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ORIGINAL PAPER

Spectral analysis of pharmaceutical formulations prepared according to ancient recipes in comparison with old museum remains

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Abstract A study of the composition of the remains of ancient ointments from museums was undertaken to enable understanding of the preparation techniques. Comparison of ancient recipes from different historical periods and spectroscopic characteristics of inorganic and/or organic remains recovered in museum vessels enabled preparation of ancient pharmaceutical–cosmetic formulations. *Farmacopea Augustana* by Occo was one the most important books studied for the 14 formulations prepared in the laboratory. Three formulations are discussed in detail and raw materials and new preparations were proposed for ozone ageing. The most important micro Raman results are discussed. The spectra of the raw materials lipids, beeswax, and resins are discussed; beeswax and pig suet (*axŭngia*) Raman spectra were found to be similar, but different from those of the aged oils. SERS was applied to ancient ointments and galbanum and the Raman spectra are reported and discussed for the first time.

Keywords Recipe books · Pharmacopoeia · Ointments · Raman spectroscopy · SERS

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Introduction

Although interest in scientific treatment of analytical data obtained from ancient remains preserved in Italian and foreign institutions and museums is relevant, until now study of the composition and understanding of the technologies of preparation of ancient findings is scanty and fragmentary.

Recent progress in instrumental techniques has enabled the detailed composition of the material to be clarified and possible means of preparation of the materials can be suggested. On the basis of analytical data, the possibility of establishing the nature of raw materials and their formulations becomes even more likely.

In the framework of an Italian National Research Project (MIUR Prin07) entitled *"Colors and balms in antiquity—from chemical study to a knowledge of techniques in cosmetics, painting and medicine"*, our research group has built the basis for study of the remains of ancient cosmetics, pharmaceuticals, and paintings. In particular:

- visual inspection of vessels, and sampling in national and international museums;
- spectroscopic analysis (FT-IR, micro-Raman) for characterisation of inorganic and/or organic remains;
- identification and study of ancient published and unpublished bibliographic sources;
- translation from classical and vernacular Latin followed by interpretation of the raw materials cited and their function in the formulation;
- identification of currently available materials which were used in antiquity;
- preparation or acquisition of raw materials currently not available; and

- modern reproduction of ancient formulations on the basis of the ancient sources have been taken into consideration.

The first step faced was acquisition of ancient remains, that is, sampling on the spot from the vessels to be studied. Therefore, samples were taken from Aboca Museum (Sansepolcro (AR), Italy): 68 blue ceramic jars of Spanish provenance (XVIII century) were inspected, on each of these a label reporting an ancient formulation name was observed (e.g.: ung. rosatum). Thirty of the jars contained a suitable amount of residue, of which nine were the object of the study. After sampling, the materials were analysed by Raman microscopy and FT-IR spectroscopy to distinguish the organic and the inorganic components. Taking into account the labels on the containers, we proceeded to research on ancient similar formulations. In particular, we searched ancient recipe books—problems with the manuscripts and the printed books were their difficult availability and obtaining permission to use them. In rare cases they were photographed or reproduced in digital format; sometimes they were property of ancient institutions and not readily accessible.

Subsequently, it was necessary to examine the recipe books starting from the classical age until to the beginning of scientific chemistry and pharmacology, to critically compare the materials found, to understand their nature, their possible alteration with time, novelty in comparison with preceding versions, and the technological achievements of an age in comparison with the preceding ones. Study of the same formulation from different times showed the evolution and adaptation to the historical period.

Many ancient books and manuscripts reporting recipes from the period between 1597 and 1872 were considered [1–6]. The codices and printed books considered (some are the property of institutions such as the *Farmacopea Augustana* by Occo, in the Faculty of Pharmacy, University of Modena and Reggio Emilia) were examined in detail.

For each source, the desired recipes were sought and then, if necessary, translated and interpreted. In fact, some texts are in vernacular or Latin (*Farmacopea Augustana* by Occo), French (*Abrégé de Matière médicale et de Thérapeutique* by C. Binz), or Spanish (*Farmacopea Hispanica*), and careful translation was required, because the meaning of terms has changed with time.

