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COLORS AND BALMS IN ANTIQUITY: FROM THE CHEMICAL STUDY TO THE KNOWLEDGE OF TECHNOLOGIES IN COSMETICS, PAINTING AND MEDICINE

BOOK OF ABSTRACTS

Aboca Azienda, Sansepolcro (Arezzo), 2-3 December 2010

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INTRODUCTION

Recent developments in archaeometry have seen an increasing interest in the scientific investigation not only on precious or artistic heritage objects as paintings, coins, statues, but also on residues of amorphous materials found in archaeological or historical vessels related to various aspects of everyday life in past societies.
The chemical study of these materials represents a shortcut to gain a picture of the technology, social customs, diet and rituals in the context in which they were used. The characterisation of such materials, if interpreted together with the information derived from the critical study of historical documents and of "site evidences", allows us to reveal a lot on the preparation, conservation and uses of the investigated substances.
In particular, the application of an increasingly wider array of analytical tools to a large series of case studies has shown how the chemical investigation of residues of medicines and make-ups that are found in stone, ceramic or glass containers is an extraordinary source of information about their making process and, more in general, about, chemical and pharmaceutical knowledge and practices in antiquity.
For example, the funerary objects sometimes found in exceptionally good state of conservation in Egyptian tombs often include toilet tools and make-up receptacles which have been studied as an important source of archaeological information, to investigate the customs in the everyday life during the Ancient Egypt. These studies have confirmed that cosmetics and make up where used in ancient times not only for aesthetic purpose, but also with a religious or healing meaning, and played an important role during rituals and burial ceremonies, having in some cases a real therapeutical action .

The PRIN07 project *Colors and balms in antiquity: from the chemical study to the knowledge of technologies in cosmetics, painting and medicine* (2009-2010) has focused on the study and the chemical understanding of the materials used in the course of ancient times to craft cosmetics, medicines and paint materials. The aim was to contribute to the reconstruction of the evolution of science, technology and knowledge in the course of the centuries, tracing the role and the uses of various materials in past societies, and at planning conservation strategies.
The final conference of the project organised in conjunction with Aboca Spa, attempts to reach conclusions, highlight the achievements, identify gaps and discuss future research related to the chemical-physical study of archaeological-historical medical and cosmetic preparations. The included contributions focused on the following themes:

- characterisation of residues of cosmetics in archaeology
- characterisation of residues of historical medical preparations
- decay processes in archaeological residues
- round robin exercises in archaeometry
- interpretation of archaeometric data in conjunction with historical documents to reconstruct ancient recipes and formulations.

Program

Thursday, December 2nd

14.30 Registration

15.00-15.30: Opening of the Workshop: Presidente Aboca Spa Valentino Mercati, Prof.ssa Maria Perla Colombini

15.30-16.00 F. Silvano "Cosmetics in Ancient Egypt"

16.00-16.20 A. Nevin, I. Osticioli, C. D'Andrea, D. Comelli, L. Brambilla, S. Goidanich, L. Toniolo, R. Cubeddu , "Fluorescence Spectroscopy, Imaging and Vibrational Spectroscopy for the analysis of complex materials: study of selected constituents found in paint and cosmetics"

16.20-16.40 P. Baraldi C. Baraldi, G. Freguglia, M.C. Gamberini, "Auctoribus curae fuere lapides mortariorum quoque nec medicinalium tantum aut ad pigmenta pertinentium. (Pliny 36, 43)"

16.40-17.30 Coffee break + poster session

17.30-17.50 M.C. Gamberini, G. Freguglia, C Baraldi., P. Baraldi. "Cosmetic and Pharmaceutical Formulations: from Past to Present."

17.50-18.10 C. Baraldi, M.C. Gamberini, G. Freguglia, P. Baraldi, "Raman techniques applied to ancient cosmetic and pharmaceutical preparations."

18.10-18.30 L. Zoia, E.-L. Tolppa, L. Pirovano, A. Salanti, M. Orlandi "^{31}P-NMR identification and characterization of lipids in archaeological unguents"

18.30-18.50 I. Degano "Museum Aboca balms: ipertext presentation of the PRIN project results"

20.30 Social dinner

Friday, December 3rd

9.00-9.20 M. Rocchi, E. Ribechini, F. Modugno, I. Degano, M.P. Colombini, "Analytical study of ancient pharmaceutical preparations".

9.20-9.40
C.Riedo, D.Scalarone, O. Chiantore "Pyrolysis-GC/MS for the identification of organic components in historical recipes"

10.10–10.30 R. Stacey, D. Hook, "The composition of some Roman ointments in the collections of the British Museum".

10.30-10.50 L. Brambilla, S. Goidanich, P. Baraldi, F. Modugno, J.J. Lucejko, C. Canevali, P. Gentile, "Heterogeneous powders from Pompei and Ercolano sites: a multi-analytical characterisation**"**

10.50-11.30 Coffee break + poster session

11.30–11.50 N. Garnier, D. Frère, L. Hugot, "Characterisation of archaeological organic "perfumes" from Etruria and Sardinia (7th – 5th c. BC). Assessment of the 3-year research program Perhamo"

11.50-12.10 K.L. Rasmussen, **"**Tracing the academics in medieval monasteries"

12.10-12.30 M. Fantuzzi, "The use and production of organic colouring in painting techniques"

12.30-12.50 C. Miliani, D. Buti, A. Romani, D. Domenici, B.G. Brunetti, A. Sgamellotti "Non invasive in situ study of colours in Pre-Hispanic codex"

Lunch

14.30-15.00 M.P. Colombini, F. Modugno, M.C. Gamberini, E. Ribechini, "Presentation of round robin results and discussion"

15.00 M.P. Colombini: Concluding remarks

16.00 Visit to ABOCA Museum

Index of Oral Presentations

Index of Posters

COSMETICS IN ANCIENT EGYPT

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Abstract

This paper will focus on the functional aspects of cosmetic art known to us from Egypt. The ancient Egyptians attached great importance to cosmetics which men and women wore to make themselves attractive and alluring but also to venerate and propitiate the gods. I will discuss here mainly the personal uses of cosmetics, touching only slightly on ritual and ceremonial aspects.
In primitive societies cosmetics served magic-religious purposes and the application of face paint and the desire to improve one's personal appearance is basically of sexual nature. The perpetuation of the species was the basic aim in life and, as in the animal world, humans would emphasise their sexuality in their appearance. For this reason in Egyptian funerary equipments too, cosmetics underline the sexuality of the deceased in order to unable him to undergo the vital process of rebirth in the Hereafter. The cosmetic preparations used by the ancient Egyptians included powders, ointments, perfumes which were produced from various plants and resins or minerals mixed with vegetable oil or animal fat. Several recipes in the medical papyri prescribe remedies for making hair grow, preventing it from turning grey, removing unwanted hair, wrinkles and spots, improving the skin and repelling unpleasant body odour.

