REVIEW

Not only wall paintings—pigments for cosmetics

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Abstract

Always very enlightening, the knowledge of the composition and production of ancient cosmetics has attracted the interest of diverse characterisation studies on archaeological residues in the last decades. Multi-analytical methods are the best option to attain a complete research, prioritising non-destructive techniques, and considering the complexity and the preservation of these ancient materials. X-ray diffraction, infrared and Raman spectroscopies, and electron microscopy with X-ray emission analysis are some of the most consolidated techniques to identify the composition and to reveal the technology of ancient makeups. The present review is mainly focused on the characterisation of inorganic pigments in these cosmetics, even if other ingredients of organic nature could be also included. Some more usual red, black and white components, like ochre, cinnabar, galena, cerussite and madder lake, are highlighted. A brief good practice guide for the analytical study of pigments in archaeological cosmetic residues is described at the end.

Keywords Archaeological residues · Contents · Minerals · Characterisation · Analysis

Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments (Gliozzo et al. 2021).

The first group of contributions explains how mortars have been made and used through the ages (Arizzi and Cultrone 2021; Ergenç et al. 2021; Lancaster 2021; Vitti 2021). An insight into their production, transport and on-site organisation is further provided by DeLaine (2021). Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from practical and technical standpoints (La Russa and Ruffolo 2021; Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Medieval (Murat 2021) wall paintings clarify the archaeological and historical/cultural framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red; yellow and brown ochres (Mastrotheodoros et al. forthcoming); Cu-based greens and blues (Švarcová et al. 2021); As-based yellows and reds (Gliozzo and Burgio 2021); Pb-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021); Hg-based red and white (Gliozzo 2021) and organic pigments (Aceto 2021). An overview of the use of inks, pigments and dyes in manuscripts, their scientific examination and analysis protocol (Burgio 2021) and an overview of glass-based pigments (Cavallo and Riccardi forthcoming) are also presented. Furthermore, two papers on cosmetic (this paper) and bioactive (antibacterial) pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

Introduction: looking at archaeological samples

Probably, one of the most exciting findings in archaeological or historical sites is any material related to cosmetic use, even though it is sometimes difficult to separate beauty, pharmacology and funerary practices. Information

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on cosmetic or medical products was already included in papyrus (Bardinet 1995; Manniche 1999) and ancient Greco-Roman documents, written by Dioscorides (*De Materia Medica* I.52–76), Ovid (*Ars amatoria*, Book III, and *De Medicamine Faciei Femineae*), Pliny (*Historia Naturalis*, Books XIII and XV), or Theophrastus (*De Sensibus*) (Green 1979; Pliny 1998; Wellman 1958). These descriptions explained the use and properties of some natural and artificial materials. However, the archaeometric investigations of archaeological cosmetics can contribute to shed light on several aspects of everyday life, how cosmetics were made, and the chemical know-how of ancient societies. Therefore, analysis of makeup residues remaining in glass, ceramic or stone containers, sometimes even on metallic objects, always attracted the interest of researchers since the beginning of the archaeological sciences (Chapman and Plenderleith 1926; Lucas 1930).

In the literature, some authors provided an in-depth description of materials and techniques involved in cosmetic production in antiquity (Lucas and Harris 1962; Forbes 1965; Moorey 1999); this information was also most recently revised (Olson 2009; Scott 2016; Vázquez de Ágredos-Pascual et al. 2018). When there is an opportunity to characterise archaeological residues, a correct analytical approach can improve the knowledge of these ancient materials and the technology to produce cosmetics. Besides the value of the archaeological and conservation data that can be obtained, the characterisation of such historical contents/residues needs to consider some significant analytical aspects in order to preserve material integrity (minimising sampling) and to resolve complex mixtures of compounds. Then, a multi-analytical method is the best option to achieve a characterisation as complete as possible. This research requires non-destructive or micro-destructive techniques with high selectivity and high sensitivity, in order to obtain morphological, molecular and elemental information.