The next step was to study the raw materials used in the recipes, to verify the persistence of the ingredients today and their commercial availability. For example, the gum resins were particularly difficult to purchase, e.g. sagapenum, a gum resin of oriental provenance, is no longer sold, and galbanum was difficult to acquire. Another ingredient studied with particular attention was *axŭngia*, as reported in the *Farmacopea Augustana* by Occo. After careful consideration and discarding different hypotheses (*lard, strutto, lardello*) we discovered the essentials of the raw material used in antiquity: "the ensemble of the fatty and soft parts of pig, especially those enveloping the entrails, from which the strutto is obtained (upon melting, filtration, clarification and cooling)" (Treccani Enciclopedy). Proof of the use of this ingredient, *axŭngia,* in antiquity is given by Pliny in his Naturalis Historia (XXVIII, 37–141), in which perirenal fat was extracted, because of its different functions, for example greasing cart axles and wheels and treating animal wounds.

Not all the raw materials could be bought, some had to be prepared in the laboratory, for example rose water and turnip juice, two ingredients used in the preparation of many ointments.

The ointments to be prepared were chosen on the basis of the remains found in the containers, but mainly on the basis of the preliminary results from spectroscopic analyses. Using the results from these analyses and the labels on the containers, we proceeded to the preparation of materials similar to the ancient formulations.

Fourteen preparations were reproduced in the laboratory. The final fresh preparations and their raw materials were aged by use of an ozonation procedure, to simulate the oxidation of the organic matter by ageing; finally they were studied by use of spectroscopic techniques. The ozonation procedure was performed by the University of Milan, Milano Bicocca, participating in the PRIN project.

Experimental

Sample preparation

Procedure for reproducing ancient pharmaceutical recipes

In this study, it was necessary to examine recipe books starting from the classical age until the beginning of scientific chemistry and pharmacology. The same formulation in different times was sought to compare its evolution and its adaptation to the age, to enable understanding of the novelties in comparison with preceding versions [1–6].

One of the most ancient books studied describing the different pharmaceutical preparations was a Pharmacopoeia: the "Farmacopea Augustana" by Adolfo Occo dated 1597 [1]. The volume originates from a collection of pharmaceutical books, the property of the Department of Pharmaceutical Science, University of Modena e Reggio Emilia, Modena, Italy. In this ancient text, the raw materials, the recipes, and their functionality are reported. "Farmacopea Augustana" is an important ancient book, a pharmacopoeia, therefore a collection of officially recognized recipes followed in

the preparations by pharmacists or physicians of that period.

By comparing the same recipe studied in ancient bibliographic sources from different historical periods, despite modification of the operating methods, it should be possible to understand the mains procedures used in ancient pharmaceutical formulations. Sometimes, the recipes consisted in a mixture of olive oil, pig suet, or beeswax as ingredients, with occasional addition of water or perfumed flower water. In general, after heating of the basic mixture below the melting temperatures of lipids or beeswax, fresh plant parts (rose petals, shoots, etc.) or inorganic powders were added until the consistency of an ointment was obtained. In this way, different ointments with different pharmaceutical–cosmetic functionality were prepared.

Reconstructions of ointments were performed by following and adapting the ancient recipes studied in this work.

Preparation of reference ointments

For the nine museum remains considered in this study, the same ointment was sometimes prepared by following recipes of different historical periods, differing in the presence or absence of some raw materials and the methods of preparation. Therefore, to take this variability into consideration, 14 pharmaceutical–cosmetic formulations were prepared in our laboratory.

The Latin inscriptions on the containers of the nine museum remains collected from Aboca museum vessels (XVIII century, Spain) with their inventory numbers and the corresponding laboratory reproduced formulations are listed in Table 1.

Three ointment preparations are reported here, and the analysis of these ointments is discussed.

Rosatum ointment preparation

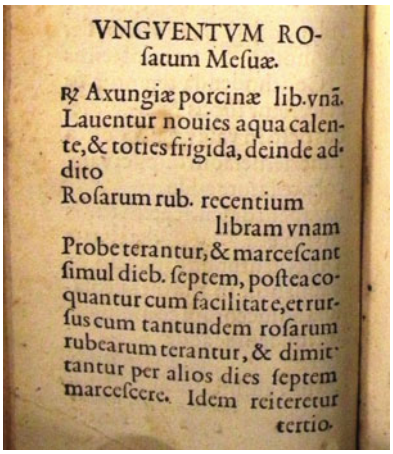
As an example of an ancient recipe, the "unguentum rosatum" of Adolfo Occo (formulation I_A in Table 1) is reported below. As a demonstration of the difficulty of preparing formulations by use of a modern procedure, the ancient text of the latter is reported (Fig. 1), with its literal translation and the present laboratory procedure.

