

MicroRaman and infrared spectroscopic characterization of ancient cosmetics

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ABSTRACT

By FT-IR and microRaman spectrometry a large number of black to gray powders have been analysed. The studied remains were found inside Pompeian unguentaries situated in depository of “Casa Bacco”.

By the analytical results it has been possible to understand the different nature and composition of the materials employed in preparation of ancient cosmetic powders. Dark black powders were essentially composed of amorphous carbon probably due to the carbonisation of vegetal or animal tissues. By using different starting materials or by adding different powders to the black carbon other hues could be also obtained. Particularly, this study enabled to gain a complete and unambiguous composition characterization of these old cosmetics.

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1. Introduction

The complementary spectroscopic techniques, such as Fourier transform infrared (FT-IR) and microRaman spectroscopies are valid techniques in maximizing the amount of informations provided by complex matrices like the remains in archaeological holders.

A better knowledge of archaeological sample composition can be achieved by the spectroscopic data study. In some cases it is possible to suppose the manufacturing as well as the degradation process.

The difficulty in analysing archaeological samples is due to their composition which generally involves a mixture of different inorganic and organic materials, some times degraded by the environmental conditions. Therefore, only a set of analytical techniques can characterize such samples properly, the black eyeliners.

During the ancient times, the black eyeliners showed great interest [1,2]. In ancient Egypt, black eyeliners were the cosmetics preferred above all the others, generally used to emphasize eyes. The use of the so-called *mesdemet* was not only in cosmetic, but also in magic-religious and hygienic field [3].

Many of the black eye paints, the *koahs*, were composed of galena, stibine or antimony sulfide, cerussite [4] and even of laurionite and phosgenite as reported in literature [5,6].

Greek and Roman civilizations made at their own this type of cosmetic. In these civilizations another black eye paint was used: the so-called *fuligo* (black smoke), rarely reported in literature [1]. These products seem to come from the combustion of vegetables or animal bones and they were used to mark the eyebrows and the contour of the eyelashes [1,7].

The black powders were usually conserved in glass unguentaries, in bronze or fictile unguentaries and even in *alabastra*. In some cases roman people could have mixed the colored powders with excipients such as vegetable oils (*omphacium*, line seed oil, etc.), animal fats (for ex. *oesipium*) or saliva onto bronze plates or shells for making them to adhere better on the skin.

The pertinent literature referred to ancient roman cosmetics appears abundant [5,8–22], but scanty informations concerning the chemical composition of archaeological cosmetic powders are reported. In the past, most of the scientific studies have been carried out with classical chemical analyses [5,6,23–31]. Recently, new instrumental techniques, such as non-destructive Raman microscopy and destructive gas chromatography coupled with mass spectrometer (GC-MS), have been applied and led to a peculiar characterization of cosmetic materials [32,33].

Many samples coming from Pompeii excavations have been examined. The materials, found inside brasses, glasses, ceramics and stones vessels were of different nature.

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The aim of the research was to analyse the powders in order to characterize the components, interpret the differences of ancient utilization among the compositions and to trace back the mixtures preparation technologies. Furthermore, a detailed knowledge of the principal and minor components of the materials is needed to achieve the best cosmetic products preservation inside a museum. Comparing the black powders obtained data with those from some literature [1,34,35], it could lead to the identification and characterization of some specific products used particularly in Roman cosmetology. Finally, a careful inspection of data has revealed some important considerations about the qualitative distribution of different materials.

2. Experimental

2.1. Approach to the sample

Approximately 1300 containers, classified by the archaeologists as cosmetic holders (ex: unguentaries), are suited in Casa Bacco House, in Pompei. By an initial inspection inside holders, more or less the 30% of them presented traces of substances, presumably of organic and inorganic nature. In the present study, mainly 133 black and the gray samples have been analysed.

The first problem to be faced was to decide whether the material found inside the holders was a cosmetic, a pigment or a drug. In fact, still now, the relationship between shape/material composition of the containers and their contents is an unsolvable question [36]. The archaeological discovery environment is very important so a careful inspection of the finding location is needed also to interpret the obtained analytical data.

During the study a further problem was due to sample alterations cause of external materials coming from 79 AD events Pompeii's eruption or volcanic ground prolonged contact.

2.2. Operating protocol for the preparation of the sample

The powders identified inside different types of containers were sampled with a steel spatula: a small amount was taken and put inside a plastic vial, sealed and identified by the number that was assigned by the archaeologists during the excavations (catalogue number). The same numbers were used in the heading of Table 1. This table reports the obtained results of 133 samples analysed.

Firstly, a microscope examination was carried out in order to verify whether the powders appeared homogeneous or not. These observations were taken in consideration during Raman and infrared analysis.

2.3. FT-IR and microRaman measurements

The spectrometer used was an infrared PerkinElmer 1700 equipped with a TGS detector, with 20 scans, a spectral resolution of 2 cm^{-1} , in presence of a purging system for controlling carbon dioxide and moisture and a Jasco FT-IR 4200 equipped with a DLaTGS (deuterated L-alanine-doped triglicine sulphate) detector and a 2 cm^{-1} spectral resolution in the range $4000\text{--}400\text{ cm}^{-1}$. This instrument automatically calculated the proper number of scans in order to obtain a suitable S/N ratio.

The KBr pellets were prepared by weighing 1 mg of powder and 100 mg of pure reagent KBr, mixing them together for 1 min, putting the mixture inside a steel die and pressing for 1 min the die at the pressure of 1 MPa. The pellets were carefully extracted and inserted inside the support in the instrument compartment.

For the Raman investigations the samples were used as they were. The instruments used were a Labram of the Jobin-Yvon Horiba equipped with a red laser with wavelength 633 nm,

adopting the following conditions: maximum power 5 mW (at the source), a 632.8 nm laser, CCD detector with 1026×256 pixels, resolution 5 cm^{-1} ; and a Jasco NRS 2000 with a 488 nm laser, 330×1100 pixels CCD, resolution 2 cm^{-1} , maximum power 2 mW. The spectra were recorded from 2000 to 100 cm^{-1} with a spatial resolution of $1\text{ }\mu\text{m}$. The accumulation time and the number of scans changed according to the intrinsic strength of the Raman signal. Furthermore, GRAMS/AI 7.02 was used for Raman spectra elaboration.