Before any physicochemical analysis of the materials, a previous thorough study by stereomicroscopy and optical microscopy (with polarised light too) can provide data on the possible mineral components (Eastaugh et al. 2008), as well as on the presence of organic components and other materials (i.e. from plants) in the archaeological contents. Moreover, current image software to treat photomicrographs can highlight significant details of the cosmetic residue composition. This initial observation can be also useful to isolate particles of different compositional nature, to characterise them individually, avoiding the heterogeneity of this type of materials.

X-ray diffraction (XRD) is one of the most frequently used methods in the study of cosmetics, because it allows the mineralogical phases to be identified, especially if they are about well-crystallised components. Due to the scarce quantity of archaeological materials and to the requirement of analysing micro-samples, synchrotron radiation (SR) offers a variety of methods to analyse archaeological makeups, including XRD (SR-XRD), but also infrared spectroscopy (SR-IR) and X-ray absorption near edge structure (SR-XANES) (Dooryhée et al. 2004).

Two vibrational (Raman and Fourier transformed infrared (FTIR)) spectroscopies can also provide useful information to characterise molecular structures and to identify some components, mainly because both techniques can be non-invasive and work with micro-samples. Both methods are well suited for the characterisation of non-crystalline (i.e. amorphous) materials.

Electron microscopy contributes to complete the characterisation, improving data on microstructure, phases and elemental composition. Scanning electron microscopy (SEM) is the most utilised, including chemical analysis with energy-dispersive X-ray spectrometry (EDS). Current electron microscopes can be equipped with an electron backscattering diffraction (EBSD) detector, which allows crystallised phases to be identified (Pérez-Arantegui and Larrea 2015). Transmission electron microscopy (TEM) is used to study some crystal phases or defects.

Finally, elemental composition can be determined by X-ray fluorescence spectroscopy (XRF) or by inductively coupled plasma atomic emission spectrometry (ICP-AES). The last method provides bulk composition of the cosmetic material, whereas the former technique can be non-invasive and applied in micro-areas.

Examples of the utilisation of all these analytical techniques to characterise pigments in cosmetics will be shown in the next sections of this paper. Nevertheless, we have to consider that most archaeological cosmetics are mixtures of inorganic and organic components. In this second category, oils, fats or resins can frequently be present and the use of mass spectrometry (MS) is required to provide a complete characterisation of the residues (Ribechini et al. 2011).

According to early descriptions (Green 1979; Bardinet 1995; Pliny 1998; Manniche 1999; Wellman 1958), ancient cosmetics were combinations of several ingredients of different properties and nature (organic and inorganic). Most described mixtures corresponded to products formed with powder pigments, or with oils and/or resins (probably perfumes or unguents). For instance, Greek and Roman preparations were divided into seven categories: balsams or unguents (*myra*), cerates (*keromata*), pain-stilling unguents (*acopa*), liquid unguents (*epichrismata*), unguents with vegetable powders (*malagmata*), dusting powders (*parapasta*) and cosmetic powders made by aspersion (*diapasmata*) (Forbes 1965). The different components, carefully mixed by specialists, provided suitable properties: texture, astringency, scent, or colour. As well as their original compositional complexity, important

transformations can appear in archaeological cosmetics due to ageing and postdepositional modifications. Then, oxidation, chemical bond breaking, substitution, volatilisation of some components and other possible reactions should be considered to correctly characterise the archaeological residues.