Pig suet (from a Venetian butcher), 30 g, was washed alternately in hot and cold water nine times and was then blended in a mortar with 30 g fresh rose petals for 5 min. The mixture obtained was left for 7 days in a dark glass container at room temperature, then heated to 70–80 °C for 60 min. Then the mixture was filtered and the solid was squeezed to obtain the juice. Another 30 g rose petals were added to the filtrate and ground in a mortar for 5 min. The entire procedure

Table1 Correspondence among ancient ointments from Aboca museum and formulations reproduced in our laboratory

UNGUENTUM ROSATUM Inv. N. 50509			***UNGUENTUM POPULEON Inv. N. 50023***	***UNGUENTUM PRO IGNE Inv. N. 50015***	
I_A [1]	I_B [4]	I_C [6]	II_A [1]	III_A [2]	III_B [2]
Pig suet			Pig suet	Pig suet	
			Poplar buds		
Fresh red roses			Poppy	Turnip juice	
			Viola		
Rose water		Rose water	Henbane	Olive oil	
			Deadly nightshade		
Sweet almond oil			Houseleek	Beeswax	
			Lettuce		
		Beeswax	Burdock	Silver litharge	
			Red wine		

OXIMEL SIMPLEX Inv. N. 50010 Inv. N. 50025		***MEL ROSATUM Inv. N. 50054***		***UNGUENTUM ALTHEA Inv. N. 50007 Inv. N. 50030***		***UNGUENTUM COLOPHONIA Inv. N. 50017***	
IV_A [1]	IV_B [3]	V_A [3]	V_B [1]	VI_A [1]	VI_B [3]	VII_A [1]	VII_B [5]
Skimed honey		Decoction of roses		Marsh mallow		Colophony	
				Linseed			
				Fenugreek		Olive oil	
		Skimed honey		Beeswax		Beeswax	
Vinegar				Pine resin		Mastic	
				Olive oil		Galbanum	
			Green of roses		Pig suet	Incense	
					Curcuma powder		Gumarabic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tertio.

Rosatum ointment according Mesue

Take one pound of pig suet.
Wash nine times in hot water and other nine times in cold water, then add fresh roses petals one pound.
Blend and keep the roses petals macerate tougher with pig suet for 7 days, then cook with ability and again blend with the same quantity of roses petals and keep macerate for other seven days.
Do it again a third time. After fourth times mix all tougher without the roses petals.
(Add): Juice six ounces of red roses and almond oil three ounces.
Gently cook until consistence of the juice.

Fig. 1 Part of the Latin recipe of *unguentum rosatum* from *"Farmacopea Augustana"* of Occo (I_A formulation in Table 1) and its literal translation

was repeated four times, collecting the four filtrates. To the final filtrate 5.4 g sweet, almond oil (product of Marco Viti, Italy) and 10.8 g of rose water (distilled from red roses in our laboratory) were added and the ointment was cooled to room temperature. A total of 21 days was necessary.

As an alternative, a second version of Rosatum ointment without oil was prepared, but with beeswax (formulation I_B in Table 1)

Colophony ointment preparation

Beeswax (from a Pisa beekeeper, 12 g) and 75 g olive oil (from a Sicilian farmer) were separately heated a b.m. at 70 °C, then mixed together. Colophony (6 g, from Portugal, sold by Zecchi, FI, Italy), 3 g mastic (*Pistacia lentiscus*, from Greece, sold by Minardi, RA, Italy), and 3 g incense (*Boswellia carterii*, from Ethiopia, sold by Minardi, RA, Italy), previously blended in a mortar, were added to the mixture with stirring. When the mixture was molten, 3 g galbanum (*Ferula Galbaniflua*, from Iran, sold by La via dell'Incenso-Italy) was added with warming (70 °C) and stirring. Finally, the ointment was cooled to room temperature until its complete solidification.

An alternative recipe involved mixing colophony and gum arabic only (formulation VII_B in Table 1).

Pro igne ointment preparation

Pig suet (10 g, from a Venetian butcher) was washed alternately in hot and cold water nine times and then blended in a mortar, the mash was heated to 70–80 °C for 3 h and subsequently blended and heated for 2 and 30 min, respectively. Olive oil (8.33 g, from a Sicilian farmer), pig suet, and 10 g turnip juice (common trade product) were mixed and heated to 80 °C. The mixture was filtered and, still at 80 °C, 7.5 g beeswax (from a Pisa beekeeper) cut into small pieces was added with stirring over 10 min. Ointment III_B was obtained in this way.