FLUORESCENCE SPECTROSCOPY, IMAGING AND VIBRATIONAL SPECTROSCOPY FOR THE ANALYSIS OF COMPLEX MATERIALS: STUDY OF SELECTED CONSTITUENTS FOUND IN PAINT AND COMETICS

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Abstract

Historical paints and cosmetics may contain a range of organic and inorganic materials and advances in analytical methods have contributed to a better understanding of the technology used for their preparation. Materials studied include natural gums, oils, glues, waxes and a variety of inorganic and organic pigments and colourants. Fluorescence spectroscopy and fluorescence imaging techniques can provide indications regarding the presence of organic materials on the surfaces of a variety of different types of objects and illustrative examples of applications of fluorescence spectroscopy for the study of cultural heritage will be given. However the interpretation of fluorescence spectra and a rationalisation of results from imaging analysis may be complex. For this purpose, we present analysis of a series of raw materials used in cosmetics and for paint prior to and after artificial ageing, and an interpretation of changes in fluorescence following oxidation is given on the basis of results from analysis with Fourier Transform Infrared Spectroscopy and Raman spectroscopy. Further, limitations and advantages of the use of fluorescence spectroscopy for the analysis of complex materials will be given.

"AUCTORIBUS CURAE FUERE LAPIDES MORTARIORUM QUOQUE NEC MEDICINALIUM TANTUM AUT AD PIGMENTA PERTINENTIUM" (PLINY 36, 43)"

Our authors are interested in stones for making mortars, and not only in officinal mortars or those used for colors.

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Abstract

A very important phase for reconstructing ancient technology and human activities is the analysis of artifacts. It can supply a lot of information, but sometimes the data obtained are not understandable. On the other hand an amount of written information is available since the classical antiquity. Some of the authors are considered not to be scientists and therefore their data are neither used nor interpreted.
Beyond published texts some unpublished manuscripts are known that could be very interesting. Other documents include ancient translations from other languages, such as the greek papyrii, and the Arabian documents from Spain, documents regarding trade and history of countries, icones in ancient paintings, tools used for paintings and other activities. In more recent times it is to recall, the *secreti*, the books for treating diseases, where the subjects not only concern medicine, but include preparation of pigments, dyes, lakes, cosmetics, alloys inks…
Their contents can be very old, some being composed much before Christ and re-written many times, and translated and sometimes erroneusly read.
The transcription, understanding and interpretation of these recipes can help in understanding:
the ancient paintings, decorations, alloys, textiles and cosmetics;
the presence of some compounds as a consequence of past treatments and restorations;
thhe survival of some compounds, not necessary for the formulate, but added for some forgotten reasons, such as folklore, superstition, faith, magic;
the degradation of some parts of artworks due to time and environment.
These items have been followed in examining an unpublished miscellanea from the Biblioteca Estense Universitaria in Modena.

COSMETIC AND PHARMACEUTICAL FORMULATIONS: FROM PAST TO PRESENT

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Abstract

The interest devoted to the scientific treatment of analytical data obtained from ancient founds preserved in Italian and foreign institutions and Museums is nowadays relevant. However, till now the study of the composition and the understanding of the preparation technologies of ancient founds is scanty and fragmentary.
Now, the progress of instrumental techniques enables the material composition to be cleared in details and to advance a possible re-proposition of the handiworks. On the basis of analytical data, the possibility to establish the nature of raw materials and the formulations, becomes even more concrete.
In the framework of the PRIN project the unit of Modena has thrown the basis for the study of ancient cosmetic, medical and pictorial founds, in particular:

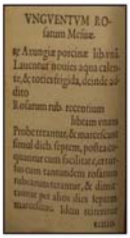
1) Identification and sampling of ancient remains in national and international Museums and of handiworks not purely cosmetic or medical.
2) Spectroscopic studies (FT-IR, micro-Raman and XRF) for the characterisation of inorganic and/or organic remains recovered in unguentaries and in containers of ancient workshops.
3) Identification and study of the ancient published and unpublished bibliographic sources: translation from Latin and vernacular followed by an interpretation of the function of raw materials.
4) Identification in the actual market of the materials used in antiquity.
5) Preparation or acquirement of raw materials not available on the market.
6) Reproduction in a modern perspective of ancient formulations on the basis of the ancient sources.

The first step faced was the acquirement of ancient founds, that is the sampling on the spot of samples to be studied. Therefore, samples were taken at the Museum Aboca (Sansepolcro, Arezzo). At the Aboca Museum about 68 pots were inspected and 30 exhibited a fair amount of residue of which 9 were the object of the study.
After sampling, the materials were analysed by Micro-Raman and FT-IR in order to have a first screening of them, that is to determine whether they were of organic or inorganic origin and which compounds were present. In this way we got a first idea of what the materials were. Thanks to the spectroscopic analyses and to the labels on the containers, we proceeded into the research of ancient similar formulations.

Therefore, it was necessary to examine the recipe books starting from the classical age till to the beginning of scientific chemistry and pharmacology in order to critically compare the materials found, to understand their nature, their possible alteration undergone with time, the novelties in comparison with preceding versions, the technological acquirements of an age in comparison with the others. From the study of the inscriptions reported on the containers and the interpretations carried out, the period of actualisation of the formulation was hypothesised. The study of the same formulation in subsequent times has shown the evolution and the adaptation to the age.
Many ancient books and manuscripts reporting recipes concerning the subject in the period between 1597 and 1872 have been considered, the most interesting of these was *Farmacopea Augustana* by Occo, 1597. For each source, the desired recipes were searched for and then, if necessary, translated and interpreted. In fact, some texts are in Latin or vernacular (*Farmacopea Augustana* by Occo), French (*Abrégé de Matière médicale et de Thérapeutique* by C. Binz) or Spanish (*Farmacopea Hispanica*), and the translation must be careful, since the meaning of the terms at the time was searched [1-7].
The next step was to study the raw materials used in the recipes, that is to verify the persistence of the ingredients today and their availability in commerce. The ointments to be prepared were chosen as a function of the remains found in the containers, but mainly on the basis of the results of the spectroscopic analyses. Those reproduced in the laboratory were many, sometimes the preparations have been made in double or triple, according to the sources of different historical periods. Here is reported an example of an ancient ointment reproduced in laboratory.
Example, Unguentum Rosatum: ancient latin recipe, Italian transalation, scientific procedure.