In many cases the samples were heterogeneous and therefore the surface was carefully investigated by recording Raman spectra in different points having different shades. The spectra were compared with those from an in-house database and from other databases available on-line [37–40].

3. Results and discussion

3.1. Analysis of data

The obtained data are reported all together in Table 1. Cause of the high number data, the discussion was organized in different groups, even if this distinction cannot be so sharp.

The adopted groups were: black (ex: 2440, 5824B, 12974C) and gray powders (ex: 5824E, 10809 XIII), iron-based materials (ex: 9027, 12012, and 37957), pink powders (ex: 13052C), white pigments (ex: 7147 and 12355) and organic compounds (ex: 1106 and 13086).

In all cases it must be considered that the material inside the containers could be contaminated by earth components and by the materials deriving from the 79 AD eruption. Among these, many compounds must be included, such as silicates (Egyptian blue, excepted of course). However, many silicates were identified thanks to their good crystallization, recording good Raman spectra. These results are reported in Table 1. In reality, the silicates presence cannot be clearly attributed to volcano ash or intentional addition to the content. Silicates such as diopside could have formed during ceramics firing or have eruptive origin; therefore, it is important to check the container materials. Considering the black materials, in many cases, a great proportion of carbon was determined: this was the principal component of the ancient Pompeian eyeliner. Amorphous carbon is easily identifiable by the two strong and broad bands at about 1600 and 1380 cm^{-1} attributed to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{C})$, respectively [41]. In the studied unguentaries, the extensive presence of carbon permitted the identification of this black powder as *fuligo* and not as the famous and precious *kohl*. Carbon is frequently associated with apatite: this fact could be attributed to the use of carbon derived from carbonisation of animal residues in a controlled atmosphere [10], otherwise, carbon origin could also derive from the carbonization of vegetable products. In some cases apatite was present when carbon was not. In these instances apatite mineral can be invoked. In all cases, the characteristic bands of the phosphate ions at 965 and 432 cm^{-1} are well identified (Fig. 1). The trace level of calcite (main band at about 1084 cm^{-1}) could be referred to the preparation technique, by grinding the ingredients in presence of water, or derived from the material constituting the mortar and the pestle.

Concerning the gray powders, the impression is that the original powder could have been white one and, as a consequence of the 79 AD event, the fall of black carbon particles or black minerals has turned its colour.

Some particular substances, just detected as painting materials in "Casa dei Casti Amanti" and "Officina pigmentaria", were found. Among them jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, was characterized (Fig. 1). This is a yellow basic iron sulphate already identified in Egyptian

Table 1
Composition of the samples examined according to the microRaman and FT-IR techniques

Catalog number	Aspect of content	MicroRaman	FT-IR
609B	Big white, black, gray, pink, yellow grains	CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Feld, αFeO(OH), Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , [TiO ₂ /Ru] ^a	CaCO ₃ /Ca, Sil
609C	Big white and black grains	C, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, TV
747	Black powder	C	AA, C, Sil, W
1046–1086	White, red, black grains	C, CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Sil
1106	Brown grains	Org	W
1612B	Brown powder	C, CaCO ₃ /Ca, PH, Sil	CaCO ₃ /Ca, Fe ₂ O ₃ , Sil
1944C	White and brown slivers	Feld, Ca(SO ₄) ₂ (H ₂ O)	Feld, CaCO ₃ /Ca
2049	Gray powder	Ca ₅ (PO ₄) ₃ (OH), C, CaCO ₃ /Ca, Fe ₂ O ₃ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Org, Sil
2191	Gray, white, red grains	Ca ₅ (PO ₄) ₃ (OH), Bi, C, CaCO ₃ /Ca, KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
2440–2475	Black powders	C, CaCO ₃ /Ca	C, CaCO ₃ /Ca, [Sil]
3250–5824N			
2445	Fine black powder	[Ca ₅ (PO ₄) ₃ (OH)], C	C, Org
2446	Gray powder	C, CaCO ₃ /Ca, Fe ₂ O ₃ , PH, Sil	CaCO ₃ /Ca, Pb(CO ₃), Sil, W
2825	White and gray grains	CaCO ₃ /Ca, Fe ₂ O ₃ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Org, Sil
2826	White and gray grains	Ca ₅ (PO ₄) ₃ (OH), C, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	Sil
3897–11432D	Black powders	C	C
4197B	Gray powder	Fe ₂ O ₃ , KAlSi ₃ O ₈	[CaCO ₃ /Ca], Org, Sil
4737B	Dark gray powder	TiO ₂ /An, C, KAlSi ₃ O ₈ , SiO ₂	CaCO ₃ /Ca, K(NO ₃), Org, Sil
4905	Brown and white powder	TiO ₂ /An, C, CaCO ₃ /Ca, Fe ₂ O ₃	CaCO ₃ /Ca, Sil
5281	Big pink, white, gray, black and green grains	C, CaCO ₃ /Ca, Pb(CO ₃), Sil	CaCO ₃ /Ca, Sil
5656A	Pink, black, white and gray grains	TiO ₂ /An, Aug, Bi, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	Ca ₅ (PO ₄) ₃ (OH), CaCO ₃ /Ca, Fe ₂ O ₃ , K(NO ₃), SiO ₂ , Sil
5730	Homogeneous powder with black, white and gray grains	CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Feld, Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Sil
5738G	Gray powder	Ca ₅ (PO ₄) ₃ (OH), C, CaMg(CO ₃) ₂ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	Ca ₅ (PO ₄) ₃ (OH), CaCO ₃ /Ca, Sil
5824B	Black powder with glass slivers	Fe ₂ O ₃	CaCO ₃ /Ca, Sil
5824E	Gray powder	CaMgSi ₂ O ₆ , CaMg(CO ₃) ₂ , Fe ₂ O ₃ , KAlSi ₃ O ₈ , SiO ₂	CaCO ₃ /Ca, Sil
5824M	Gray and black grains	TiO ₂ /An, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Org, Sil
6363A	Gray powder	CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Fe ₂ O ₃	CaCO ₃ /Ca, Sil
7147	Fine powder with big blue grains	C, Pb(CO ₃), Cu ₂ (CO ₃)(OH) ₂	Org
7220	Black, white and gray powder	Ca ₅ (PO ₄) ₃ (OH), C, CaCO ₃ /Ca, KAlSi ₃ O ₈	C, CaCO ₃ /Ca, SiO ₂
7524	Black white powder with slivers	Pb(CO ₃)	[CaCO ₃ /Ca], Pb(CO ₃)
8197C	White and gray powder	C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Sil
8205A	Very fine white, black and pink grains	C	[CaCO ₃ /Ca], αFeO(OH), Fe ₂ O ₃ , Sil
8569	Gray powder	C, CaCO ₃ /Ca, CaMg(CO ₃) ₂ , KAlSi ₃ O ₈ , glass	CaCO ₃ /Ca, Sil
8659	Gray powder	Ca ₅ (PO ₄) ₃ (OH), C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
8728	Big gray slivers	C, Cu ₂ (CO ₃)(OH) ₂	C, Cu ₂ (CO ₃)(OH) ₂ , Org
8886–15637	Fine black, white and pink grains	C, CaCO ₃ /Ca, Fe ₂ O ₃ , Sil	CaCO ₃ /Ca, Sil
8998	Black powder	C, CaCO ₃ /Ca, Fe ₂ O ₃	CaCO ₃ /Ca, K(NO ₃), Org, Sil
9027	Brown powder	NaAl(Si ₂ O ₆)(H ₂ O), CaAl ₂ Si ₂ O ₈ , C, αFeO(OH), Fe ₂ O ₃ , Pb ₂ PbO ₄ , KAlSi ₃ O ₈ , We	αFeO(OH)
9511	Red powder with white, gray, black and red grains	CaCO ₃ /Ca, Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , SiO ₂ , Sil	Fe ₂ O ₃ , SiO ₂
9685A	Gray powder	Ca ₅ (PO ₄) ₃ (OH), Aug, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Mg ₂ (SiO ₄), SiO ₂ , KAlSi ₃ O ₈	Ca ₅ (PO ₄) ₃ (OH), [C], CaCO ₃ /Ca
9767bisA	Bright gray powder with glass slivers	Aug, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , glass	CaCO ₃ /Ca, Sil
10419A	Fine powder with white, pink, green, black and yellow grains	C, CaCO ₃ /Ca, EB	CaCO ₃ /Ca, Org [Est]
10583B–10794I	Black powders	C	C, CaCO ₃ /Ca, Org [fats], W
12241A–12496			
13086–13584A			
11994Q			