A second formulation (III_A in Table 1) was prepared differing from this one only by addition, at room temperature, of litharge powder.

Spectroscopic instrumentation

In this study freshly prepared and ozone-aged samples were analysed by FT-IR, micro-Raman, and SERS (surface-enhanced Raman scattering). The results of the analyses are reported in the next section, with some spectra of the compounds characterized.

For the FTIR/ATR measurements a Vertex 70 (Bruker) FT-IR spectrophotometer, equipped with a deuterium triglycine sulfate (DTGS) detector, was used. Settings: resolution 4 cm^{-1}; apodization weak. The spectral range was 4,000–600 cm^{-1} and the number of scans was 32 for each spectrum. The spectra were obtained in ATR mode with a Perkin–Elmer Golden-Gate accessory.

Micro-Raman spectra were measured using a Labram (Jobin–Yvon Horiba) instrument equipped with a red laser of wavelength 632.8 nm, under the following conditions: maximum power 2 mW at the sample, CCD detector with 1,026×256 pixels, resolution 1 cm^{-1}, scan time from a few seconds to some minutes, depending on the intrinsic intensity of the signal.

The aqueous silver colloid used in the SERS experiments was prepared by reduction of silver nitrate (Aldrich, 99.998% purity) with sodium citrate (Aldrich, 99% purity), by following the Lee–Meisel method [7]. An aqueous solution of the sample of interest (2×10^{-4} mol L^{-1}; 1 mL) was added to an equal volume of the silver colloid. Colloid aggregation was induced by addition of 35 mL 1 mol L^{-1} aqueous NaCl (Aldrich, 99.999% purity). For the aqueous solutions 18 MΩ water was used.

One drop of the final colloid mixture was placed on a glass slide and the Raman spectrum was recorded with the instrument cited above. The power used was 0.5–1.5 mW and the recording time was 2–5 s.

FT-Raman spectra were recorded by use of a Bruker Multiram spectrometer, equipped with a FRA 106 FT-Raman module and with a near IR continuous-wave Nd-YAG laser operating at 1,064 nm in backscattering. The laser was focused on an approximately 100 μm×100 μm area of the sample and a liquid nitrogen-cooled germanium detector was used. Approximately 2,000 scans with a resolution of 4 cm^{-1} were averaged for each sample. Maximum power at the sample was approximately 15 mW.

The program GRAMS/AI 7.02 was used for processing of IR and Raman spectra (baseline correction, spike deletion).

Results and discussion

Characterization of pharmaceutical ingredients

The laboratory samples discussed above were exposed to ozonation, as an artificial ageing treatment, with the purpose of simulating oxidation of the organic matrix by ageing. Therefore, fresh and ozone-aged samples are compared and discussed [8].

In Fig. 2 the micro-Raman spectra of ozone-aged beeswax, pig suet, and olive oil are compared. The Raman spectra of beeswax and pig suet (*axŭngia*) are similar, but different from those of the aged oils. Characteristic of the pig suet are the ester C=O stretching band at 1,745 cm^{-1}, and the peak at 1,658 cm^{-1} from aliphatic unsaturation. These bands are of very low intensity for the beeswax. Again, the C–C skeletal stretching at 1,101 cm^{-1} is much stronger in animal fat, as also is the CH_2 rocking at 893 cm^{-1}. In addition, the relative intensities of two peaks near 1,440 (deformation of the CH_2 group) and 1,300 cm^{-1} (twisting of the CH_2 group) are quite different: the two bands for the pig suet have the

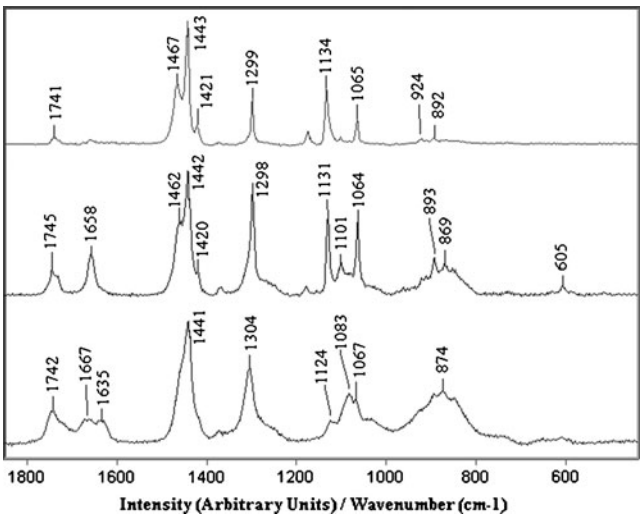


Fig. 2 From the bottom: Raman spectra of ozone-aged olive oil, pig suet and beeswax