Many different pigments were used in cosmetics throughout history. Ochres were materials to colour faces, hands or bodies in red, orange or yellow hues (Roebroeks et al. 2012; Hodgskiss and Wadley 2017). The two most common Egyptian eye paints were malachite (a green copper carbonate) and galena (black lead sulphide); the last one was specially popular (Lucas 1930; Lucas and Harris 1962). The analyses carried out in Mesopotamian materials from the cemetery of Ur allowed azurite, malachite, haematite and pyrolusite to be identified (Bimson 1980). Green, blue and white cosmetic powders (mixtures of mineral phases) were found in 3rd-millennium BCE stone flagons at Shahr-i Sokhta (Sistan, Iran) (Vidale et al. 2016). In antiquity, the poisonous properties of some cosmetic ingredients seemed to be less important than the colour; then, products like red mercury sulphide and black or white lead compounds (galena and cerussite) were included in the cosmetic box. However, other black components (soot or carbon black) and white powders (clays) could substitute them in some periods. Even other infrequent white products were found in archaeological cosmetics. White lumps found inside a Chinese first-millennium BCE bronze jar were prepared with monohydrocalcite from cave moonmilk; it was one of the components to prepare a face cream (Han et al. 2021). However, cassiterite (tin oxide) was found in the contents of a small Roman tin canister, which contained a cosmetic cream (Evershed et al. 2004). Freshwater pearl powder was also used in an ancient Chinese cosmetic found in a tomb of the Late Northern Song dynasty (1074–1111 CE) (Yu et al. 2017). Calcite and gypsum were also identified in many ancient contents, often with the aim of lightening the colour, but sometimes as alteration or contamination products. Then, a review of some of the most common pigments found and characterised from archaeological residues is expounded below.

Earth pigments in cosmetics

Coloured iron compounds are probably among the most ancient materials used as pigments (see Domingo Sanz and Chieli 2021) in this topical collection), including ritual and symbolic purposes (Zilhão et al. 2010; Zilhão 2012; Roebroeks et al. 2012; Hodgskiss and Wadley 2017). Earth pigments, also called ochres, comprise compositionally heterogeneous materials coming from ferruginous rocks, and they contain iron oxides, like haematite (α-Fe_2O_3), or hydrated iron oxyhydroxides, like goethite (α-FeOOH); generally, those reds are haematite-rich, and goethite uses

to be the major component of yellow ones. For an in-depth description of this type of earth pigments, see the paper by Mastrotheodoros et al. (forthcoming) in this topical collection.

Perhaps due to their natural abundance, ochres are among the earliest pigments used; however, few studies address these materials as cosmetics. Kiehn et al. (2007) analysed samples from seven prehistoric mines in Botswana (Southern Africa), which could be the sources of the iron oxide used as an appreciated cosmetic during the Late Stone Age and Iron Age in this area. They tested the feasibility of using specular haematite (or specularite, Fe_2O_3) as geochemically fingerprinting of the archaeological source, by means of instrumental neutron activation analysis (INAA) of the heavy mineral fraction.

Haematite was identified by Raman spectroscopy in the red pigments that covered the surface of cosmetic sticks found in Xiaohe cemetery (1980–1450 BCE) at Xinjiang, China (Mai et al. 2016). These objects were usually found in women tombs and they could be a primitive crayon for makeup or painting.

According to historical sources, Forbes (1965) described the use of earth pigments in preclassical societies. Mesopotamian people used red ochre as face powder; however, Sumerians preferred yellow earth, also called "golden clay" or "face bloom". In the classical makeups, Roman women employed several mineral substances for the rouge, and Forbes (1965) suggested red chalk (reddish limestone) among them.

Through the combination of several analytical techniques, Huq et al. (2006) found iron oxides in Punic makeup materials dating from the fourth to the first centuries BCE. They used Raman spectroscopy and SR-XRD to characterise the mineral components, identified as haematite in four of the analysed samples; optical microscopy and atomic absorption spectrometry were also applied to complete the study. In addition to iron oxides, these samples contained quartz, and some clay minerals (detected by XRD). Then, the authors suggested a natural source of the red pigment.