Table 1 (Continued)

Catalog number	Aspect of content	MicroRaman	FT-IR
10690C	Black, white and gray grains	TiO ₂ /An, CaMg(CO ₃) ₂ , [Fe ₂ O ₃], Fe ₂ ³⁺ Fe ²⁺ O ₄ , glass	Ca ₅ (PO ₄) ₃ (OH), CaMg(CO ₃) ₂ , K(NO ₃)
10809III	Gray powder	NaAl(Si ₂ O ₆)(H ₂ O), CaCO ₃ /Ca, αFeO(OH), Fe ₂ O ₃	CaCO ₃ /Ca, [Org], Sil
10809XIII	Black powder	NaAl(Si ₂ O ₆)(H ₂ O), C, Mg ₂ (SiO ₄), αFeO(OH)	CaCO ₃ /Ca, K(NO ₃), Sil
10809XXII	Beige powder	CaCO ₃ /Ca, Fe ₂ O ₃ , KFe ³⁺ (SO ₄) ₂ (OH) ₆ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, K(NO ₃), Sil
10809XXVIII	Gray powder	[Ca ₅ (PO ₄) ₃ (OH)], C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	Org
10830C	Gray powder	[Ca ₅ (PO ₄) ₃ (OH)], C, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , [Fe ₂ ³⁺ Fe ²⁺ O ₄]	CaCO ₃ /Ca, Al ₂ Si ₂ O ₅ (OH) ₄
11294D	Black, white, gray and red grains	[Ca ₅ (PO ₄) ₃ (OH)], C, CaCO ₃ /Ca, Feld, Mg ₂ (SiO ₄), Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	CaCO ₃ /Ca, Sil
11338	Green slivers with white and red points	Cu ₃ (CO ₃) ₂ (OH) ₂ , Ca(SO ₄) ₂ (H ₂ O)	[CaCO ₃ /Ca], Ca(SO ₄) ₂ (H ₂ O)
11342–56204	Black and white powders	C, Sil	CaCO ₃ /Ca, Sil
11485–11486	Big grains with blue crusts	[Ca ₅ (PO ₄) ₃ (OH)], Cu ₃ (CO ₃) ₂ (OH) ₂ , CaCO ₃ /Ca	CaCO ₃ /Ca, Org [fats]
11994L	Fine black, white and red grains	CaCO ₃ /Ca, Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Sil
11994M	Gray, white and red grains	C, CaMgSi ₂ O ₆ , CaMg(CO ₃) ₂ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	[CaCO ₃ /Ca], Sil
11994T	Large white, black and red grains	CaCO ₃ /Ca, Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , SiO ₂	CaCO ₃ /Ca, Org
12000A	White, black and red particles	CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	CaCO ₃ /Ca, Sil
12012	Blue, black, white, yellow and red grains	C, CaMg(CO ₃) ₂ , [EB], αFeO(OH), Fe ₂ O ₃ , Sil	Ca(CO ₃)/Ar, CaCO ₃ /Ca, Sil
12045B–8179D	Dark gray powders	CaCO ₃ /Ca, Sil	CaCO ₃ /Ca, Sil
15791–21517			
55987			
12080A	Gray powder	Aug, CaCO ₃ /Ca, Fe ₂ O ₃ , [Fe ₂ ³⁺ Fe ²⁺ O ₄], KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
12108B	Dark gray powder	Ca ₅ (PO ₄) ₃ (OH), Aug, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
12132B	Dark gray powder	C, CaCO ₃ /Ca	CaCO ₃ /Ca, K(NO ₃), Org, Sil
12132F	Dark gray powder	C, CaCO ₃ /Ca, Fe ₂ O ₃ , SiO ₂	CaCO ₃ /Ca, [Org], Sil
12132N	Dark gray powder and black grain	NaAl(Si ₂ O ₆)(H ₂ O), TiO ₂ /An, Ca ₅ (PO ₄) ₃ (OH), CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	Sil
12148D	Black and white grains	CaCO ₃ /Ca, Sil	C, CaCO ₃ /Ca, Sil
12355	White, gray and black grains	C, Pb(CO ₃), Cu ₂ (CO ₃)(OH) ₂	Cu ₂ (CO ₃)(OH) ₂ , Org
12408A	Red orange powder	CaCO ₃ /Ca, Fe ₂ O ₃ , Sil	CaCO ₃ /Ca, Sil
12425	Dark gray powder	C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈ , SiO ₂	CaCO ₃ /Ca, Sil
12487	Gray powder	Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	Sil
12497	Fine black powder	C, CaMg(CO ₃) ₂	C, Sil
12777D	Red orange powder	Ca ₅ (PO ₄) ₃ (OH), αFeO(OH), Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, αFeO(OH), K(NO ₃)
12834	Black powder	C, CaCO ₃ /Ca, [Fe ₂ ³⁺ Fe ²⁺ O ₄], Fe ₂ O ₃ , SiO ₂	Org
12974C	Black powder	C	Ca ₅ (PO ₄) ₃ (OH), [Org], K(NO ₃)
12982B	Beige powder	glass	Org
13052C	Pink red powder	n.d. ^b	n.d. ^b
13270	White powder	CaCO ₃ /Ca, Ca(SO ₄) ₂ (H ₂ O), Fe ₂ O ₃	CaCO ₃ /Ca, Ca(SO ₄) ₂ (H ₂ O)
13271H	Gray, black and white grains	NaAl(Si ₂ O ₆)(H ₂ O), Ca ₅ (PO ₄) ₃ (OH), Aug, [CaCO ₃ /Ca], CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	Ca ₅ (PO ₄) ₃ (OH), K(NO ₃), Sil
