Characterization of residues found within some Roman *unguentaria* glass artefacts: preliminary results of a multi-disciplinary approach

IOANA MARIA CORTEA
OVIDIU ȚENTEA

Abstract:
Despite the large number of *unguentaria* vessels generally discovered in Roman archeological sites, very little information is available concerning the nature and chemical composition of the products that were originally contained within these artifacts. In this study a combined non-destructive approach that included Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and X-ray fluorescence was used for the characterization of some brownish-black residues preserved in a series of glass *unguentaria* recovered from excavations at the Roman baths from Mălăiești. The obtained results highlighted the presence of different inorganic substances (an earth-based pigment rich in iron and manganese oxides, admixed with traces of lead- and mercury-based compounds) impregnated with an organic binder such as animal glue and possible natural essential oils, a powdered product associated most probably with a cosmetic/pharmacological use. The study allowed a first insight into the composition and origin of these ancient remains, providing important clues that may help to understand the original function of these *unguentaria* vessels.

Rezumat: Rezultate preliminare ale unui studiu multidisciplinar privind reziduurile identificate în câteva fragmente de *unguentaria*
În ciuda numeroaselor vase *unguentaria* găsite în siturile arheologice romane, se știe puțin despre natura și compoziția chimică a conținutului lor original. În acest studiu, s-au folosit metode nedistructive (spectroscopie FTIR, spectroscopie Raman și fluorescență cu raze X) pentru a analiza reziduuri preservate intr-o serie de vase de sticla unguentaria descoperite la baile romane de la Malaiesti. Rezultatele au relevat prezența diferitelor substanțe anorganice, inclusiv un pigment pe bază de pământ, bogat în oxizi de fier și mangan, împreună cu urme de compuși de plumb și mercur. Aceste substanțe au fost amestecate cu un liant organic, posibil clei de origine animală și uleiuri esențiale naturale. Produsul a avut probabil utilitate în cosmetică sau farmacologice. Acest studiu oferă informații valoroase asupra compoziției și originii acestor rămășițe antice, oferind indicii importante care pot ajuta la înțelegerea funcției inițiale a acestor vase *unguentaria*.

Keywords: Roman glass, *unguentarium*, ancient residues, FTIR, Raman, XRF
Cuvinte cheie: sticla romana, unguentarium, reziduuri antice, FTIR, Raman, XRF

Introduction

The small ceramic bottles *unguentaria* (sometimes referred to as *lacrimaria* or *balsamaria*) are common artifacts found at Hellenistic and early Roman sites. Frequently found in burial sites throughout the Mediterranean area, *unguentaria* were probably used as grave offerings, or played a certain role during the funerary ritual[1]. *Unguentaria* have also been found in public and residential areas, as vessels for everyday use, and as offerings in religious sanctuaries - mainly to hold scented "holy" oils, unguents and perfumes[2]. While most *unguentaria* found in burials are often intact or only partly damaged, the ones found in settlement contexts are in general of poor quality and therefore it is not always possible to establish their function. *Unguentaria* vary in size, from miniatures to large examples, but in general most of the artifacts fall within the range of 8-20 cm. In terms of typology, *unguentaria* were produced in two basic shapes - the fusiform or spindle shape, and the bulbous shape, the main difference between the two being the presence or absence of the foot. The discovery of glassblowing around 50 B.C.

1 Anderson-Stojanović 1987
2 Saraçoğlu 2011; Laflı and Kan Şahin 2018

determined a transition from ceramic to glass bottles. However, glass *unguentaria* are not found in large quantities until the second half of the first century A.D.[3]

Amongst Roman glass artefacts, *unguentaria* stand among the most common finds being considered cheap Roman goods. In high demand across the Roman world, these small vessels were used to store various substances. According to some authors, the closed shape and narrow mouth of the *unguentarium* bottle are more appropriate to store liquids such as wine or water, or viscous substances such as oil or honey. However, scientific analysis carried on the contents of several glass *unguentaria* discovered in various regions of Europe have also found a wide range of pigments, colorants and different organic compounds for cosmetics or pharmacological products[4], as well as a wide range of aromatic and fragrant substances from resins (such as myrrh or frankincense), flowers, spices and scented wood probably used to produce unguents, balms or perfumes[5]. If we take into account ancient text sources as well, dangerous substances (magical or toxic) used for ritual and poisoning could also have been stored in such vessels[6]. Information and recipes on cosmetic and medical products, but not only, can be found in papyrus and ancient Greco-Roman documents written by Dioscorides (*De Materia Medica*), Ovid (*Ars amatoria*), Pliny (*Historia Naturalis*) or Theophrastus (*De Sensibus*).