In red makeups, the presence of several minerals, together with iron oxides, seems to be common. These minerals could come from the source of the natural red pigment, or be added to modify the hue to produce paler shades. Red ochres with calcite and some quartz were highlighted by R.E. Jones (Carington-Smith 1982), studying a pink powder found inside a Roman globular *unguentarium* recovered from Knossos. Similar results were obtained through the analysis of the contents in two different Roman objects (a glass *unguentarium* and shell fragments) from Iberia, verifying the presence of red ochre mixed with other components (Pérez-Arantegui et al. 1996). In this case, an analytical multi-technique approach by XRD, FTIR and particle-induced X-ray emission (PIXE) was also performed. In the

glass vessel (first century CE, Isings 11 form (Isings 1957), Fig. 1), gypsum and calcite were found together with red ochre. However, the remains of reddish powders on shell fragments (dated to 100 CE, Fig. 2) showed the presence of red ochre and calcium carbonate (probably calcite). The use of seashells as makeup tools is common in different ancient cultures; for instance, they were found as cosmetic receptacles in Mesopotamia (Moorey 1999), in the Punic world (Ben Younès-Krandel 1992; Karmous et al. 1996) and in Roman cities (Bejarano Osorio et al. 2019).

FTIR spectroscopy has demonstrated to be a valuable method for the structural characterisation of this type of pigments, in spite of its limitations, and it provides additional information on organic components (Lettieri and Giannotta 2017). Raman microscopy was particularly advantageous to determine the presence of constituents in trace levels within the sample examined, sometimes not possible by FTIR; this method identified the presence of iron oxides in some Pompeiian *unguentaria* (Gamberini et al. 2008).

Earth pigments for cosmetics could be sold as small balls in ancient markets. Vázquez de Ágredos-Pascual et al. (2019) characterised some coloured materials found in the Roman market from Magdala (Lower Galilee), dated to first century. CE; they identified red and yellow ochres, haematite and jarosite (an iron-hydroxysulphate mineral) by light microscopy, SEM–EDS and FTIR spectroscopy.

The use of ochres in cosmetics spreads all over the world and chronologies. Doménech-Carbó et al. (2012) studied residues contained in 31 miniature ceramic vessels found in a burial in Teotihuacan (Central Mexico), its chronology dates from approximately 200–350 CE (*Tlamimilolpa* period). For the full characterisation of these samples, a multi-analytical

Fig. 2 Shell fragment found in archaeological excavations of *Caesaraugusta* (Zaragoza, Spain), dated to 100 CE

approach was performed, using light microscopy, SEM-X-ray microanalysis, TEM, XRD, voltammetry of microparticles, FTIR spectroscopy, UV–Vis spectrophotometry and gas chromatography (GC)-MS (this last method to identify organic products). Several earth pigments, iron-based compounds, were found as components of these pre-Hispanic cosmetics: haematite, jarosite and goethite. Once again, these products appeared mixed with quartz, clays, feldspars or some minor impurities (like ilmenite, barite, manganese oxides or zircon). Yamada et al. (1997) analysed red cosmetics found in several ancient burials from the third to the sixth centuries CE in three separate geographical areas of Japan, also confirming the use of iron oxides.

Beauty or toxicity? The role of mercury and lead

Red colour of cosmetics was also provided by the bright red mineral, cinnabar (a mercury sulphide, α-HgS), or its synthetic version, vermilion, in spite of its toxicity (see Gliozzo (2021) in this topical collection). Cinnabar was found in four samples of the red Punic makeups analysed by Huq et al. (2006), following the analytical procedure already cited. According to classical texts, this red compound appeared in the toilet box for the rouge of Roman women (Forbes 1965). Vázquez de Ágredos-Pascual et al. (2019) also identified cinnabar in a medium-red ball from the first-century CE Magdala market, which could be used as pigment or cosmetic. Mercury sulphide was also detected, as minor component mixed with iron oxides, in pre-Hispanic cosmetics (Doménech-Carbó et al. 2012); in this case, the compound was identified by voltammetry of microparticles and polarised light microscopy. Significant quantities of mercury were