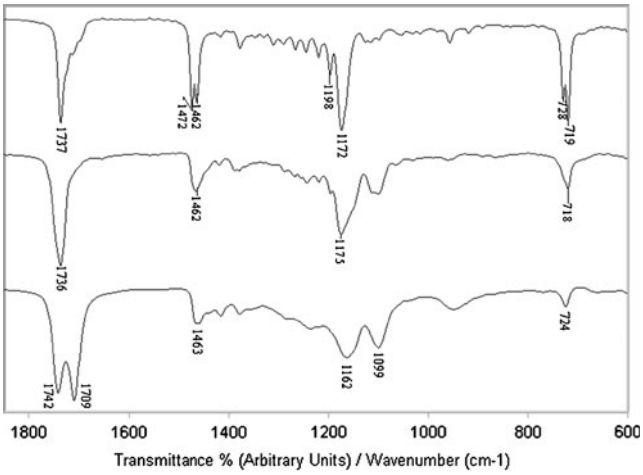
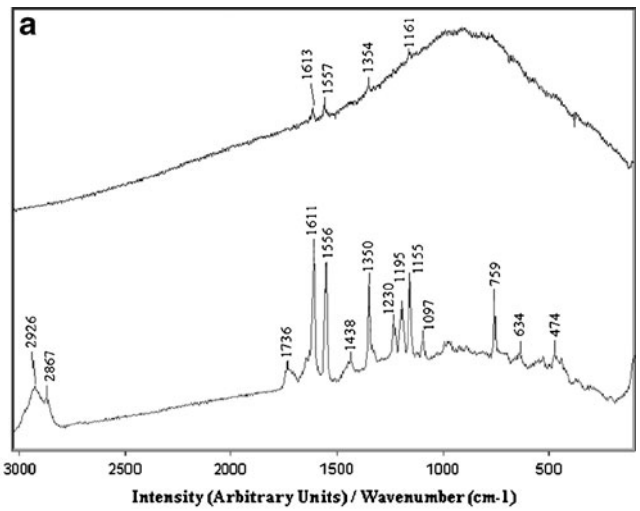


Fig. 3 From the bottom: FT-IR/ATR spectra of ozone-aged olive oil, pig suet and beeswax



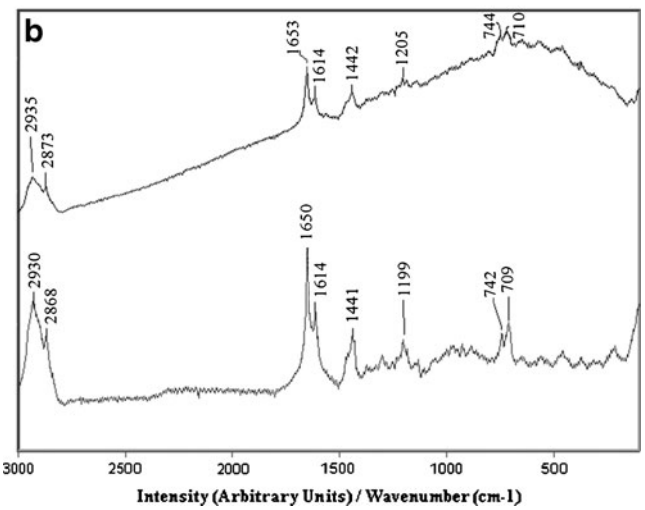


Fig. 4 Comparison of the Raman spectra of galbanum (**a**) and colophony (**b**) without (*top*) and with (*bottom*) use of SERS

same intensities, but not those for the beeswax. Moreover the CH_2 twisting mode band at 1,298 cm^{-1} from the pig suet has an evident shoulder at 1,300 cm^{-1} which can be associated with the in-plane deformation of $=CH_2$ [9, 10].