Ancient residues preserved in Roman glass unguentaria have been the subject of an increasing number of studies in recent years. However, in general, the remains in archaeological *unguentaria* vessels are not easy to characterize due to their complex composition that usually involves a mixture of different organic and inorganic compounds, frequently degraded by the environmental conditions and the long burial time[7]. An in-depth characterization of the various materials that may be present in such samples requires in most cases the use of a multi-analytical methodology capable to provide morphological, molecular and elemental information. In this paper residues occurring on the inside of some Roman *unguentaria* glass artefacts discovered in the Roman fort and baths from Mălăieşti (Romania) have been investigated via a combined non-destructive approach that included Fourier transform infrared (FTIR), Raman and X-ray spectroscopies. These easily accessible spectroscopic techniques stand among the most frequently used analytical tools in conservation and heritage science as they offer a series of advantages such as relatively low-cost, immediate response in terms of results and high selectivity and sensitivity[8]. Moreover, these techniques work well on micro-samples, including non-crystalline (i.e. amorphous) materials, and are non- or minimally-invasive depending on the experimental setup[9]. Vibrational spectroscopies such as FTIR and Raman provide key insights into the molecular structures of the investigated samples, allowing in certain situations the exact identification of the various organic and inorganic compounds that may be present based on their chemical signatures (fingerprints), while X-ray fluorescence (XRF) provides fast and accurate elemental characterization.

The main aim of this study was to obtain a detailed characterization of the different components present in the remains found as amorphous residues adhering to the interior walls of some of the Roman *unguentaria* recovered from the archeological site from Mălăieşti. By comparing the information obtained with those from the literature we may obtain a better understanding of the nature and composition of the materials employed in the preparation of these ancient presumed cosmetic powders. Not least, the obtained data could help us gain more insights into the function of these *unguentaria* vessels, expanding thus our knowledge about Roman daily life and culture.

Archaeological context

A network of fortifications constructed by the Roman army in the northwest of Muntenia during their conquest campaigns in Dacia[10] includes the Roman fort from Mălăiești (Prahova County, Romania.) Archaeological research in the Roman fort from Mălăiești began at the end of the 1930s, when detailed topographical plan of the entire area, including, among others, the Roman fortification and the baths were made by Constantin Zagoriţ. However, the first systematic archaeological research was carried out only in 1954 by Grigore Florescu and Expectatus Bujor[11]. During the most recent archaeological research, that took place between 2011 and 2019, the baths were completely excavated[12], along with the fortification system and two barracks in the *praetentura.* The baths at

3 Anderson-Stojanović 1987
4 Gamberini et al. 2008; Pérez-Arantegui et al. 2009; Knapp et al. 2021; Pérez-Arantegui 2021
5 Alcock 1980; Ribechini et al. 2008
6 Derrick 2018
7 Gamberini et al. 2008; Pérez-Arantegui et al. 2009
8 Cortea et al. 2022
9 Gamberini et al. 2008; Pérez-Arantegui 2021
10 Țentea and Matei-Popescu 2015
11 Țentea and Călina 2019
12 Țentea et al. 2017

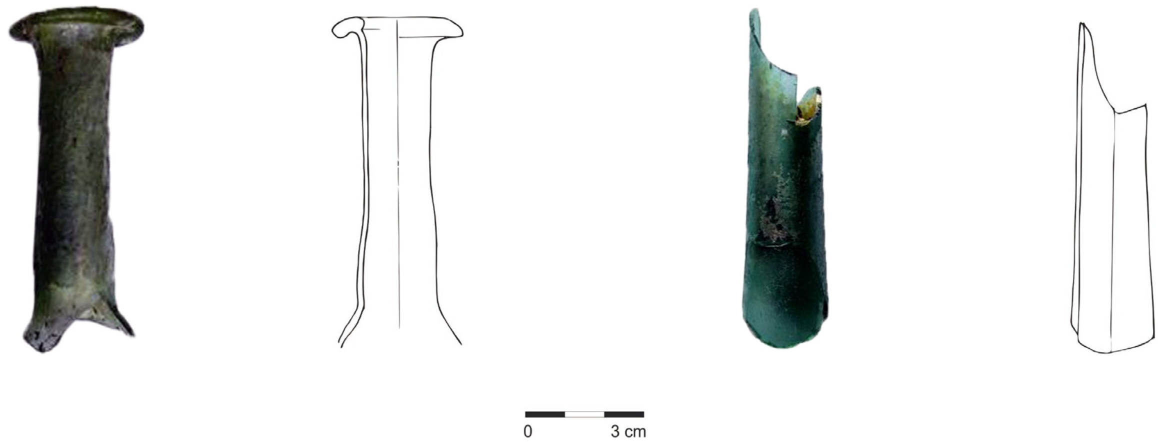

Figure 1. Some of the glass finds discovered at the Roman fort and baths from Mălăieşti.

Mălăiești are located 50 m west of the fort and provide the image of a *balneum* prototype, closely resembling the baths at Pietroasele, *Arutela* and Bumbești. The fort as well as the baths were built around 102 A.D. and their functioning lasted until 118 A.D.[13]

During the last excavation that took place at the Roman fort and baths at Mălăieşti, 160 fragments of glass were found amongst other remarkable artifacts, such as a relatively well-preserved bronze vessel[14]. Most of the glass fragments recovered (Fig. 1) could be attributed to objects with a specific function, including beakers, bowls, jugs, *unguentaria*, cups, bottles, jars, window panes or intact beads[15]. The larger group of glass artifacts is represented by *unguentaria,* with most of these discovered in the bathhouse. Two distinct types—Isings 82a1 and 28b[16]—have been determined in terms of typology, with the first form being relatively prevalent throughout the Roman Empire in the first century and the early second century A.D.