Unguentum Rosatum - Farmacopea Augustana of Occo

Vernacular Version:



Italian Version:

Unguento rosato sec. Mesuè
Prendi: sugna di maiale una libbra
Lava nove volte in acqua calda e altrettante volte in acqua fredda, poi aggiungi Rose rosse recenti una libbra.
Triturare bene e lasciare macerare i petali di rose e la sugna per 7 giorni, dopo cuoci con abilità e di nuovo tritura con altrettante rose e lascia macerare per altri sette giorni
Fai lo stesso una terza volta.
La quarta poi versa tranne le rose.
(Aggiungi:)Succo di rose rosse sei once
Olio di mandorle dolci tre once
Cuoci a fuoco lento fino a consistenza di succo.

Laboratory version:

Adeps Suillus	30 grams
Fresh red roses	30 grams x 3
Rose water	10.8 grams
Sweet almond oil	5.4 grams

1) The adeps suillus was washed 9 times alternatively in hot and cold and then was blended in a mortar with fresh rose petals for 5 minutes.
2) The mash obtained was let aside for 7 days in a dark glass container at ambient temperature.
3) After 7 days the mash was heated to 70-80°C for 60 minutes.
4) After one hour the mash was filtered with fine mesh colander and the solid was squeezed to obtain the juice.
5) To the filtrate other rose petals were added and ground in a mortar for 5 min.
6) The preparation procedure was repeated twice more.
7) The fourth time the preparation was filtered and to the filtrate sweet almond oil and rose water were added .

References

1. Farmacopea Augustana by Occo, 1597.
2. Della Summa dei secreti Universali by Timoteo Rosselli, 1619.
3. Secreti Nobilissimi del Nuovo Autore detto il Greco, 1641.
4. Ricettario Fiorentino, 1789.
5. Farmacopea Hispanica, 1826.
6. Nuovo Formulario Magistrale by A. Bouchardat, 1864.
7. Abrégé de Matière médicale et de Thérapeutique by C. Binz, 1872.

RAMAN TECHNIQUES APPLIED TO ANCIENT COSMETIC AND PHARMACEUTICAL PREPARATIONS

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Abstract

Complementary spectroscopic techniques, such as FT-IR and Micro-Raman spectroscopies are valuable means for maximizing the amount of information provided by complex matrices like the remains in archaeological containers. The difficulty in analyzing 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.

We report the results of the vibrational spectroscopy techniques, such as Raman microscopy (laser 632 nm), FT-Raman spectroscopy (laser 1064 nm) and FT-IR/ATR with a golden gate accessory, of a first approach to the analysis of the ancient samples. The analytical results showed the importance of micro-Raman Spectroscopy in discriminating between inorganic and organic materials, thereby underlining the complexity of pharmaceutical and cosmetic matrices.

Raman microscopy is the most suitable technique in order to identify minor inorganic components and contaminants at the micrometric scale inside these complex matrices[1]. On the basis of the FT-IR and micro-Raman spectra, it was possible to identify some specific old cosmetic materials and some binders used in cosmetic preparations.

In particular, Raman microscopy was able to identify the presence of constituents at the trace levels or compounds having vibrations at low wavenumbers within the sample examined, that it is not possible with normal FT-IR technique[2]. This technique can easily identify compounds like lead oxide, red lead, cinnabar, rare minerals, (etc.) that could give interesting information about the original composition of the formulate and the provenance of the raw materials.

Concerning the organic materials, their possibility of identification is very different from that of inorganic ones. Some compounds were rapidly degraded, some others persisted till to present day, often unchanged (e.g. wax). Historical samples are subjected to ageing and degradation process that make difficult to recognize the raw material originally present. For understanding the possible changes undergone by materials during ageing, a specific database of spectra must be available.

In the project PRIN 2007 "Colours and balms in antiquity" some thirty raw materials were chosen among oils (e.g. olive, almond, and palm oil), gums (e.g. gumarabic), animal fats and waxes, commonly employed in the ancient preparations. The raw materials and the reference formulations prepared in the

laboratory, were artificially aged. The reference Raman spectra have supplied an interesting database.
The use of Surface-Enhanced Raman Spectroscopy (SERS) enabled to increase Raman signal and to decrease the background fluorescence for some samples. This techniques exhibits new perspectives for the study of organic and inorganic compounds in the field of cultural heritage[3,4].

References

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2. M.C. Gamberini, C. Baraldi, F. Palazzoli, E. Ribechini, P. Baraldi, Vib. Spectrosc., **47** (2), 82, (2008).
3. M. Leona, J. Stenger, E. Ferloni, J.R.S., **37**, 981, (2006).
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^{31}P-NMR IDENTIFICATION AND CHARACTERIZATION OF LIPIDS IN ARCHAEOLOGICAL UNGUENTS

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Abstract

New methods for obtaining compositional information have been explored. In this study the characterization of archaeological unguent samples was achieved by ^{31}P labeling, using the derivatizing agent 2-chloro-4,4,5,5-tetramethyldioxaphospholane [1]. Lipids containing hydroxyl, aldehyde and carboxyl groups were selectively tagged with ^{31}P and then detected with good resolution using ^{31}P-NMR by exploiting the 100% natural abundance and wide chemical shift range of ^{31}P [2]. After standardizing the reaction conditions, using representative compounds, the derivatization approach was used in order to profile the lipids in the archaeological unguents. The unguents are a complex mixture of natural compounds composed by a lipid base (wax, vegetable oils and animal fat) and a series of natural different ingredients. In order to analyze the lipid base, a preliminary extraction procedure should be applied. The separation procedure is based on a chloroform/methanol extraction, followed by a liquid/liquid (hexane/water-ethanol) separation. After this procedure, the samples were then submitted to ^{1}H-NMR and ^{31}P-NMR analyses. The analyses were able to individuate the presence of vegetable oils, animal fat, beeswax and coniferous resins. In particular, this result was achieved by the detection of: primary, secondary and ω-1 alcohols markers of beeswax; diacyl (1,2-DG and 1,3-DG) and monoacyl (1-MG) glycerols markers of triglycerides; abietic acid groups marker of resin. Moreover the identification and quantification of aldehydes, ketones and double bonds were helpful in the assessment of the degree of oxidation. The individuation and the characterization of these components and its degradation compounds induced by ageing, is important for understand the ancient pharmaceutical techniques and to assess the state of conservation.