The Raman spectrum of pig suet does not change noticeably during ozone-ageing, despite what happens to beeswax. In particular, for pig suet a decrease in intensity of the 1,659 cm^{-1} band occurs, as a consequence of partial oxidation of double bonds, and an increase of the 1,745 cm^{-1} band, probably arising from oxidation products. Because the band at 1,659 cm^{-1} because of fatty acid double bonds was still present, as revealed by the micro Raman spectrum, it is clear that the ozonation should be protracted. Concerning the ozonated wax, two kinds of Raman spectra were recorded. The first corresponds to the fresh wax (Fig. 2), the second, less frequently observed on the sample surface, shows an intensity increase of the band at 1,421 cm^{-1} and a decrease of the band at 1,443 cm^{-1}. These bands are attributed to CH_2 deformation and the changes could be assigned to different hydrocarbon chain length.

Unlike the FT-IR spectrum, beeswax has a very characteristic spectrum, so it is more difficult to distinguish the lard from the oils than from the beeswax (Fig. 3). The application of both techniques can aid correct identification of the ingredients [11].

Regarding the resins used in the past in pharmaceutical formulations, because they have, or develop, fluorophores that hinder Raman microscopy, they have most often been analysed by FT-Raman spectroscopy. However, it is known in the literature that is possible to reduce fluorescence by application of SERS techniques [12]. Studies carried out with these techniques have emphasized that they can help in identifying resins such as galbanum and colophony. The spectra of galbanum and colophony with and without the SERS solution applied are compared in Fig. 4.

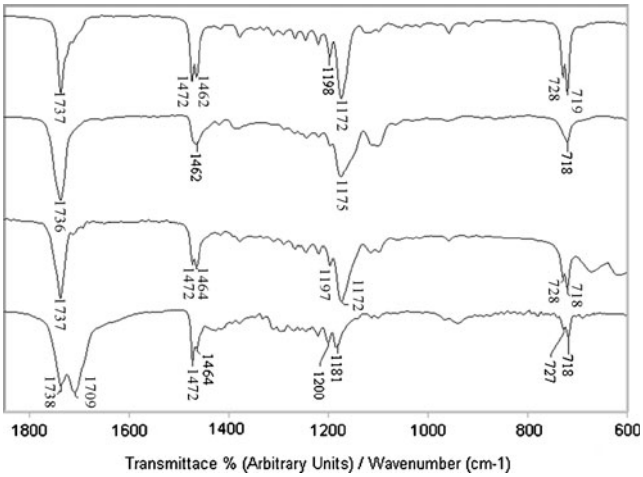


Fig. 6 From the bottom: comparison of the FT-IR/ATR spectra of ointment no. 50,509 and ozon-aged rosatum ointment preparation I_C, pig suet and beeswax

The characteristic bands for identification of resins are discussed below. Because colophony is believed to contain abietic acid as a major constituent, the 1,650 cm^{-1} band is readily assigned to the *cis* diene component. The C=C stretching band at 1,614 cm^{-1} and the CH deformation band at 1,441 cm^{-1} have been reported [13, 14].

Concerning the characterization of resin from *Ferula galbaniflua* by Raman spectroscopy, the literature is scanty and so the characterization is reported here for the first time. The spectrum of galbanum contains two very strong bands at 1,611 and 15,56 cm^{-1} because of C=C stretching in the aromatic ring. The strong band at 1,350 cm^{-1} involves ring stretching and CH deformation. Also characteristic are a series of three medium-intensity bands at 1,230, 1,195 and 1,155 cm^{-1} attributable to ring stretching, CCH deformation, and ring breathing, respectively. Finally the medium peak at 759 cm^{-1} is attributable to C–C ring stretching.

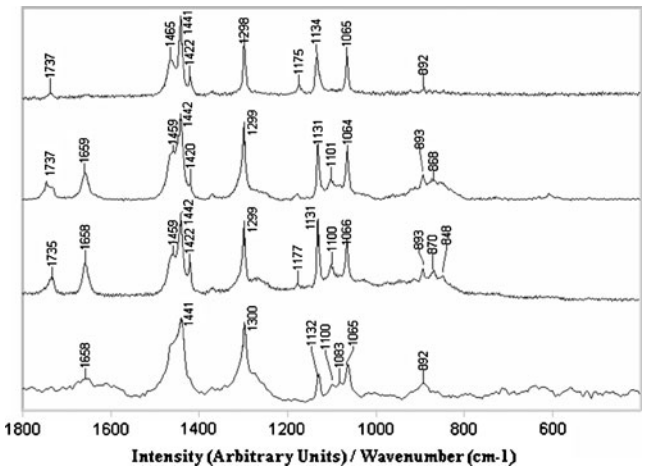


Fig. 5 From the bottom: comparison of the Raman spectra of ointment no. 50,509 and ozon-aged rosatum ointment preparation I_B, pig suet and beeswax