The above-mentioned discoveries are not rare. Glass *unguentaria* are common findings across the Roman province of Dacia, such vessels being discovered in various sites including *Histria*, *Tomis*, *Apulum, Alburnus Maior* or *Ulpia Traiana Sarmizegetusa*. Most of these artifacts come from funerary contexts and usually in association with other inventory categories (metal, coins, and ceramics)[17]. While the majority of the *unguenatria* discovered until now falls within common typologies like the candlestick-type, rare pieces have also been found such as the glass *unguentarium* with a high tubular foot coming from *Argamum*[18].

What is particular in the case of the most recent discoveries at Mălăiești, is the fact that some of the *unguentaria* fragments recovered from the site are still containing part of their original contents in the form of a brownish-black solid amorphous material. In terms of research, most of the studies published until now on the topic of Roman glass artifacts found on the present territory of Romania, including the ones focused on *unguentaria*, discuss the chronological, morphological and typological characteristics of the artifacts, and to a lesser extent, their chemical composition[19]. However, studies focused on the characterization of residues found inside Roman glass *unguentaria* have not been published up to this date as far as we know. On this topic, there are only a limited number of publications that deal with the chemical characterization of ancient residues found in some Late Neolithic ceramic vessels[20].

The presence of original content was found in two vessels. The first is represented by a neck from a dark green *unguentarium* (fig. 1/11). Its chemical composition places it in the group of plant ash glass, implying that it could be recycled[21]. The second vessel (fig. 1/4) that was examined is a green *unguentarium* with a folded-out rim and a cylindrical, narrow neck. Its chemical composition is unique from the other fragments which were analyzed and shows relatively high concentrations of lime (8.3 weight percent CaO), magnesia (1.3 weight percent MgO), and

13 Țentea, 2018
14 Angheluță et al. 2022
15 Țentea et al. 2023
16 Isings, 1957
17 Damian and Simion 2007; Boţan et al. 2010
18 Boţan et al. 2010
19 Bugoi et al. 2021
20 Kramberger et al. 2021
21 Bugoi et al. 2023

Figure 2. Glass unguentaria fragments investigated in this study.

strontium (1100 ppm SrO)[22]. This could mean that the fragment was made from recycled glass and that it belongs to the types Foy Série 3.2 and/or Foy Série 2.1[23], both of Egyptian origin.

Materials and methods

Samples

Residues of brownish-black color, preserved on the inside of some of the glass *unguentaria* excavated at the baths from Mălăiești (Fig. 2), have been investigated via combined FTIR, Raman, and XRF analysis. Residue samples were gently scratched from the interior surface of several *unguentaria* vessels using a scalpel and then ground in a mortar. All the analyses were carried out on powder with several spectra recorded on each sample. In all cases, it must be considered that the material inside the *unguentaria* could be contaminated to a certain degree by the site environment.

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was carried in attenuated total reflection (ATR) mode, using a SpectrumTwo FTIR spectrometer (PerkinElmer) equipped with a GladiATR accessory (monolithic diamond ATR crystal, Pike Technologies). Spectra were recorded by accumulating 32 scans at 4 cm^{-1} resolution in the 4000–380 cm^{-1} mid-infrared region. Data processing was carried out in Essential FTIR Spectroscopy Software Toolbox (Operant LLC). For spectra analysis INFRA-ART Spectral Library was used[24] as well as data available in the literature.

Raman spectroscopy

Raman spectra were recorded using a Wasatch Photonics system (WP 785 ER Raman) equipped with a standard fiber optic probe, providing a spatial resolution of 7 cm^{-1}. A near infrared diode laser (785 nm) was employed as excitation source. The laser spot size is ~170 µm, while the collection area is 1 mm diameter at 11 mm working distance (lens to sample). Acquisition time was on the order of 5 s and the laser power on the order of a few mW on the samples. All the spectra have been acquired in the absence of room lights to avoid any interference. Data collection was carried out in ENLIGHTEN Raman spectroscopy software (Wasatch Photonics) while data processing was carried out in OriginPro. Raman spectra were assigned following published data, including the ones in the RRUFF database[25].

X-ray fluorescence (XRF)

XRF measurements were performed using a portable energy-dispersive instrument from Bruker-TRACER III-SD, provided with a Rh anode X-ray tube and a 10 mm^2 X-Flash Silicon Drift Detector (SDD). The detection mode was universal, optimized for the mid-energy range of the 0-40 keV domain, experimental parameters being set at 40 kV tube voltage, 10.6 µA current intensity, 60 s analysis time, without filter. Data analysis was carried in ARTAX

[22] Bugoi et al. 2023
[23] Foy et al. 2003
[24] Cortea et al. 2023
[25] Lafuente et al. 2016

software, using standard Bayesian deconvolution. All spectral data were normalized with respect to the Rh Kα line of each sample.