References

[1] A. Granata, D.S. Argyropoulos. "2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins". *J. Agric. Food Chem.* **1995**, *43*, 1538-1544.
[2] F.M. Dayrit, O.E.M. Buenafe, E.T. Chainani, I.M. De vera. "Analysis of Monoglycerides, Diglycerides, Sterols, and Free Fatty Acids in Coconut (*Cocos nucifera* L.) Oil by ^{31}P NMR Spectroscopy". *J. Agric. Food Chem.* **2008**, *56*, 5765-5769.

ANALYTICAL STUDY OF ANCIENT PHARMACEUTICAL PREPARATIONS

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Abstract

The identification of the substances and the processes used in the past for formulating of medical, cosmetic and pharmaceutical preparations is of great interest in the context of archaeometric researches aimed to reconstruct the evolution of science, technology and knowledge in the course of the centuries, and to trace the role and the uses of various materials in past societies.
The presented results are relative to the chemical analysis of organic natural substances in samples collected from vessels belonging to historical collections of pharmaceutical preparations (17^{th}-19^{th}): the Aboca museum of Sansepolcro (Arezzo, Italy), the Real Cartuja de Valldemossa (Palma, Majorca, Spain) and the Museum of S. Agostino (Palazzo Tursi, Genova, Italy).
This research was part of the national project Prin07: *Colors and balms in antiquity: from the chemical study to the knowledge of technologies in cosmetics, painting and medicine* (Cofin2007).
Analyses have been performed by gas chromatography-mass spectrometry (GC/MS), aimed at separating and identifying significant molecular markers to be used to assess the composition of the materials. The research focused on lipid and terpenic compounds, which are the main components in the majority of the ancient pharmaceutical preparations investigated. The presence of fatty acids, diacids, hydroxy-acids, long chain alcohols and specific alkane patterns highlighted the presence of beeswax, animal fats, plant oils and pine resin. The results have been interpreted contextually with information obtained from the historical documents and ancient pharmaceutical treatises, in order to reconstruct the original recipes of the formulations.

PYROLYSIS-GC/MS FOR THE IDENTIFICATION OF ORGANIC COMPONENTS IN HISTORICAL RECIPES

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Abstract

In the present study samples of ointments collected in Spanish vessels dated from 16th and 17th century were analyzed. Part of samples comes from Aboca Museum (Sansepolcro, Arezzo, Italy). Two samples were from the Real Cartuja de Valdemossa (Palma de Majorca, Spain), stored in the ancient pharmacy of the monastery.
All samples were analyzed by Py-GC/MS with thermally assisted hydrolysis and methylation with tetramethylammonium hydroxide (TMAH). Because this study is part of multi-analytical investigation conducted in collaboration with other research groups, py-GC/MS in this context has the role of providing initial information about the composition of the sample, being a fast method which requires small amounts of material. Based on the preliminary compositional analysis a first reconstruction of original recipes could be done, followed by comparison with historical documents. In the second phase of the work, the ointments were reproduced in the laboratory following the historical sources, and the modern preparations were analyzed and results compared with historical samples. Also, modern preparations were artificially aged. In this way it is possible to understand if the py-GC/MS characterization technique is sufficient to provide the major information on the samples, or if it is necessary to employ other types of analysis.
The results obtained by py-GC/MS show that with this technique it is possible to identify lipids, waxes and natural resins in the sample. Comparison with aged and unaged standard preparations highlighted that distinction between vegetal oils and animal fats is difficult, in particular when a mixture of the two kinds of lipids is present. Aid in data interpretation is obtained from use of chemometric data treatments applied to the fatty acid relative content in the samples.

THE COMPOSITION OF SOME ROMAN OINTMENTS IN THE COLLECTIONS OF THE BRITISH MUSEUM

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Abstract

Residues from medicine containers in the collections of the British Museum have been analysed as part of a wider programme of scientific work on Roman surgical instruments. These cylindrical bronze containers have been found to contain *materia medica*, ranging from extensive extant remains of ancient ointments to possible minor deposits on the interior surfaces of the containers.

Samples from the residues have been analysed by gas chromatography-mass spectrometry (GC/MS) to identify lipid, resin and carbohydrate components. Where possible, the ointments were also analysed using X-ray fluorescence to identify any inorganic components. The results have provided evidence for ointments (and in one case possibly pills) consistent with a medical purpose. Ingredients identified include beeswax, fat, conifer resin and gum-derived sugars, plus lead and zinc. Particularly significant were the varied compositions of residues from four sections of a multi-compartment container. In one of these compartments the beeswax seems to have been prepared as the 'Punic wax' described by Pliny [1]. Experimental preparation of Punic wax following Pliny's method was undertaken in the laboratory and the product analysed to compare with the ointment residues. This paper discusses the GC-MS results of both the experimental material and the archaeological residues and their significance for the interpretation of the past use of these medicines.

References

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HETEROGENEOUS POWDERS FROM POMPEI AND ERCOLANO SITES: A MULTI-ANALYTICAL CHARACTERISATION

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Abstract

The contents of a series of vessels from the archaeological sites of Pompei and Ercolano have been analysed with the purpose of: a) studying the component materials and their degradation products; b) identifying the technology of production, and c) verifying the function and use of the products. The investigated materials are in the form of powders, and have been tentatively identified as residues of ink on the basis of the shape of some of the vessels (atramentaria) in which they were found.
Several complementary analytical techniques have been applied: optical microscopy, micro-FTIR, micro-Raman, XRD, SEM-EDS, EPR, GC/MS and Py-GC/MS
The samples resulted to be constituted of a complex mixture of inorganic phases, including gypsum or silicates, and other minor compounds. Carbon black was identified as the main mineral pigment, while no traces of iron gall ink was found. The presence of radicals probably related to the carbonaceous portion was assessed. Some metallic residues, mainly bronze and copper minerals as malachite and azurite, were identified in several samples. It is not clear whether they were intentionally added to the mixture or not.
After chemical analyses, for some samples the function and uses of the material is still unknown, while other have been confirmed to be ink residues.
The research has been carried out in the framework of the Project PRIN2007 CiBA, coordinated by Prof M. P. Colombini.