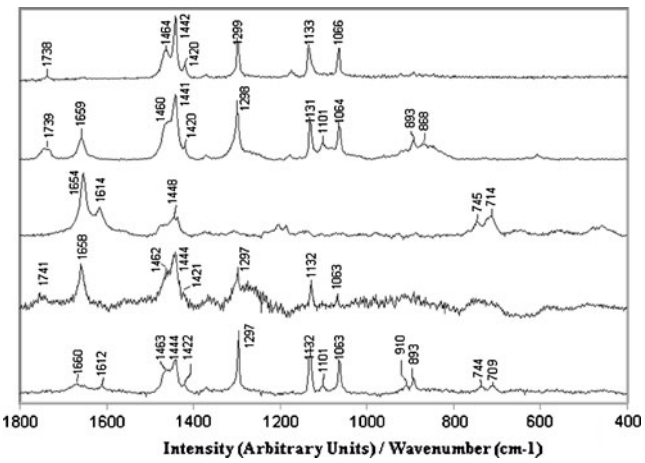


Fig. 7 From the bottom: comparison of the Raman spectra of ointment no. 50,017 and ozon-aged colophony ointment preparation VII_A, colophony, pig suet and beeswax

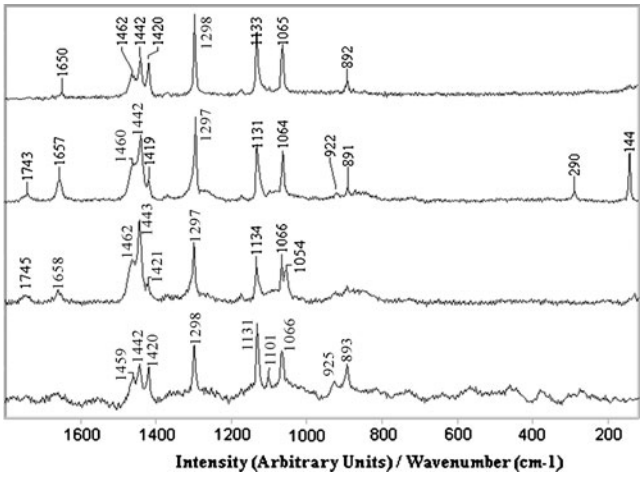


Fig. 8 From the bottom: comparison of the Raman spectra of ointment no. 50,015, ozon-aged pro igne ointment preparation III_A (two different points on the same preparation) and ozone-aged beeswax

Comparison of laboratory preparations and ancient museum ointments

To assess the possibility of identifying the raw materials mentioned above in complex matrices, measurements were conducted on samples from museum and reference samples reproduced in our laboratory.

In some cases it is quite difficult to assess their composition, because of the conservation status of the remains. In Fig. 5 the FT-Raman spectrum of an ancient ointment (bottom) is compared with the spectra of the ointment reproduced in the laboratory and the ozone-aged raw materials. In the reproduced ointment it is easier to identify animal fat as the main component and wax as a secondary component, from the intensity of 1,422 cm^{-1} band.

The spectrum of ointment 50,509 instead contains more bands typical of pig suet, in particular the band at approximately 1,100 cm^{-1}. The 1,658 cm^{-1} band is nearly absent, probably because of the ageing process that leads to almost total saturation of the double bonds of unsaturated fatty acids. The broadening of peaks at 1,300 and 1,400 cm^{-1} may be because of the presence of an oil mixed with the pig suet, but it is very difficult to confirm this by use of this technique.

In this case, FT-IR measurements can be used for better characterization of the ointment studied. In the Raman spectrum of the ancient ointment in Fig. 6, the carboxylic acid C=O stretching at 1,709 cm^{-1} can be attributed to the presence of oil; furthermore the presence of a degraded beeswax is clearly shown by the characteristic CH_3 bending doublet at approximately 1,470 cm^{-1} and of the CH_2 bending doublet at approximately 720 cm^{-1}. In this case, the IR and Raman results reveal the correspondence of the ancient ointment with formulation I_C Fig. 7.

In another cases, the spectral features indicate more clearly the presence of pig suet. For colophoniae ointment 50,017 the spectrum contains the C–H deformation band at approximately 1,444 cm^{-1}; also characteristic are the bandwidth of the peak near 1,300 cm^{-1} of the in-phase methylene twist and the intensity of two other bands—the C–C stretching mode at 1,101 cm^{-1} and CH_2 rocking at 893 cm^{-1}.