13599	Black and white grains	Pb(SO ₄), C, Pb(CO ₃)	Pb(CO ₃), Ca(SO ₄) ₂ (H ₂ O)
13972	Black, white and gray grains	Ca(CO ₃)/Ar, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , PH, Sil	Sil
14187A	Gray powder	Ca ₅ (PO ₄) ₃ (OH), Aug, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
14201	Gray powder	C, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , [Feld], Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	CaCO ₃ /Ca, Sil
15367	Dirty white powder	Feld, Ca(SO ₄) ₂ (H ₂ O), SiO ₂	CaCO ₃ /Ca, Ca(SO ₄) ₂ (H ₂ O)
15824–15833	Black, white, and red grains	CaCO ₃ /Ca, Feld, Sil	[CaCO ₃ /Ca], Sil
19183–42967			
15827–15830	White, gray, and pink grains	Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	[CaCO ₃ /Ca], Sil
15840–15842			
15832	Polychrome powder	TiO ₂ /An, C, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , SiO ₂	[CaCO ₃ /Ca], Sil
17077–10718H	Pink, yellow, gray, black grains	CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , Sil	CaCO ₃ /Ca, Sil
17879	Fine white, black and red grains	CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Sil	CaCO ₃ /Ca, Sil

Table 1 (Continued)

Catalog number	Aspect of content	MicroRaman	FT-IR
19537	Red powder with some white grains	C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Fe ₂ O ₃ , Al ₂ Si ₂ O ₅ (OH) ₄
22178	Gray powders	[Ca ₅ (PO ₄) ₃ (OH)], CaCO ₃ /Ca, Feld, SiO ₂	CaCO ₃ /Ca, Sil
22302	Small and large polychrome grains	Org	CaCO ₃ /Ca, Sil, Org [fats]
22380	Fine white, gray, black and yellow grains	CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Feld	CaCO ₃ /Ca, Sil
22411	Gray slivers and grains	C, CaCO ₃ /Ca, [Pb(CO ₃)], Sil	CaCO ₃ /Ca, Sil
22757	Fine black and white grains	Org	CaCO ₃ /Ca, Org
22818–37415	Gray powder with white and red grains	CaCO ₃ /Ca, Fe ₂ O ₃	CaCO ₃ /Ca, Fe ₂ O ₃
25830	Fine black, Gray, pink grains	CaCO ₃ /Ca, [C], CaMgSi ₂ O ₆ , Feld	CaCO ₃ /Ca, Sil
25832	Pink, red, black and white grains	C, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , SiO ₂ , Sil	Sil
25850	Fine brown earthy powder	C, CaMgSi ₂ O ₆ , Feld, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , SiO ₂	[CaCO ₃ /Ca], Sil
37957	Fine powder with slivers	C, Fe ₂ O ₃ , γFeO(OH), Fe ₂ ³⁺ Fe ²⁺ O ₄	[CaCO ₃ /Ca], Fe ₂ O ₃ , Sil
53633	Gray, white, black and reddish grains	Aug, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
53679	Gray powder	CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Sil	CaCO ₃ 7Ca
54560	Three grains: one white, one black, one gray	Cu ₃ (CO ₃) ₂ (OH) ₂ , CaCO ₃ /Ca, CaMg(CO ₃) ₂ , Feld, FeO(OH)–αFeO(OH), Fe ₂ ³⁺ Fe ²⁺ O ₄	Sil, CaCO ₃ /Ca
54640	Gray powder	Ca ₅ (PO ₄) ₃ (OH), Aug, C, Fe ₂ O ₃ , SiO ₂	Ca, K(NO ₃), Sil
55756	Fine yellow brown powder	C, Ca(SO ₄) ₂ (H ₂ O), Sil	Ca(SO ₄) ₂ (H ₂ O), C, Sil
54856	Beige gray powder	NaAl(Si ₂ O ₆)·(H ₂ O), Aug, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Mg(SO ₄) ₇ (H ₂ O), Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄	CaCO ₃ /Ca, Sil
55027	Gray powder with glass sliver	CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈ , glass	CaCO ₃ /Ca, Sil
55029	Gray powder	NaAl(Si ₂ O ₆)·(H ₂ O), Ca ₅ (PO ₄) ₃ (OH), C, CaCO ₃ /Ca, Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, Sil
55033	Gray powder	NaAl(Si ₂ O ₆)·(H ₂ O), Ca(CO ₃)/Ar, C, CaCO ₃ /Ca, CaMg(CO ₃) ₂ , glass	CaCO ₃ /Ca, Sil
55725	White, black and gray grains	NaAl(Si ₂ O ₆)·(H ₂ O), Ca ₅ (PO ₄) ₃ (OH), Aug, CaCO ₃ /Ca, CaMgSi ₂ O ₆ , Fe ₂ O ₃ , Fe ₂ ³⁺ Fe ²⁺ O ₄ , KAlSi ₃ O ₈	CaCO ₃ /Ca, [Sil]