Results and discussion

FTIR, Raman and XRF spectra were recorded on multiple residues samples collected from various areas of the inside of two *unguentaria* vessels. The obtained data are consistent, with similar results obtained on each of the investigated samples.

FTIR analysis allowed several clear identifications, the overall spectral fingerprint pointing towards the presence of an earth-based pigment. As can be seen in Figure 3-a, the FTIR spectrum registered on the black residue is dominated by a broad absorption around 1020 cm^{-1} with a shoulder at 914 cm^{-1} that can be ascribed Si–O and Al–O–H modes[26]. Small amounts of calcite could be clearly identified via the characteristic peaks observed at 1420 cm^{-1} and 713 cm^{-1}. The small peak at 796 cm^{-1} can be linked with the presence of quartz while the strong absorption around 430 cm^{-1} could represent contributions from Mn–O bond vibrations[27]. The broad band within the 3500–3100 cm^{-1} region along the peak at 1640 cm^{-1} correspond to stretching and bending vibrations of water molecules. Raman analysis (Fig. 3-b) confirmed the presence of manganese oxides[28] via the small but representative peaks observed around 551 cm^{-1} and 626 cm^{-1}. The Raman peak at 1065 cm^{-1} can be ascribed to carbonate ions while the band around 1591 cm^{-1} could be linked with the presence of brugnatellite, a magnesium carbonate mineral[29]. In terms of the elemental signature, XRF analysis (Fig. 4) indicated a rich iron and manganese content, minor amounts of calcium and traces of Ti, K, Si, Sr, S, Cu, Pb, Ba, Cr, Zn and Hg. The high iron content is most likely related to the presence of amorphous Fe-oxides and/or Fe-hydroxides, not detected via FTIR or Raman. Calcium can be clearly linked to calcite, a compound clearly identified via FTIR.

Corroborated spectral data indicates towards the presence of an iron-rich smectite (such as montmorillonite) with manganese hydroxides components, most probably a dark umber earth used as a black pigment[30]. Earth pigments, frequently admixed with other organic and inorganic components, stand among the most used ancient materials as pigments, including for Roman cosmetics[31]. Moreover, black manganese minerals, such as the ones identified in this study, have been proven to have antibacterial activity, making them ideally for cosmetic/pharmacological use[32].

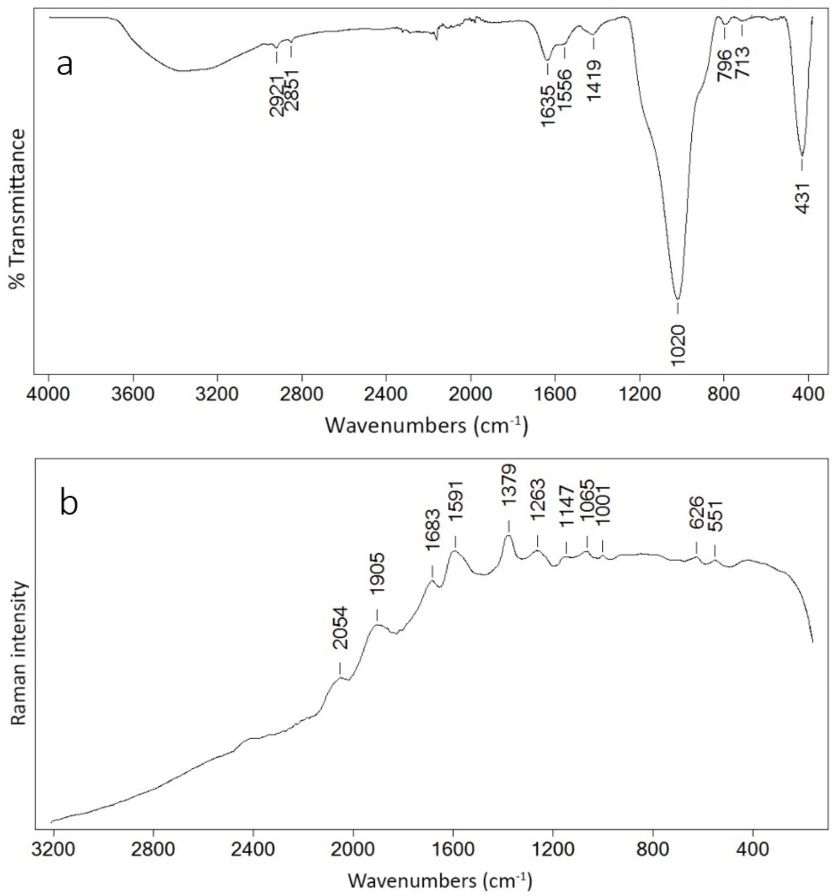

Figure 3. Representative FTIR spectrum (a) and Raman spectrum (b) registered on the brownish-black residue.