CHARACTERISATION OF ARCHAEOLOGICAL ORGANIC "PERFUMES" FROM ETRURIA AND SARDINIA (7TH – 5TH C. BC). ASSESSMENT OF THE 3-YEAR RESEARCH PROGRAM *PERHAMO*

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Abstract

The research program *Perhamo* (ANR 2008-2010, French Research Agency) was dealing with the characterisation of perfumes and oily residues from the west Mediterranea, during the 7th c. – 5th c. BC. Both approaches were investigated. The first one included the organic study of the preserved organic matter, by implementing "structural" characterization methods such as gas chromatography coupled to mass spectrometry (GC-MS). A great attention to preparation of the samples was paid in order to detect and identify major markers, minor ones and traces. Specific extractions and purification by solid phase extraction (SPE) were implemented before analysis. The second approach had to apprehend the genetic information eventually preserved in archaeological ceramics. Unfortunately, all ceramics has been broken during use or after the deposition or, if preserved entire, they were opened, allowing the penetration of modern pollutions inside. At this point, DNA investigations have been discarded for potsherds; only closed vessels are investigated.

The samples. — Two different types of series were studied, consisting even of ceramic or of glass: (1) materials from museums coming from ancient excavations (archaeological museums of the Villa Giulia, Cerveteri, Florence, Cagliari), (2) recent material directly sampled during excavation or from recent excavations (Oristano, Cabras in Sardinia, Chiusi, Marzabotto, Metaponto). Different residues were studied: visible residues preserved in the container, invisible impregnations of the ceramic inner sides, or invisible residues deposited on the inner walls of glass vessels. More than 220 objects issued mainly from tombs were sampled, even by scratching their inner sides or dissolving residues with solvents.

Chemical characterisation. — For each sample, lipidic soluble fraction and polymerised fraction were characterised by GC-MS. No general protocol has had to be implemented because of the different contents, structure and composition of the container, depositional contexts, and storage conditions following the excavations. The implemented methodology has been adapted to each sample. Also, no general rule can be established between the composition of the content and the typology of the vessel. As summary:

- pollutions are the most frequently identified preserved markers. They are due to migration from the environment of the object during

deposition (fertilisers, biocides, plastic materials) or from the museum (biocides).

- lipids are the most preserved markers. Thanks to the depositional context (pH, hygrometry, …) soluble markers, even if major in the native materials, can be completely lost. A more pertinent information can be obtained from neutral and apolar markers, that are not concerned by lixiviation, as sterols and triterpenoids *vs* fatty acids.
- among lipids, cerids are often identified. They are issued from vegetal epicuticular waxes. Nowadays, the greater sensitivity of the analytical apparatus allows their detection in almost samples.

Fatty materials identified in perfume vessel are varied: animal fats, vegetal oils, dairy products, beeswax. The preservation state of the residues allows rarely the complete identification of the native material. However, the precise purification and characterisation of sterols and triterpenoids permits the authentication of olive oil in several unguentaria, or moringa oil in an alabaster coming from Egypt, by comparison with a home-made sterol databasis. When presented as traces, the identification of beeswax is more complicated, because of the close footprint of vegetal waxes. Care has to be taken for a sure authentication of beeswax.

Glass unguentaria from Nola (South Sardinia) brought in light a wide range of content, including intense fragrant molecules including camphor and phenolic acids. Such products could reveal importations from East and South-East Asia because camphor, in such important amounts, is unknown in European and Mediterranean species. Many triterpenic markers can not be attributed to a botanical source, because of our insufficient knowledge of the composition of plants. Working with botanists seems now to be an indispensable step for the further identification and the development of biomolecular archaeology. Coniferous resin from *Pinus* sp. were widely used, even as crude oleoresins or pitch. Oriental resins such as mastic (*Pistacia lentiscus* L.) were rarely identified.

The study of several tombs from the necropolis of Sulcis (South Sardinia) revealed unexpected results. The selection of vessels before sampling and their precise examination allow a partial restitution of the burial ceremony. More surprisingly was the range of organic materials used for libations. An association of polymethoxyflavanones revealed the presence of *Citrus* sp. They were identified in association with important amounts of sugars, traducing a king of fruit paste. Such a discovery would modify our conception of importation of *Citrus* sp. from East, in correlation with palaeobotanical evidences in Cumae (4^{th} c. BC). Another oenochoe was filled with a viscous content, consisting on a mixture of *Pinus* sp. resin and bee bread. This latter was mentioned for the first time in archaeological context and its association with funerary ceremonies has to be noted.

Conclusion. — This program brought in light that ceramic vessels found in tombs have unexpected contents and uses. Oenochoe, the well-known "wine vessels" and other cantharis, seem to take another role in funerary context, because they don't contain wine, but other widely diverse substances. Also, perfume vessels (unguentaria, balsamaria or typical Etruscan arrybals and alabasters) contained

mostly fatty materials. Only glass vessels revealed a volatile and fragrant content. As conclusion of this research program, it seems to be necessary to analyse wider series of ceramics. The attribution of a role, or a use, to a vessel has to be carefully suggested because it seems that a same type of ceramics has different uses in the domestic, official and religious life (according the iconography) and in the funerary life. Thus, biomolecular archaeology seems to be an indispensable complement to each actual archaeological study.

TRACING THE ACADEMICS IN MEDIEVAL MONASTERIES

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Abstract

The medieval monasteries and friaries were centres for the academic activity in Denmark from the mid 1100's and until the reformation in AD 1536. Some monasteries and friaries also had a hospital function where sick people could be treated and nursed. Syphilis was most likely introduced in Europe for the first time shortly after Columbus and his men returned from the Americas in 1492, and we know from written sources that mercury compounds were used in the treatment of syphilis in late medieval and renaissance times. It has, however, not been known if mercury was also used in early medieval times, where leprosy was the dominant disease. In the lecture it will be shown how our measurements of mercury in medieval human bones can cast light on both the treatment of leprosy and of the academic activity in the monastery.

THE USE AND PRODUCTION OF ORGANIC COLOURING IN PAINTING TECHNIQUES

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Abstract

The historical importance of blue indigo and the interest always greater for the environmental and health protection, represent today the starting point for many experiments on the production and re-use of natural colours in the textile and pictorial sector. This work develops from the need to widen the variety of colours available in pictorial techniques, by thoroughly analysing the traditional extraction methods of the best-known vegetable dyes. The colours involved are: the yellow extracted from reseda flowers and leaves (Reseda Luteola L., in the past called Arzica) and the red obtained from the roots of madder (Rubia Tinctoria L., formerly an important source of the dye alizarin and today known as madder lake, a synthetic substitute). The vegetable raw material was obtained from an experimental cultivation near Lamoli, at the Natural Colours Museum.

