b) sample 1924-185 (c)
483 sample 1974-66. The following components are reported in the figure as follow: long-
484 chain esters (orange squares), long-chain alkanes (orange plain circles), terpenic
485 compounds (green plain circles).

486 Figure 7: (a) Score plot and (b) loading plot from the comparison of reference
487 samples and unknown jar sealants considering only compounds originating from wax
488 (esters and alkanes).

489 Figure 1

(a)

(b)

(c)

(d)

(e)

(f)

490

491 Figure 2

Figure 3

Figure 4

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500 Figure 5

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502 Figure 6

Figure 7

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