26 Madejová et al. 2017
27 Palchik et al. 2014
28 Sepúlveda et al. 2015
29 Frost and Bahfenne 2009
30 Cavallo and Barioni 2015; Cortea et al. 2022
31 Gamberini et al. 2008
32 Knapp et al. 2021

Most of the trace elements identified can be linked to various types of accessory minerals and/or natural impurities present in earth pigments, these chemical patterns/fingerprints being characteristic of a particular geological source[33]. Among the trace elements identified, Pb and Hg are more peculiar. As shown in other studies, trace amounts of Pb can be found in certain earth pigments[34], however, these small concentrations of lead could also be due to black or white lead-based compounds[35]. Lead compounds, in the form of galena (lead sulfide), cerussite (lead carbonate) or artificial white lead chlorides have been frequently found in ancient cosmetics[36]. Cinnabar (a mercury sulfide), or its synthetic version, vermilion, have also been found in ancient cosmetic boxes, frequently mixed with other pigments such as iron oxides[37]. The presence of such compounds would explain the trace amounts of Hg and S detected via XRF. Despite their toxicity, such compounds were oftentimes included in various products, for medicinal and/or cosmetic purpose, with lead-containing materials being more frequently found in archaeological sites (related to cosmetic products) than red mercury sulfide, this last one being used more limited and as a minor component only, most probably due to its rare nature and cost[38].

Some product of an organic substance[39] is also present within the investigated samples, as indicated by the small IR absorptions (Fig. 3-a) around 2921 cm^{-1} and 2851 cm^{-1} (aliphatic C–H stretch groups)[40]. The broad absorption around 1550 cm^{-1} could be linked to a protein binder (Amide II band). However, the amide I band is overlapped by the O-H bends present, making the identification of a possible proteinaceous binder not possible only by FTIR. The presence of a proteinaceous compound seems to be confirmed though by Raman, a closer look at the spectra highlighting some key spectral features (Fig. 3-b) that are typically associated with the α-helix structure of proteins - 1683 cm^{-1} (Amide I), 1263 cm^{-1} (Amide III)[41]. The Raman band at 1379 cm^{-1} assigned to CH_3 bending modes can be linked to aromatic compounds frequently found in essential oils[42]. However, at this moment an exact identification of the various organic compounds that may be present within the investigated samples cannot

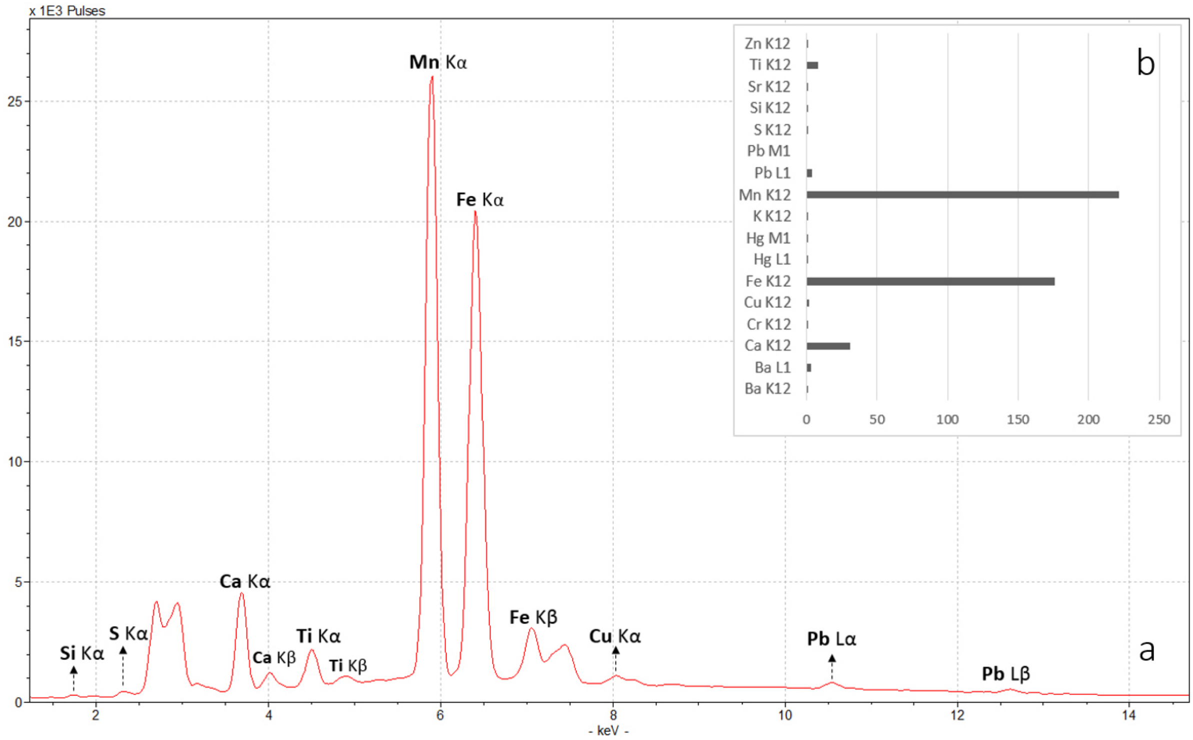

Figure 4. *Representative XRF spectrum registered (a) and elemental distribution (b)*