As an extractive method, we chose a specific process by which we can obtain the production of a pure, crystalline and bright pigment named "lake". In pictorial techniques the term lake stands for a "combined" pigment: in fact, it is composed of an organic colouring matter fixed permanently (whether or not chemically defined) and an inorganic mineral inert compound (usually a metallic salt, oxide or hydroxide, which constitutes the base or carrier).

As early as the Middle Ages, vegetable dyes were widely employed in miniature painting, so the early instructions to prepare lake appeared just in that period. Howerver, owing to the little availability of recent studies on this subject and to the difficulty of interpreting the historical sources, the research methodology of the present survey is mainy based upon new experimentations.

The many tests done on extraction were marked by rigorous consistency in the choice and selection of the raw materials and by as accurate as possible processes in order to ensure objectivity in the comparison and enhancement in the results. As far as the dyes assessment criteria are concerned, they are based upon an attentive observation of the external and technical features during the stages of the pictorial preparation and application.

The process of lake production can be divided into two steps: the extraction of colouring principles from a vegetable substance and the coagulation/flocculation of the dye extracted, which determines its sedimentation in the form of a lake.

The first series of laboratory tests run on a small scale brought, as a result, the achievement of the optimum procedures for lake extraction from reseda and madder. Good results have been obtained also in terms of dye productivity/performance and of energy saving. The pigments produced were subsequently employed to create particular colour maps in order to point out their external pictorial features. With a view to a future production on a large scale, extraction tests were done by multiplying the data of the procedures: the

results proved to be consistent with the experimental tests. Besides, thanks to its functionality, this method can be applied to the planning of a single system provided with flexible machinery and units which, at a reasonable cost, could be used in the production of other types of lakes.

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NON INVASIVE IN SITU STUDY OF COLORS IN PRE-HISPANIC CODEX

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Abstract

The scientific study of the material components and of the painting techniques of Pre-Hispanic codices is still in its infancy. Invasive analytical techniques based on sampling of the painted surfaces, that in the last decade allowed important breakthroughs in the study of Mesoamerican mural painting, were seldom applied to codices that, given their rarity and preciousness, cannot be adequately sampled. When such samplings were done in the past on some codices, they gave very scarce information due both to limited sampling and obsolete analytical techniques.

Nowadays, the development of portable and non-invasive spectroscopic techniques, as those employed in this work, allows for the identification of the ground and to the characterization and mapping of the different dyes and pigments used in codex painting.

Nowadays, thanks to the development of a variety of non-invasive and portable spectroscopic techniques, the scientific study of Pre-Hispanic Mesoamerican books can be carried out, revealing information on the constituting materials and painting technique while fully respecting their physical integrity.

In this paper we discuss a non-invasive study of the Cospi Codex, carried out by the use of the multi-technique integrated approach of MOLAB, and focused on the characterization of coloured materials (pigments, dyes and substrates) and on their use on the obverse and reverse.

The non-invasive analytical data were compared with historical references contained in Early Colonial Mexican documents showing interesting parallels and providing hints for probable identifications. The section devoted to pigments and dyes in the Náhuatl and Spanish texts of Book 11 of the Florentine Codex, written by the Franciscan friar Bernardino de Sahagún around 1576-77 on the basis of information gathered from Native Aztec elders, is particularly useful in this sense, as well as other historical sources such as Francisco Hernández's *Historia Natural de la Nueva España* (1570-77), Francisco Javier Clavijero's *Historia Antigua de México* (1780), and some modern synthesis devoted to colour use in ancient Mesoamerica.

MULTI ANALITYCAL APPROACH TO AGED COMPLEX MATRICES

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Abstract

Since a decade our research group deals with the analysis of ancient cosmetics and drugs, starting from the Roman founds [1-3]. At present some founds from pharmacies of Italy (Genua, Sansepolcro) and Spain (Majorca) amounting to the XVII century and Egyptian ointments of the II millennium b.C. from the Turin Museum are under study.
The analysis protocol provides firstly non-destructive analyses and then the more expensive and destructive analyses, such as gas-chromatography-mass spectrometry (GC-MS) methods. We report the results of the vibrational spectroscopy techniques, such as Raman microscopy (laser 632 nm), FT-Raman spectroscopy (laser 1064 nm) and FT-IR/ATR with a golden gate accessory, were identified as the most suitable techniques for a first approach to the analysis of the ancient samples. Raman microscopy is the most suitable technique in order to identify minor inorganic components and contaminants at the micrometric scale inside these complex matrices[4]. This technique can easily identify compounds like lead oxide, vermillion, rare minerals, (etc.) that could give interesting informations about the provenance of the raw materials and the original composition of the formulate. In Tab.1 are reported some data about the composition of some ancient Egyptian samples. It can be observed that Titanite is present, a mineral possibly coming from mines in Southern Egypt[5].

Table 1: Micro-Raman and FT-IR/ATR data from Egyptian samples (Turin Museum)

Sample	μ-Raman	FT-IR/ATR
4b	Fluorescence	Free fatty acids, resin, gum
5	Fluorescence	Free fatty acids, resin, gum
8	Hematite, Magnetite, Biotite, MnO2, Titanite	Clay
11	Protein, BaSO4, silicates	Free fatty acid, protein, shellac
12c	Big hematite crystals	Wax, gum, resin

Concerning to organic materials, their possibility of identification, is very different from that of inorganic ones. Some compounds were rapidly degraded, some others persisted till to present day, often unchanged (e.g. wax). Historical samples give a chemical variability like the natural products, in addiction there are the ageing and the degradation process that make very difficult to recognize the raw material originally present. For understanding the possible changes undergone by materials in ageing, a specific database of spectra must be available.

Some thirty raw materials were chosen among oils (e.g. olive, almond, and palm oil), gums (e.g. gum arabic, gum tragacanth), animal fats and waxes commonly employed in the ancient preparations. On the basis of the examination and critical interpretation of ancient literature sources (pharmacopoeias) fifteen samples based on pharmaceutical and cosmetic recipes were prepared as a reference samples. The raw materials and the reference formulations were artificially aged by using heating (in a oven at 60°C for 1 month), photo-oxidation (with ozone for 20 hours) and enzymatic degradation (by means of a pool of cellulase, lipase and laccase).