Fig. 1 Fragment of Isings 11-form *unguentarium* found in the colony of *Vitrix-Iulia-Celsa* (Zaragoza, Spain), dated to first century CE

determined by ICP-AES in red samples from ancient burials in Japan (Yamada et al. 1997); the proportions of Hg and Fe allowed the authors to classify the cosmetics into four groups, where mercury sulphide and iron oxides were the main components. However, mercury-based cosmetics are not frequently found in archaeological contents, and this evidence could be related to the limited use of these expensive and toxic compounds. By contrast, cinnabar was widely used for ancient funerary rites, maybe because of the symbolic value of red colour, or its conservative properties (see Gliozzo (2021) in this topical collection).

Lead compounds appear much more profusely in many of the archaeological contents related to cosmetic products (see Gliozzo and Ionescu (2021) in this topical collection). In order to differentiate and identify these materials, XRD (or SR-XRD) is essential, supported by other microscopy methods. Two different groups of lead-containing materials can be described according to its colour: black pigments and white products (or sub-products). An in-depth study of the contents preserved in their original vessels (dated to 2000–1200 BCE) allowed to identify black galena (PbS) and white cerussite ($PbCO_3$), together with artificial white lead chlorides (phosgenite, $Pb_2Cl_2CO_3$, and laurionite, PbOHCl) (Walter et al. 1999; Martinetto et al. 2000a, 2001); these objects belonged to the Egyptian department of the Louvre Museum (Paris, France).

Galena was used as black eye-paint in ancient Egypt since 5000–3000 BCE (Lucas 1930; Lucas and Harris 1962; Forbes 1965; Manniche 1999; Hardy et al. 2006); it was also described among the ingredients of Egyptian therapeutic recipes (Manniche 1989; Nunn 1996). Moreover, there were similar black makeups in Mesopotamia, in the classical Mediterranean, and later in the Islamic world, with medical, cosmetic or protecting purposes (Forbes 1965; Hardy et al. 2006). Egyptian cosmetics from the Louvre museum contained galena as one of the main products, proving its intentional use, and they were studied using a multi-analytical approach by XRD, SR-XRD, SR-XRF, SR-XANES, PIXE, SEM and TEM (Walter et al. 1999; Martinetto et al. 2000a, b, 2001; Ungár et al. 2002; Deeb et al. 2004; Castaing et al. 2007). The samples were thoroughly characterised, and information on composition, preparation technology, and properties of the cosmetic materials were revealed. For instance, data from TEM (Deeb et al. 2004; Castaing et al. 2007) and XRD (Ungàr et al. 2002) contributed to explain the crushing process of the black powders. The study by an electroanalytical method (amperometry) disclosed the biomedical properties of the Egyptian black makeups, also used for eye diseases (Tapsoba et al. 2010).

Another example of the ancient use of galena is provided by the Late Bronze Age "kohl box" found at Tepebağ Höyük (modern Adana, Cilicia, Turkey). This significant archaeological artefact was dated between the fifteenth and thirteenth centuries BCE and its contents were characterised by SEM–EDS (Şahin 2020). The small decorated object was made of basalt and it contained mainly lead sulphide, with some grey and white particles identified as altered lead compounds.

Lead pigments were also described in ancient cosmetics from China; early cosmetic use probably dated of the pre-Qin period (before 221 BCE) (Schafer 1956).

An indirect use of lead sulphide, synthesised from lead oxide, was highlighted through the study of an ancient hair-dyeing formula (Walter et al. 2006; Patriarche et al. 2014). The recipe was described in texts since the Greco-Roman period, and the data from X-ray micro-diffraction and scanning transmission electron microscopy (STEM) showed the presence of PbS nano-crystals within the hair, causing the blackening.

Galena was also identified through XRD and SEM in a fourth-century CE glass vessel from Late Roman Palestine (Grüner 2002). As well as PbS, $PbCO_3$ (cerussite) and $PbSO_4$ (anglesite), common products of galena alteration, were identified in these Palestinian contents.