33 Popelka-Filcoff et al. 2007
34 Cortea et al. 2022
35 Pérez-Arantegui 2021
36 Pérez-Arantegui and Cepriá 2014
37 Gliozzo 2021; Pérez-Arantegui 2021
38 Pérez-Arantegui 2021
39 Pérez-Arantegui et al. 2009
40 Pérez-Arantegui et al. 1996
41 Rygula et al. 2013
42 Jentzsch et al. 2015

be achieved by vibrational spectroscopy only. Due to the complex molecular pattern of the samples (mixture of various organic compounds in trace amounts, with different levels of degradation), solvent extraction or more sensitive analytical techniques such as Gas Chromatography–Mass Spectrometry (GC-MS)[43] or Laser Induced Fluorescence (LIF)[44] are needed.

Conclusions

Using a combined non-invasive approach that included FTIR, Raman and XRF analysis, it was possible to characterize the remains found inside some glass *unguentaria* recovered from the Roman baths from Mălăiești that were still containing part of their original contents in the form of a brownish-black solid amorphous material. Corroborated results allowed a clear identification of some specific compounds, providing important insights that may help to understand the original function of these *unguentaria* vessels. In particular, FTIR analysis has been able to determine the presence of an earth-based pigment rich in iron and manganese oxides, most probably a dark umber. Some accessory minerals such as calcite and quartz could also be identified via FTIR, along some minor organic components, confirmed via Raman as proteinaceous materials. Some aromatic compounds, possibly linked with the use of natural essential oils, were also inferred. The chemical signature obtained via XRF analysis highlighted key trace elements, some liked to the geological origin of the earth pigments, some with the presence of other inorganic compounds based on lead and mercury. Grounded on the rich set of information obtained, some hypothesis can be made on regard the original product contained and its function, the above preliminary findings pointing towards a powdered product for cosmetic/pharmacological use. This study is a first attempt to characterize ancient remains preserved in Roman *unguentaria* vessels discovered in archeological sites in Romania, and is intended to be continued in future systematic research studies. Better knowledge and a complete and unambiguous identification of the investigated residues would require the use of more sensitive techniques in order to be able to clearly identify all the mineralogical phases present, as well as the specific organic fractions still preserved in this complex matrix. Moreover, such exact findings, correlated with ancient recipes found in Greco-Roman documents could open new directions of research, such as the recreation of ancient perfumes and scents, a direction aligned with the most recent trends in the field - olfactory heritage.

Acknowledgment

This work was supported by the Romanian Ministry of Research, Innovation and Digitization, CCCDI—UEFISCDI, under grant number PN-III-P2-2.1-PED-2021-3576, within PNCDI III, and under Program 1—Development of the National Research-Development System, Subprogram 1.2—Institutional performance—Projects to finance the excellence in RDI, SUPECONEX grant number 18PFE/30.12.2021.

References

Alcock, J.P. 1980. Classical Religious Belief and Burial Practice in Roman Britain. *Archaeological Journal* 137, 1: 50-85. DOI: https://doi.org/10.1080/00665983.1980.11078480

Anderson-Stojanović, V.R. 1987. The Chronology and Function of Ceramic Unguentaria. *American Journal of Archaeology* 91(1): 105-122. DOI: https://doi.org/10.2307/505460

Angheluță, L.M., Țentea, O., Ghervase, L., Cortea, I.M., Dinu, M., Ratoiu, L.C. and Pârău, A.C. 2022. Integrated multi-analytical study of the bronze vessel from Mălăiești Roman fort, *Journal of Ancient History and Archaeology* 9(1): 185-198. DOI: https://doi.org/10.14795/j.v9i1.743

Boţan, S.P., Paraschiv, D. and Nuţu, G. 2010. Vase de sticlă romane şi romano-bizantine descoperite în nordul Dobrogei. *Arheologia Moldovei* 33: 217-242. DOI: https://doi.org/10.11588/amold.2010.0.29853

Bugoi, R., Panaite, A. and Alexandrescu, C.G. 2021. Chemical Analyses on Roman and Late Antique Glass Finds from the Lower Danube: The Case of Tropaeum Traiani. *Archaeological and Anthropological Sciences* 13: 148. DOI: https://doi.org/10.1007/s12520-021-01310-7

[43] Ribechini et al. 2008
[44] Ghervase and Cortea 2023

Bugoi, R., Țentea, O., Manea, I. 2023. A Window Into Roman Glass From The Beginning Of The 2nd C. AD - An Archeometric Study Of Selected Vitreous Finds Discovered In The Roman Fort And Baths From Mălăieşti, Romania. *Archaeological and Anthropological Sciences. - in press*

Cavallo, G. and Gianoli Barioni, K. 2015. Black Earths from Veneto and Piedmont (Northern Italy): Origin, Composition and Potential Use in Different Painting Techniques. *Heritage Science* 3: 5. DOI: https://doi.org/10.1186/s40494-015-0035-4

Cortea, I.M., Chiroșca, A., Angheluță, L.M. and Serițan, G. 2023. INFRA-ART: An Open Access Spectral Library of Art-Related Materials as a Digital Support Tool for Cultural Heritage Science. *Journal on Computing and Cultural Heritage* 16(2). DOI: https://doi.org/10.1145/3593427

Cortea, I.M., Ghervase, L., Rădvan, R. and Serițan, G. 2022. Assessment of Easily Accessible Spectroscopic Techniques Coupled with Multivariate Analysis for the Qualitative Characterization and Differentiation of Earth Pigments of Various Provenance. *Minerals* 12(6): 755. DOI: https://doi.org/10.3390/min12060755

Damian, P. and Simion, M. 2007. Funerary Practices in the Necropolises belonging to the ancient communities at Alburnus Maior. *Acta Terrae Septemcastrensis Journal* 6(1): 141-153.