By comparing the spectrum of ancient colophoniae ointment with the reference spectra, it is possible not only to distinguish the presence of pig suet, although of low intensity, but also to observe four bands compatible with the presence of pinaceae resin or colophony. Because of aliphatic and aromatic unsaturation, C=C stretching bands can be observed at 1,660 and 1,612 cm^{-1} and C–C stretching bands at 744–709 cm^{-1}. For preparation VII_A the intensity of the band at 1,658 cm^{-1} contains a contribution from the presence of pig suet (mild ozonation) and it was necessary to apply a spectral subtraction of the pig suet spectrum from that of the formulation to observe the presence of colophony.

In some cases it is possible to distinguish the kind of ingredient. The Pro Igne 50,015 spectrum (Fig. 8, bottom) corresponds perfectly to the typology of ozone-aged beeswax (Fig. 8, top) and is different from that in Fig. 2. The spectrum shows, in fact, variation of the relative intensities of the CH_2 deformation bands at 1,442 and 1,420 cm^{-1}. The spectrum of 50,015 also contains a band at 1,101 cm^{-1} which is typical of pig suet so it is possible to suppose its presence.

Table 2 Museum ointment spectral information

Aboca Ointment	FT-IR/ATR	Raman techniques
50,509 Ung rosatum	Degraded wax	Pig suet
50,023 Ung populeon	Pig suet	Pig suet or wax, cinnabar (HgS), quartz
50,015 Ung pro igne	Wax	Degraded wax (plus pig suet), sulfides, gudmundite (FeSbS)
50,010 Oximel simplex	Ester	Vegetable carbon, (PbO)
50,054 Mel rosatum	Oxalates, silicates	Hematite, magnetite, apatite, carbon, silicon carbide (SiC)
50,025 Melle	Calcite, quartz	Gypsum, carbon, PbO
50,007 Ung althea	Degraded wax, gum	Fluorescence
50,030 Ung althea	Degraded wax, gum	Fluorescence
50,017 Ung colophoniae	Degraded wax, resin	Degraded pig suet, colophony, TiO_2 (rutile), calcite, syngenite, crystobalite

As demonstrated by the analysis, the ozone treatment turned out to be relatively mild and to cause only limited oxidation of some of the components.

Raman microscopy has been proved to be a suitable technique for identifying inorganic components in museum ointments (Table 2). Among the inorganic components, the discovery of gudmundite is interesting. Gudmundite is a mineral usually found in association with native antimony. Deposits of this mineral are not widespread.

Furthermore, after only having examined a Raman database containing spectra of fresh and aged ingredients, it was possible to identify and distinguish some organic ingredients, even if in some samples the problem of fluorescence was still present.

In other cases insufficient amounts of the remains resulted in identification of products from ageing and environmental contaminants only (nos 50,054 and 50,010).

Conclusions

Some pharmaceutical formulations have been re-prepared in the laboratory in accordance with ancient sources and one of the first Pharmacopoeias, that by Occo. A series of 14 ointments were formulated and proposed for ageing. FT-IR and micro Raman spectra of the new and aged formulations were recorded and compared to identify the changes undergone by some components. Three formulations (unguentum rosatum, colophony, and pro igne) are discussed in detail. The raw materials lipids, beeswax, and resins, in particular, are discussed and changes are attributed to reactions. The same compounds were then sought in the recently prepared formulations. The presence of pig suet has been identified from its Raman bands at 1,658 cm^{-1} (aliphatic unsaturation), at 1,101 cm^{-1} (C–C skeletal stretching), and at 893 cm^{-1} (CH_2 rocking).

The Raman technique is revealed to be a useful method for screening ancient preparations for distinguishing organic and inorganic matrices, and for characterization of raw materials in ancient and re-prepared formulations. In the work discussed in this paper SERS was applied for the first time to ancient ointments. In particular, galbanum has been characterized by Raman spectroscopy for the first time—two very strong bands at 1,611 and 1,556 cm^{-1} (C=C stretching) and a strong band at 1,350 cm^{-1} (ring stretching and CH deformation) were observed. Also characteristic were a series of three medium-intensity bands at 1,230, 1,195, and 1,155 cm^{-1}, attributable to ring stretching.

The spectra recorded made it necessary to acquire reference spectra under the same conditions by working on raw materials that were possibly used in the past. We propose to build a database of spectra of lipids, waxes, carbohydrates, and proteins and their degradation products.

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