Later use of galena was also verified in products from Islamic Middle-Age Iberia. A small glass vessel (Fig. 3) was found in an archaeological context dated to eleventh to twelfth centuries CE in Albarracin (Teruel, Spain); it contained black powders, which were analysed by voltammetry of immobilised microparticles and SEM–EDS, and identified as lead sulphide (Pérez-Arantegui and Ceprá 2014). The contents of two glass *unguentaria* found in the Renaissance level (sixteenth century CE) of an archaeological excavation in Zaragoza (Spain) were analysed in the same study (Pérez-Arantegui and Ceprá 2014), but other lead compounds (especially lead sulphate) were found in this case, maybe the results of some ageing and alteration of the original material. In faraway lands, galena was found in several pigments of the pre-Hispanic cosmetics from Teotihuacan (Central Mexico), studied by Doménech-Carbó et al. (2012).

Probably because of its toxicity, or maybe its lack of availability in some places, galena was substituted by other

Fig. 3 Small glass vessel from the archaeological site of the medieval Islamic castle in Albarracin (Teruel, Spain), eleventh to twelfth centuries CE

black pigments in different periods and societies. Soot was used as black eye-paint in Greco-Roman makeups (Forbes 1965). Gamberini et al. (2008) used micro-Raman and IR spectroscopy to characterise some black and grey compounds found inside Pompeiian *unguentaria*, and they found amorphous carbon (*fuligo* or black smoke) in these powders. Cersoy et al. (2016) proposed a method using synchrotron-based techniques to distinguish amorphous and crystalline phases in this type of carbon black samples. Charcoal was also found mixed with galena in pre-Hispanic cosmetics, maybe to reduce PbS toxicity (Doménech-Carbó et al. 2012).

White lead pigments can be also found among ancient makeups. Early use of white lead minerals was already verified by the analysis of some cosmetic samples from the Royal cemetery of Ur (c. 2500 BCE), stored in the British museum, where cerussite was detected, mixed with malachite, in a green powder (Bimson 1980). Sotiropoulou et al. (2010) studied and analysed lead pigments and tools used in Akrotiri (Thera, Greece) during the Early, Middle and Late Cycladic Bronze Age (c. 3000–1600 BCE), by XRF and XRD; they also found lead carbonates among the compounds, but the cosmetic use of these products could not be verified.

Vidale et al. (2012) analysed the contents of a stone flagon found in Shahdad (Kerman, Iran) and dated of the fourth millennium BCE or slightly later. They identified mainly artificial lead carbonates (cerussite and hydrocerussite), using XRD, SEM–EDS, FTIR and thermogravimetric analysis (TGA). This study confirmed again that wet chemical processing of lead compounds was already common in the third millennium BCE.

Cerussite, together with synthetic lead chlorides (phosgenite and laurionite), was characterised in the contents of Egyptian 2000–1200 BCE objects (Walter et al. 1999; Martinetto et al. 2000a, 2001; Deeb et al. 2004; Castaing et al. 2007). As well as the use of techniques as SR-XRD, SR-XRF, PIXE, SEM and TEM for the analysis of these samples, the data performed by SR-IR micro-spectroscopy provided information on spatial location of phosgenite and, especially, on the interaction between lead compounds and the organic components of the cosmetics (Cotte et al. 2005).

Greek women whitened their faces with lead carbonate, and this compound was also among the preferences of Roman ladies (Forbes 1965). The analysis of the contents of several objects from Greece and Paestum (Italy), dated to the Hellenistic period, confirmed the use of white lead compounds in these makeups (Welcomme et al. 2006). In this case, cerussite ($PbCO_3$) and hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) were found in the samples; the mixture of both compounds was known as *psimythium* (in Greek) or *cerussa* (in Latin) and it implied the intentional synthesis of hydrocerussite, whose formulation was already described in classical texts (Wilner 1931). Lead carbonates were also determined in Pompeiian samples of cosmetics (Gamberini et al. 2008).