Derrick, T. 2018. Little Bottles of Power: Roman Glass Unguentaria in Magic, Ritual, and Poisoning, in: A. Parker and S. Mckie (eds.) *Material Approaches to Roman Magic: Occult Objects and Supernatural Substances*: 33-44, Oxford: Oxbow Books.

Frost, R.L., Bahfenne, S., and Graham, J. 2009. Raman and Mid-IR Spectroscopic Study of the Magnesium Carbonate Minerals - Brugnatellite and Coalingite. *Journal of Raman Spectroscopy* 40(8): 855-860. DOI: https://doi.org/10.1002/jrs.2152

Foy, D., Picon, M., Vichy, M., Thirion-Merle, V. 2003. Caractérisation des verres de la fin de l'Antiquité en Mediterranée occidentale: l'émergence de nouveaux courants commerciaux. in: Foy, D. and Nenna, M.D. (eds) Échanges et commerce du verre dans le monde antique. Actes du colloque de l'AIHV, Aix-en-Provence et Marseille, Juin 2001. Monographies Instrumentum 24. Monique Mergoil, Montagnac, pp 41–85.

Gamberini, M.C., Baraldi, C., Palazzoli, F., Ribechini, E. and Baraldi, P. 2008. MicroRaman and Infrared Spectroscopic Characterization of Ancient Cosmetics. *Vibrational Spectroscopy* 47(2): 82-90. DOI: https://doi.org/10.1016/j.vibspec.2008.02.005

Ghervase, L. and Cortea, I.M. 2023. Lighting up the heritage sciences: the past and future of laser-induced fluorescence spectroscopy in the field of cultural goods. *Chemosensors* 11(2): 100. DOI: https://doi.org/10.3390/chemosensors11020100

Gliozzo, E. 2021. Pigments — Mercury-Based Red (Cinnabar-Vermilion) and White (Calomel) and Their Degradation Products. *Archaeological and Anthropological Sciences* 13: 210. DOI: https://doi.org/10.1007/s12520-021-01402-4

Isings, C. 1957. *Roman glass from dated finds*. Groningen: J.B. Wolters.

Jentzsch, P.V., Ramos, L.A. and Ciobotă, V. 2015. Handheld Raman Spectroscopy for the Distinction of Essential Oils Used in the Cosmetics Industry. *Cosmetics* 2(2): 162-176. DOI: https://doi.org/10.3390/cosmetics2020162

Knapp, C.W., Christidis, G.E., Venieri, D., Gounaki, I., Gibney-Vamvakari, J., Stillings, M. and Photos-Jones, E. 2021. The Ecology and Bioactivity of Some Greco-Roman Medicinal Minerals: The Case of Melos Earth Pigments. *Archaeological and Anthropological Sciences* 13: 166. DOI: https://doi.org/10.1007/s12520-021-01396-z

Kramberger, B., Berthold, C. and Spiteri, C. 2021. Fifth Millennium BC Miniature Ceramic Bottles from the South-Eastern Prealps and Central Balkans: A Multi-Disciplinary Approach to Study Their Content and Function. *Journal of Archaeological Science: Reports* 38: 102993. DOI: https://doi.org/10.1016/j.jasrep.2021.102993

Laflı, E. and Kan Șahin, G. (eds.) 2018. *Unguentarium. A terracotta vessel form and other related vessels in the Hellenistic, Roman and early Byzantine Mediterranean - An International Symposium*. Izmir: Dokuz Eylül University. Epub.

Lafuente, B., Downs, R.T., Yang, H. and Stone, N. 2016. The Power of Databases: The RRUFF Project, in: T. Armbruster and R.M. Danisi (eds.) *Highlights in Mineralogical Crystallography*: 1-30. Berlin, München, Boston: De Gruyter (O). DOI: https://doi.org/10.1515/9783110417104-003

Madejová, J., Gates, W.P. and Petit, S. 2017. IR Spectra of Clay Minerals, in: W.P. Gates, J.T. Kloprogge, J. Madejová and F.Bergaya (eds.) *Developments in Clay Science* (vol. 8): 107-149. Amsterdam: Elsevier.