Abbreviations: AA, aliphatic acids; TiO₂/An, Anatase; Pb(SO₄), Anglesite; CaAl₂Si₂O₈, Anortite; Ca₅(PO₄)₃(OH), Idrossiapatite; Ca(CO₃)/Ar, Aragonite; Aug, Augite [(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆]; Cu₃(CO₃)₂(OH)₂, Azurite; EB, Egyptian blue; Bi, Biotite [K(Mg,Fe)₃[AlSi₃O₁₀(OH,F)₂]]; C, Carbon; CaCO₃/Ca, Calcite; Pb(CO₃), Cerussite; CaMgSi₂O₆, Diopside; CaMg(CO₃)₂, Dolomite; Mg(SO₄)₇(H₂O), Epsomite; Est, Ester; Feld, Feldspar; Fo Mg₂(SiO₄), Forsterite; αFeO(OH), Goethite; Ca(SO₄)₂(H₂O), Gypsum; Fe₂O₃, Hematite; KFe³⁺₃(SO₄)₂(OH)₆, Jarosite; Al₂Si₂O₅(OH)₄, Kaolinite; γFeO(OH), Lepidocrocite; Cu₂(CO₃)(OH)₂, Malachite; Fe₂³⁺Fe²⁺O₄, Magnetite; Pb₂PbO₄, Minium; K(NO₃), Niter; KAlSi₃O₈, Orthoclase; Org, Organicals; PH, Phosphate; SiO₂, Quartz; TiO₂/Ru, Rutile; Sil, silicates; TV, Terreverte; W, wax; We, wellsite [Ca,K,Na)₁-2(Si,Al)₈O₁₆(H₂O)].

^a All the abbreviations in the square brackets indicate a trace level.

^b n.d., not detected.

paintings [42] and also in Spain [43]. Its spectrum is complex and have been analysed in detail by Frost and coll. [44]. Other interesting findings were anglesite PbSO₄ and epsomite MgSO₄·7H₂O. These sulphates can be identified by their strongest band at 977 and 982 cm⁻¹, respectively, attributed to the sulphate symmetric stretching group.

These types of minerals are not ascribable to the existence of Italian mineral sites. In fact, they can be interpreted as degradation products of other materials, such as magnesite, dolomite and cerussa, in presence of sulfur dioxide from surges or from the modern acid rains [35,45]. The rare occurrence of minium Pb₃O₄ could be bound to its use as a pinkish material as a fards. As alternative, it could be due to cerussa degradation by heating during the violent 79 AD surges. In this case, the excavation context could be important for understanding this aspect.

The presence of iron compounds class, such as hematite Fe₂O₃, goethite αFeOOH, lepidocrocite γFeOOH (Fig. 1) and magnetite Fe₃O₄, in some case could derive from a proper addition of an ochre, in order to obtain a fard. In other containers these compounds can derive from a contamination due to earth components.

Sometimes, the pink particles identified inside some containers and not pertaining to iron oxides can be ascribed to the famous

purpurissum or to its fake, a madder extract. However, neither the infrared nor the Raman spectrum have been obtained (pink-red powder 13052C). Only in Raman microscopy it was observed that the particles were highly fluorescent.

Some words must also be devoted to the presence of white pigments inside the powders. The occurrence of aragonite, orthorhombic CaCO₃ (Fig. 2) and dolomite CaMg(CO₃)₂ is analogous to the painting material findings [46]. These carbonates can be easily distinguished by their IR or Raman spectra. In the microRaman spectra the fundamental CO₃⁼ vibration is observed at 1084 cm⁻¹ for calcite and aragonite and approximately at 1095 cm⁻¹ for dolomite.

The two calcium carbonates can be identified by deformation bands at 712 cm⁻¹ for calcite and 713, 699 cm⁻¹ for aragonite. Even if their IR spectra are different, particularly for the deformation band at 875 for calcite, 880 cm⁻¹ for dolomite and 855 cm⁻¹ for aragonite.

Among white substances, cerussite (CO₃⁼ symmetric vibration at 1052 cm⁻¹) (Fig. 3) could come from a hydrocerussite carbonation (band at 1037 cm⁻¹), the proper component of cerussa [32]. Its presence can be a clear indicator for cosmetic uses, since it is well known that its use in mural painting is not advisable.