Concerning the raw materials, only few showed fluorescence in Raman microscopy, but this decreases sharply with the artificial ageing process (Fig.1). This fact could be due to the loss of fluorophores.

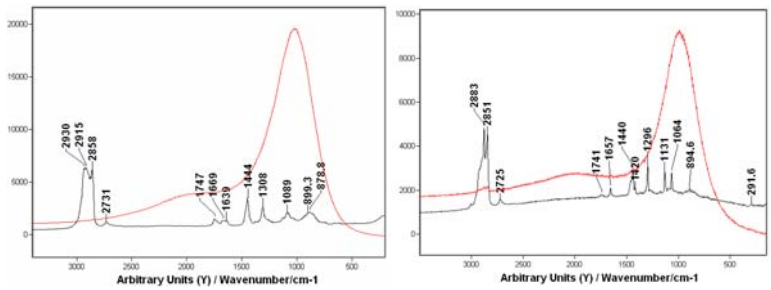

Figure 1. Decrease in micro Raman fluorescence: on the left extra virgin olive oil (red) and extra virgin olive oil thermally aged (black); on the right a pharmaceutical formulation (red) and the same aged with ozone (black).

The artificial ageing produces different alterations according to the type of ageing (Fig.2). Among the first results we reported the analysis of Pompeii sample already identified as palm oil by GC-MS[2]. The comparison with our database showed correspondence with palm oil enzymatically degraded (Fig.3). This indicates that this database is interesting in recognising the organic materials into archaeological holders.

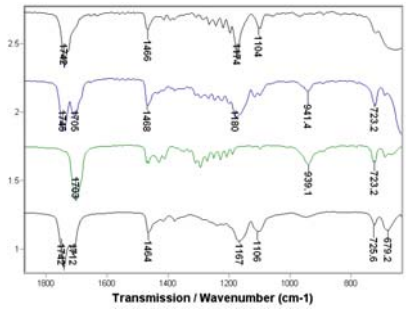

Figure 2. FT-IR/ATR spectra: thermally treated palm oil, fresh palm oil, enzymatically treated palm oil, photo-oxydated palm oil (from top).

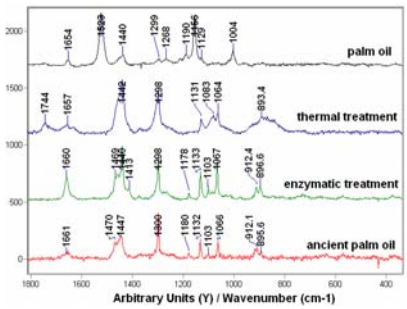

Figure 3. Micro-Raman spectra: palm oil, thermally treated palm oil, enzymatically treated palm oil, Pompeian sample (from top)**.**

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CHARACTERIZATION OF PRE-HISPANIC COSMETICS FOUND IN A TOMB OF THE ANCIENT CITY OF TEOTIHUACÁN (MEXICO)

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Abstract

A number of materials of organic and inorganic nature are usually contained in the small ceramic pieces found in the toms belonging to the high society of the archaeological site of Teotihuacán (Mexico) dated back to the Preclassic and Classic period (ca. 200 BC-750 DC). Minerals finely powdered used as pigments are the materials more frequently present. Besides them, organic products are found. All these substances have been associated by archaeologists and art historians with cosmetics and scents used in sacred rituals.

The present contribution shows the preliminary results obtained in a study devoted to the chemical characterization of the materials contained in small ceramic pieces that were found in the burials 105 and 108 placed in a tomb of the multiethnic *Teotihuacanian* district of *Teopancazco* (Manzanilla, 2009:21-42). A series of 31 samples including pigments, some of them attached to a clayey stamp, minerals and organic materials have been analyzed. For this purpose a multi-technique approach has been applied that includes light microscopy (LM), scanning electron microscopy-x-ray microanalysis (SEM-EDX), voltammetry of microparticles (VMP), x-ray diffraction (XRD), FTIR spectroscopy, Gas Chromatography-Mass spectrometry (GC-MS) and Pyrolysis-Gas Chromatography-Mass spectrometry (Py-GC-MS).

Pigments identified simultaneously by LM, SEM-EDX, XRD, FTIR and VMP are summarized in table 1

Table 1.- Pigments and minerals identified as major components.

Minerals identified	**Sample reference**
Galena (PbS)	16,17,20,26,27
Haematite (Fe_2O_3)	1,5,7,3,4
Red earth (clay minerals)	1,2,5,7,9-11,14,15,19,21,22, 24 ,25,28-31
Umber raw	23
Hydrated iron oxide ($Fe_2O_3.nH_2O$)	3,4,8

Jarosite ($KFe_3(SO_4)_2(OH)_6$)	3,4,12,13
Cinnabar (HgS)	8,10,15
Carbon (C)	16,20,26,27
Mica	16,18
Pumice	6

The results obtained put in evidence that iron oxide and earth based minerals, covering a wide color palette ranging from red-orange-pink-ochre-brown, were used for cosmetic purposes in this ancient civilization. It is interesting to remark the identification of the mineral Jarosite, a potassium-iron basic sulphate ($KFe_3(SO_4)_2(OH)_6$), in some of the yellow samples. Cinnabar (HgS), identified by VMP, has been found in small amounts in some of the reddish samples. The low content in which cinnabar has been found in the analyzed samples suggests that this material was deliberately mixed with other pigments in order to reduce its toxicity.

Identification of galena (PbS), at first time in the city of Teotihuacán, as pigment used for cosmetic purposes is of particular relevance as this mineral has been scarcely found in Mesoamerican sites in a funerary context. Occurrence of this mineral far of this archaeological site significantly limited its use. It should be noted that the closer deposits of this mineral are located in *Michoacán* (Northern Mexican region). Nevertheless, the bigest deposits of this mineral are found in the North American states of Illinois and Missouri (Fagan, 1991:372; Swanton, 1987:528-535). This is the reason of the limited use of this valuable mineral that was reserved to high public figures of this ancient society. On the other hand, the fact that galena has been found mixed with carbon, in an attemt to reduce its toxicity, suggests that the ancient teotihuacans had some empirical knowledge about the negative effect of this mineral on health. Similar combination is found in other ancient Mediterranean cultures (Mesopotamia and Egypt). For instance, the *khol* used for profiling the eye-line (Janot et Vezie, 1999:217-232; AA.VV, 2002: 38-39).