Palchik, N.A., Moroz, T.N., Grigorieva, T.N. and Miroshnichenko, L.V. 2014. Manganese Minerals from the Miassovo Freshwater Lake: Composition and Structure. *Russian Journal of Inorganic Chemistry* 59: 511-518. DOI: https://doi.org/10.1134/S0036023614050131

Pérez-Arantegui, J. 2021. Not only wall paintings—pigments for cosmetics. *Archaeological and Anthropological Sciences* 13: 189. DOI: https://doi.org/10.1007/s12520-021-01399-w

Pérez-Arantegui, J., Cepriá, G., Ribechini, E., Degano, I., Colombini, M.P., Paz-Peralta, J. and Ortiz-Palomar, E. 2009. Colorants and Oils in Roman Make-Ups-an Eye Witness Account. *TrAC - Trends in Analytical Chemistry* 28(8): 1019-1028. DOI: https://doi.org/10.1016/j.trac.2009.05.006

Pérez-Arantegui, J. and Cepriá, G. 2014. Suitability of the Voltammetry of Immobilized Microparticles to Detect and Discriminate Lead Compounds in Microsamples of Ancient Black Cosmetics. *Electrochimica Acta* 138: 247-255. DOI: https://doi.org/10.1016/j.electacta.2014.06.085

Pérez-Arantegui, J., Paz-Peralta, J.A. and Ortiz-Palomar, E. 1996. Analysis of the Products Contained in Two Roman Glass Unguentaria from the Colony of Celsa (Spain). *Journal of Archaeological Science* 23(5):649-655. DOI: https://doi.org/10.1006/jasc.1996.0061

Popelka-Filcoff, R.S., Robertson, J.D., Glascock, M.D. and Descantes, Ch. 2007. Trace element characterization of ochre from geological sources. *Journal of Radioanalytical and Nuclear Chemistry* 272: 17-27. DOI: https://doi.org/10.1007/s10967-006-6836-x

Ribechini, E., Modugno, F., Colombini, M.P. and Evershed, R.P. 2008. Gas Chromatographic and Mass Spectrometric Investigations of Organic Residues from Roman Glass Unguentaria. *Journal of Chromatography A* 1183(1-2): 158-169. DOI: https://doi.org/10.1016/j.chroma.2007.12.090

Rygula, A., Majzner, K., Marzec, K.M., Kaczor, A., Pilarczyk, M. and Baranska, M. 2013. Raman Spectroscopy of Proteins: A Review. *Journal of Raman Spectroscopy* 44(8): 1061-1076. DOI: https://doi.org/10.1002/jrs.4335

Saraçoğlu, A. 2011. Hellenistic and Roman unguentaria from the necropolis of Tralleis. Anadolu (Anatolia) 37: 1-42. DOI: https://doi.org/10.1501/andl_0000000381

Sepúlveda, M., Gutiérrez, S., Campos Vallette, M., Standen, V.G., Arriaza, B.T. and Cárcamo-Vega, J.J. 2015. Micro-Raman Spectral Identification of Manganese Oxides Black Pigments in an Archaeological Context in Northern Chile. Heritage Science 3: 32. DOI: https://doi.org/10.1186/s40494-015-0061-2

Țentea, O. 2018. Baths and Bathing in Dacia under Trajan, in: C.S. Sommer and S. Matešić (eds.) *Limes XXIII Proceedings of the 23rd International Congress of Roman Frontier Studies Ingolstadt 2015*: 133-137. Mainz: Nünnerich-Asmus Verlag.

Țentea, O. and Călina, V. 2019. Peisajul arheologic al castrului Mălăiești. *Cercetări Arheologice* 26: 169-196. DOI: https://doi.org/10.46535/ca.26.06

Țentea, O., Manea, I. and Rațiu, A. 2023. The glassware from Mălăiești Roman fort and bath. *Journal of Ancient History and Archaeology* 10(1). DOI: https://doi.org/10.14795/j.v10i1.856

Țentea, O. and Matei-Popescu, F. 2015. Why There? The Preliminaries of Constructing the Roman Frontier in South-East Dacia. *Acta Musei Napocensis* 52(1): 109-130.

Ţentea, O., Raţiu, Al., Duca, M., Cîmpeanu, A. and Sidon, R. 2017. Sfârleanca, com. Dumbrăveşti, jud. Prahova [castrul Mălăieşti]. *Cronica Cercetărilor Arheologice - Campania 2016*, 129-130.

Lista ilustrațiilor

Figura 1. Unele dintre obiectele de sticlă descoperite la castrul roman și băile de la Mălăiești.
Figura 2. Fragmentele de *unguentaria* de sticlă investigate în acest studiu.
Figura 3. Spectru reprezentativ FTIR (a), respectiv Raman (b) inregistrat pe reziduurile brun-negricioase.
Figura 4. Spectru XRF reprezentativ inregistrat (a) și distribuția elementelor (b)

IOANA CORTEA
Centre of Excellence for Restoration by Optoelectronic Techniques (CERTO),
National Institute of Research and Development for Optoelectronics - INOE 2000,
Măgurele, Romania
ioana.cortea@inoe.ro

OVIDIU ȚENTEA
Department of Archaeology, National Museum of Romanian History,
Bucharest, Romania
ovidiu.tentea@gmail.com