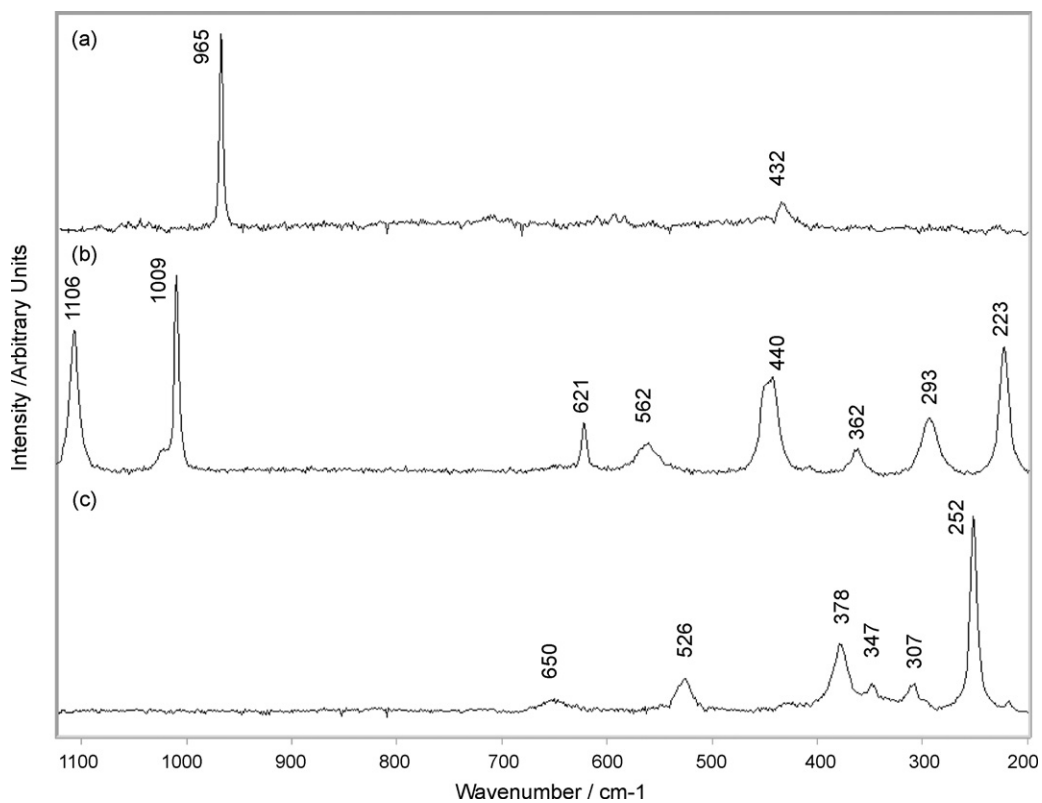


Fig. 1. MicroRaman spectra of: (a) apatite (holder n. 2049); (b) jarosite (holder n. 10809 XXII) and (c) lepidocrocite found in holder n. 37957.

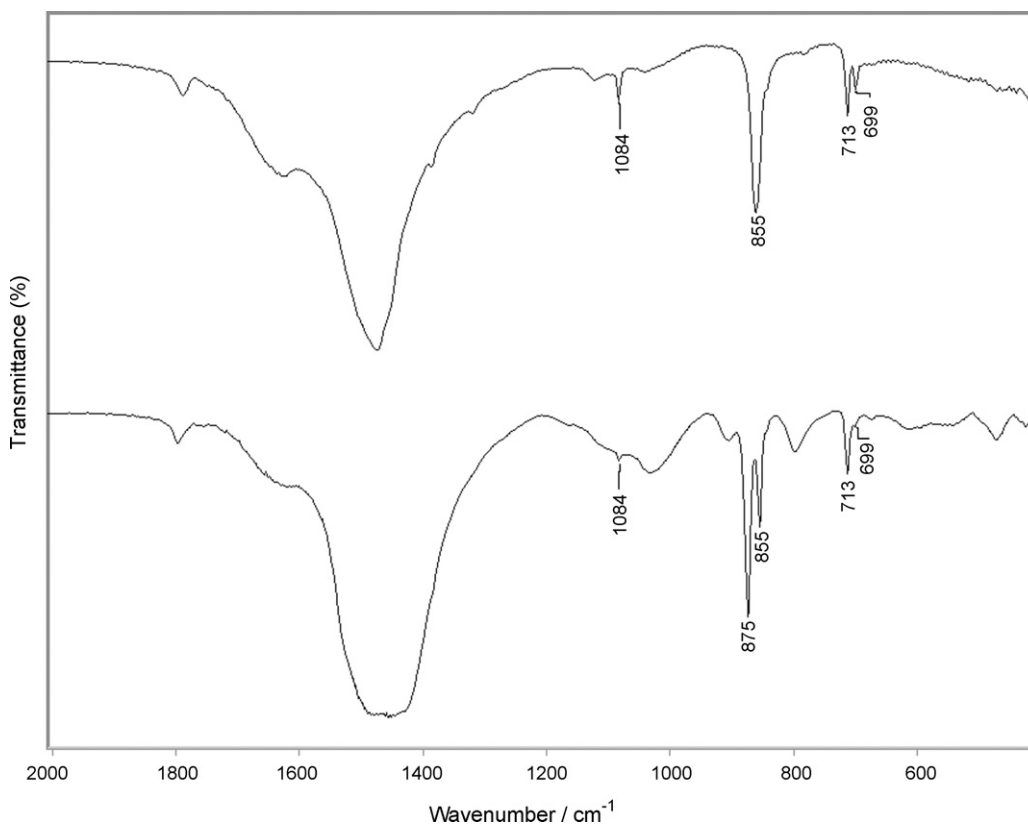


Fig. 2. Comparison between FT-IR reference aragonite and sample spectrum n. 13972 (from top).