A completely different research on lead-based cosmetics can be taken by means of lead isotopic analysis, because isotope rates could help to identify sources of galena. Shortland et al. (2000) investigated the origin of lead found in Egyptian eye-paint samples and they concluded that it was probably from Gebel Zeit on the Red Sea coast of Egypt. Ghazi (1994) used ICP-mass spectrometry (ICP-MS) to determine the lead concentration and isotope ratios in eighteenth to nineteenth centuries CE traditional cosmetics from Omaha tribe (USA). Other investigations on ancient cosmetics were focused on absolute dating of lead carbonates by radiocarbon, through accelerator mass spectrometry (AMS), studying ancient Egyptian and Greek white cosmetics from the Louvre museum in Paris (Beck et al. 2018).

Another lead compound, red lead (*minium*), also appeared among products of Roman makeup (Wilner 1931), but it has not been identified in archaeological cosmetics until now. However, Baraldi et al. (2020) that studied some rare pink and red pigments in Punic samples collected in Sicilian museums identified an unusual lead chromate block.

What about organic pigments?

Diverse organic compounds from plants were described as ingredients in ancient cosmetics (Wilner 1931; Forbes 1965; Scott 2016), but very few ones have been analytically characterised in archaeological contents. For instance, henna (*Lawsonia inermis*) could be used to colour hands, feet, nails and the hair in ancient Egypt (Lucas 1930; Scott 2016). However, pink or violet-pink materials were occasionally found in ancient cosmetics. Pink compounds, identified as madder lake, were found in Punic cosmetic materials dated to the second half of the first millennium BCE (Karmous et al. 1996; Huq et al. 2006). We have also examples of these archaeological contents in several Roman *unguentaria* and cosmetic tools, studied by diverse analytical techniques (Mazzocchin et al. 2003; Hottentot and Van Lith 2006; Van Elslande et al. 2008a; Pérez-Arantegui et al. 2009; Palamara et al. 2016; Marcaida et al. 2017; Bejarano Osorio et al. 2019). In all cases, the results highlighted the use of madder lake. This pigment was known since antiquity (Schweppe and Winter 1997; Chenciner 2000; Daniels et al. 2014), and its role as cosmetic product was reported in Greco-Roman texts (Wilner 1931; Forbes 1965). Its identification is frequently challenging due to its scarcity and the low amounts typically found in archaeological contents.

Madder and other alizarin-containing plants produce one important red dye. In Europe, many of these plants belong to the large *Rubiaceae* family, which contain alizarin and related anthraquinones as the main colouring components (the most important being purpurin, munjistin, pseudopurpurin,

xanthopurpurin and rubiadin) (Schweppe and Winter 1997). In order to characterise this madder-based pigment, samples from archaeological contents were studied by mass spectrometry methods: laser desorption-ionisation (LDI-MS), electron ionisation (EI-MS) and high-performance liquid chromatography (HPLC–MS), or by voltammetry, to identify the organic dye. Other options of madder identification can be data acquisition by spectrofluorometry (Claro et al. 2008), ultraviolet–visible (UV–Vis) absorption spectrometry (Daniels et al. 2014) and Raman spectroscopy (micro-Raman and surface-enhanced Raman scattering (SERS)) (Van Elslande et al. 2008b; Marcaida et al. 2017). This last method (SERS) is suitable for the identification of madder lake because it needs small amounts of sample to perform the analysis (Leona et al. 2006); for instance, Pompeiian pink and purple pigments were characterised in only 5-mg samples (Marcaida et al. 2017).