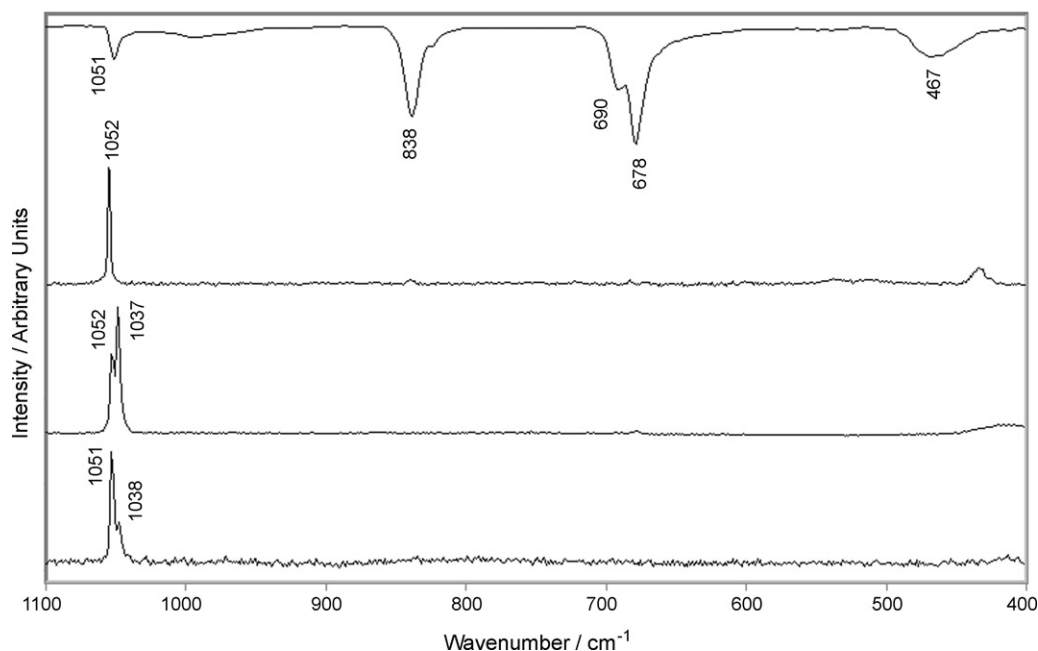


Fig. 3. FT-IR spectrum of an old C. Erba hydrocerussite, Raman spectra of cerussite, an old hydrocerussite by C. Erba and an historical cerussa sample (from top).

At the time, cerussa was employed as a foundation and probably because of its cost, it was substituted with gypsum for the lower level social classes. This is the reason of the frequent ascertainment of gypsum inside unguentaries [47].

Once more, it is evident that for a Roman there was not a clear difference between painting and cosmetic materials, in particular, in organic compounds remains, a closer examination of the binders could help in understanding the use of the pigment. Generally, the

wax and fats binders have been used in the ancient cosmetic materials.

Among the organic detected compounds, it is useful to distinguish between binders and other classes of compounds. Binders can survive a long period of time or partially give alteration products [48,49]. The original binders can be reconstructed from the found degradation compounds. The IR spectrum in Fig. 4 exhibits a band at 1737 cm^{-1} and a less

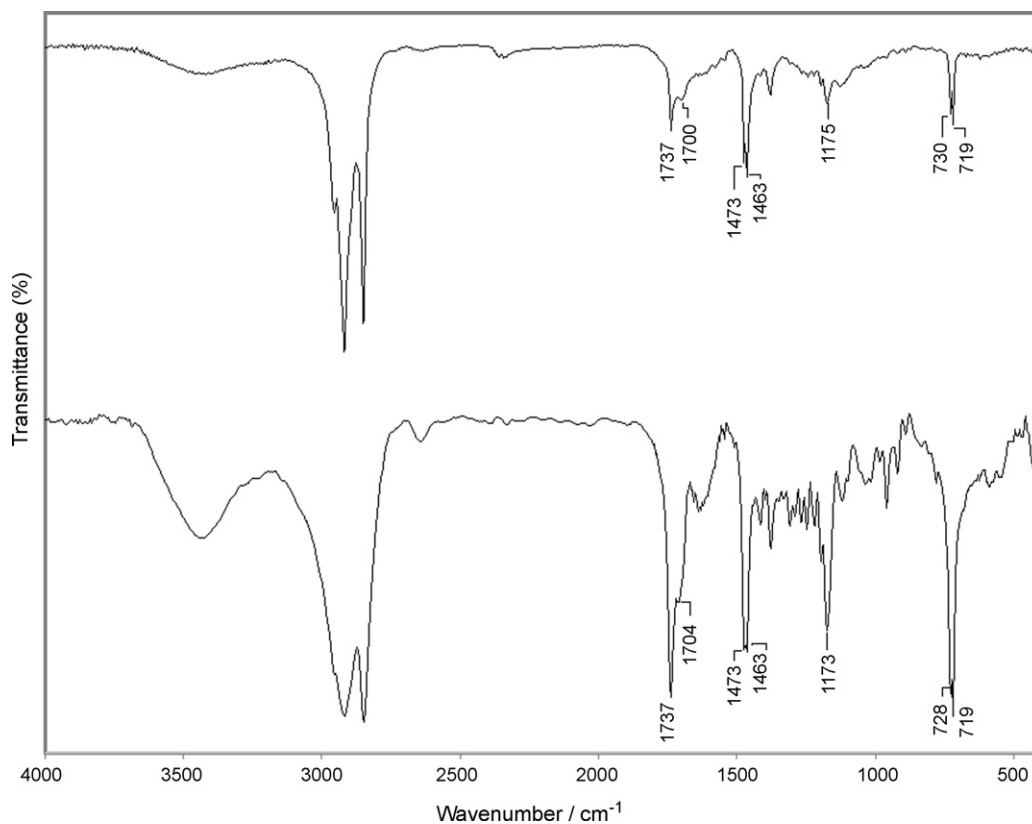


Fig. 4. Comparison between beeswax FT-IR reference spectrum and sample spectrum n. 13086 (from bottom).