Nevertheless, the use of madder in the form of pigment needs the contribution of a mordant that reacts with the dye, and, in this way, the colourant can precipitate on the inorganic component to produce the lake. Therefore, the complete characterisation of pink cosmetics requires identifying the inorganic constituent (the mordant). For this purpose, SEM–EDS represents an efficient analytical tool. This method highlights the micro-structure of the inorganic particles and their elemental composition. In the analysed archaeological pink cosmetics, the mordant uses to be an aluminium silicate (Marcaida et al. 2016), probably from pure white clay. However, in some cases, madder was precipitated on an almost pure aluminium hydroxide (Pérez-Arantegui et al. 2009); this example corresponded to pink powders adhered to the surface of a Roman bronze cosmetic tool, probably dated fifth century CE.

Besides the inorganic mordant, the reddish madder lake (Fig. 4) was usually diluted with a white component, gypsum ($CaSO_4·2H_2O$) or calcite ($CaCO_3$), to be used as cosmetic. The characterisation of all these components also improves the knowledge on the abilities and techniques to prepare cosmetic materials in different historical periods.

Safflower (from *Carthamus tinctorius* L. petals) could be used to produce ancient Chinese cosmetic rouge (Wouters et al. 2010). Dyeing silk or cotton with safflower was described in the literature, but differences between Chinese descriptions of dye and red cosmetics (*yanzhi*) are sometimes confused (Trombert 1997), and limited analytical research of Chinese archaeological cosmetics has been still published (Han et al. 2021).

Good practice guide

In this conclusive section, the analytical steps required for accurate characterisation of archaeological cosmetics are described. The procedure explained below regards pigments,

Fig. 4 Light-pink powders found in a Roman globular glass *unguentarium*, dated to the middle of the first century CE (*Vitrix-Iulia-Celsa*, Zaragoza, Spain)

while the analytical approach to organic components such as oils, fats and resins is beyond the aim of this review.

If we suspect that an archaeological object could contain any residues related to makeup, the first task is the visual examination of these contents and their thorough observation with light microscopy before deciding to sample the materials. This initial step allows also having a first description of the possible components. Simple features, like colour, amorphous or crystalline aspect, shape, size and light reflexion, can be very helpful to make next decisions.

Firstly, good practice requires archaeometric objectives to be properly structured, such as material identification, production technology definition, source of the components, or conservation. After this essential step and the initial description, we can proceed to plan the sampling strategy, for instance to choose non-invasive methods or microsampling, to extract only part of the contents or to empty the materials out of the vessel, to decide to analyse the powders, as a whole, or to isolate particles of different nature.

At this step, if some organic components (oils, fats, resins) were suspected, a second analytical procedure should be also followed to characterise these compounds, usually through chromatographic methods, mass spectrometry and FTIR spectroscopy.

As we have seen in the previous sections, there is not a single method to answer all the possible questions related to the identification of materials and technology used to produce ancient cosmetics. The utilisation of several analytical techniques can provide the best complementary results to achieve the research objectives. We should also take into account if non-invasive analytical results or microsampling data will be significant enough and representative of the studied materials to accomplish the research aims.

The choice of the analytical methods and their application sequence have to be decided before beginning the characterisation, with the purpose of making every effort to preserve the heritage-material integrity or to limit the destruction of the archaeological contents to a minimum.

Then, optical microscopy, XRD, FTIR, Raman spectroscopy and SEM–EDS can provide enough information to characterise the cosmetic residues (mineralogy, microstructure, and molecular composition). XRF and ICP-AES can highlight the elemental composition of these materials. Other specific data (like isotope analysis, crystal defects, or surface reactions and alterations) can be provided by additional less-conventional techniques (such as TEM, SR-XRD, SR-XANES). Finally, the study will not be probably finished with the pigment characterisation, and the research will have to be completed with the identification of the organic components (for instance by FTIR, HPLC–MS, GC–MS, or LDI-MS).

Data availability Data sharing is not applicable to this review article as no new data were created or analysed in this study.

Code availability Not applicable.

Declarations

Conflict of interest The author declares no competing interests.

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