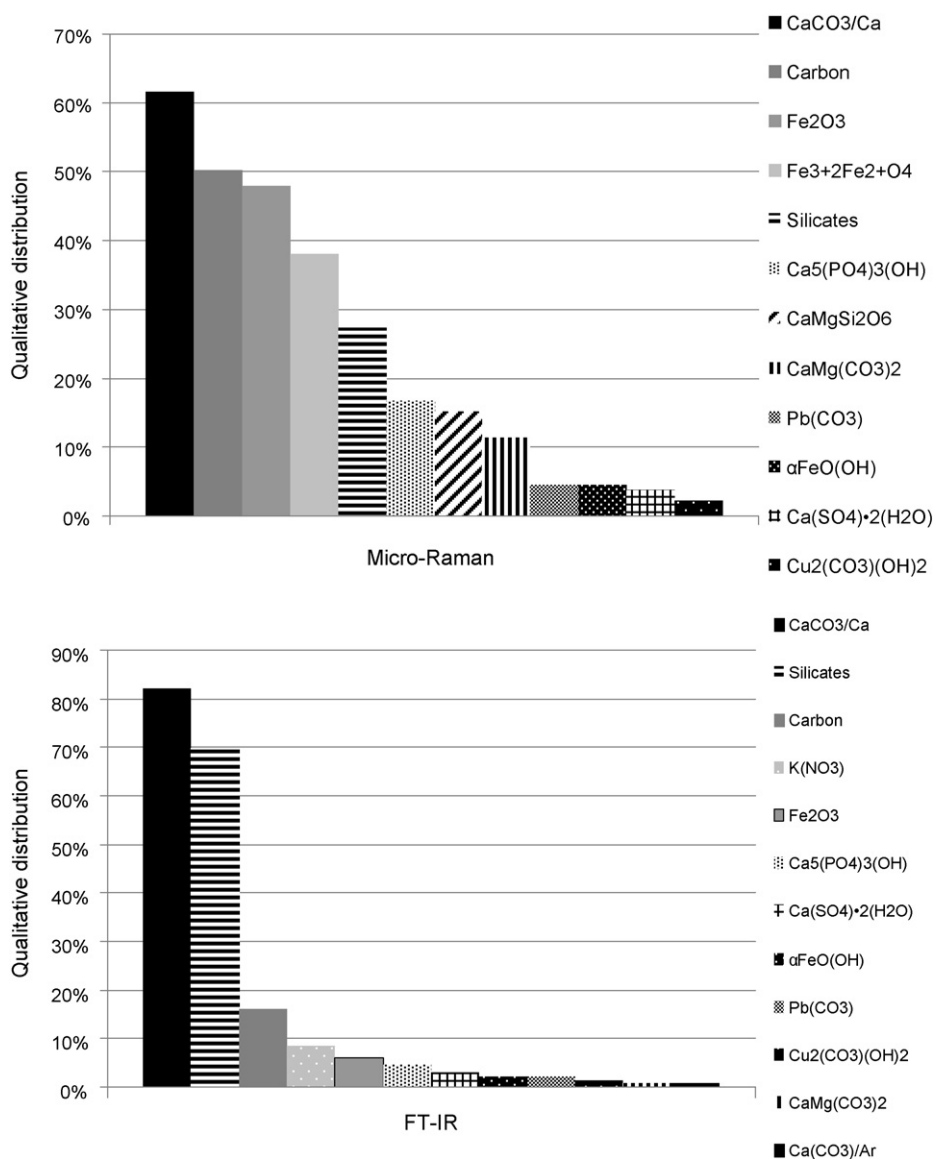


Fig. 5. Histograms of the qualitative distribution percentage in the examined samples: (a) according to the Raman technique; (b) according to the FT-IR technique (**Abbreviations:** Ca(CO₃)/Ar, Aragonite; CaCO₃/Ca, Calcite; Pb(CO₃), Cerussite; CaMg(CO₃)₂, Dolomite; αFeO(OH), Goethite; Ca(SO₄)·2(H₂O), Gypsum; Fe₂O₃, Hematite; Ca₅(PO₄)₃(OH), Idrossiapatite; Fe₂³⁺Fe²⁺O₄, Magnetite; Cu₂(CO₃)(OH)₂, Malachite; K(NO₃), Niter.).

intense band at 1700 cm⁻¹ referable to the wax ester bond and to free fatty acids, respectively. Double symmetric and antisymmetric C–H deformation (1473, 1463 cm⁻¹) and –CH₂ rotation (730–719 cm⁻¹) bands are fairly visible. In some cases the wax degradation was revealed with the free fatty acid formation.

Other compounds can be related to the extreme degradation of organic compounds, such as the frequently assessed potassium nitrate. Moreover, in a near future other analysis regarding the organic components will be taken into consideration.

For the purpose of comparison between data obtained by IR and Raman techniques, in Fig. 5 is reported in form of histograms the qualitative distribution percentage of the main compounds revealed from the spectral analysis.

As can be observed, different compounds and different percentages can be revealed by the results of the two techniques. This can be attributed mainly to their different spatial resolution high for Raman microscopy (up to 1 μm) and low for FT-IR transmittance measurements.

4. Conclusion

On the basis of the FT-IR and microRaman spectra, it has been possible to identify some specific old cosmetic materials and some binders (ex: wax) used in cosmetic preparations. In particular, Raman microscopy has been able to determine the presence of constituents in trace levels within the sample examined, not possible with FT-IR technique.

In the study of ancient black powders, the main result was the identification of the principal black component: the amorphous carbon, which, in the case of black eyeliners of Pompeii, has been characterized as *fuligo*. The ascertained presence of accessory materials, such as apatite, could allow to formulate an hypothesis about the preparation techniques and the source materials.

Many contamination and/or degradation products like silicates or minium are ascertained of being ascribed to the 79 AD events.

A special meaning has the occurrence of cerussa, a well cited foundation in the classical authors. The presence of cerussa could be markers for clearly identify a cosmetics product, since cerussa

was never used in wall painting. Instead, aragonite, dolomite and jarosite, some products even used in wall paintings, indicate a loose distinction between cosmetic and painting materials in Roman world.

The investigation in cultural heritage is a multidisciplinary work that needs the contribution of different research fields. The scientific method is fundamental to carry out a detailed and complete study, based on undoubted results. The combination of FT-IR and microRaman spectroscopies has been successfully used in providing the informations for a correct characterization of the contents inside holders. From these results, it has been possible to achieve a better knowledge and a complete and unambiguous identification of the investigated archaeological samples.

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