SEM examination of the particles of carbon pigment enabled the recognition of typical morphologies of wood, probably from the native pinaceae species of Ocote (*Pinus montezumae)*.

Other interesting finding is related to the presence of mica in some of the studied samples. This mineral was probably added to those of the cosmetics containing fragant substances in order to mantain the scent for longer periods of time due to the excelent thermal properties of this mineral (González, 2009:53).

Concerning the samples containig organic substances, FTIR spectroscopy and chromatographic techniques enabled the identification of a diterpenoid resin probably used as binding medium of the pigments.

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STUDY AND PREPARATION OF ANCIENT COSMETIC AND PHARMACEUTICAL FORMULATIONS IN A PRESENT PRESPECTIVE

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Abstract

The study of ancient cosmetic and pharmaceutical formulations involved the examination of several recipe books starting from the classical age till to the beginning of scientific chemistry and pharmacology. The study of the same formulation in subsequent times has shown the evolution and the adaptation to the age. Many ancient books and manuscripts reporting recipes concerning the subject in the period between 1597 and 1872 have been considered[1-7].
Study of the ancient remains found inside unguentaries and of the raw materials used in the recipes has been necessary. Not all the raw materials could be bought, some needed to be prepared in the laboratory, such as the rose-water and the turnip juice, two ingredients used in the preparation of many ointments.
The ointments to be prepared were chosen as a function of the remains found in the containers, but mainly on the basis of the analytical results coming out from ancient remains analysis. Those reproduced in the laboratory were many, sometimes the preparations have been made in double or triple, according to the sources of different historical periods (Tab. 1). The total number of the ointments reproduced was fourteen.

Table 1: Ointments reproduced in laboratory and their corresponding ancient Aboca remains.

UNGUENTUM ROSATUM Aboca N° Inv. 50509			***UNGUENTUM POPULEON Aboca N° Inv. 50023***	***UNGUENTUM PRO IGNE Aboca N° Inv. 50015***	
I_A	I_B	I_C	II_A	III_A	III_B
Adeps Suillus			Adeps Suillus	Adeps Suillus	
			Poplar buds		
Fresh red roses			Poppy	Turnip juice	
			Viola		
Rose water		Rose water	Henbane	Oil	
			Deadly nightshade		
Sweet almond oil			Houseleek	Wax	
			Lettuce		
		Wax	Burdock	Silver litharge	
			Perfumed wine		

OXIMEL SIMPLEX Aboca N° Inv. 50010 N° Inv. 50025		***MEL ROSATUM Aboca N° Inv. 50054***		***UNGUENTUM ALTHEA Aboca N° Inv. 50007 N° Inv. 50030***		***UNGUENTUM COLOPHONIA Aboca N° Inv. 50017***	
IV_A	IV_B	V_A	V_B	VI_A	VI_B	VII_A	VII_B
Skimed honey		Decoction of roses		Marsh mallow		Colophony	
				linseed			
				Fenugreek		Oli	
		Skimed honey		Wax		Wax	
Vinegar				Pine resin		Mastic	
				Oil		Galbanum	
			Green of roses		Adeps Suillus	Incense	
					Curcuma powder		Gum arabic

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3. Secreti Nobilissimi del Nuovo Autore detto il Greco, 1641.
4. Ricettario Fiorentino, 1789.
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WOOD TAR AND WOOD RESINOUS EXTRACTS AS INGREDIENTS OF EGYPTIAN EMBALMING MATERIALS: A GC/MS STUDY.

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Abstract

Studying the chemical composition of organic biomaterials associated to archaeological artefacts can give an important contribution both to archaeological and ethnographic studies and to a better knowledge and conservation of the objects.
Wood-derived substances as wood tar, wood pitch and resinous wood extractives can be are often encountered as ingredient of mummification balms used in ancient Egypt in funerary rituals and for the preservation of the body. Analyses of the remains of resins, tars and pitches can answer questions relating to their botanical natural origins, in addition to their modes of acquisition, preparation and geographical provenience.
In particular, the use of pitch obtained from conifer wood and of terpenic resins as colophony and mastic has been reported, and the use of terpenic materials obtained from cedar wood has been hypothesized, also on the base of historical documents [1,2].
Plinius and Herodotus (Plinius the Elder Historia Naturalis libro XVI; Erodotus, Storie II 76-88; Diodorus Siculus, Bibliotheca Historica) cite a "*pix liquida*" derived from a wood called "cedrium" as a material used in Egypt for mummification, that has been interpreted as cedar wood.
In this context, we compared by GC/MS the composition of terpenic extracts and pitch obtained from pine (Figure 1) and cedar wood, before and after induced ageing.
The research included also scientific investigation of Egyptian embalming materials, obtained from archaeological expeditions in Egypt carried out by Department of Historical Sciences of the Ancient World of University of Pisa, and sampled from archaeological remains conserved at the Natural History Museum of University of Florence and from the Museum of Anatomy of University of Pisa. The results were interpreted and compared with reference materials in order to assess the origin of the substances used to prepare the embalming mixtures.

MULTIANALYTICAL CHARACTERIZATION OF COSMETICS IN ARCHAEOLOGICAL REMAINS FROM THE ROMAN PERIOD IN THE IBERIAN PENINSULA

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Abstract

Ancient cosmetics contained complex mixtures of very different organic and inorganic substances. Most information on the preparation of these cosmetics comes from classical texts. A good number of the cosmetics studied and described in the literature correspond to products formed of oils and/or resins, probably used as perfumes or unguents, or of powder pigments (such as ochre, lead white or cinnabar). However, although recently the analysis of products contained in archaeological objects has identified some ingredients, still little is known about how the whole cosmetics themselves were prepared.

The chemical study of the materials preserved in some glass unguentaria and other metallic tools from the Roman period, found in the Iberian Peninsula (colony of Celsa, Zaragoza, Spain), highlighted the use of several substances included in diverse combinations and allowed us to understand their preparation. Different complementary analytical techniques (SEM-EDX, Py-GC/MS, GC/MS and LDI-MS), all entailing the use of an extremely small sample size, were used to identify the organic and inorganic components of the ancient cosmetics.

The results revealed different preparations of make-ups, coloured by pigments of organic and inorganic nature (madder lake and hematite) and with completely different matrixes (scented oils and gypsum). These cosmetics had been prepared thoroughly, the ingredients carefully selected and their properties and possibilities for good cosmetic use had been understood. The final product would bring together and exploit the properties of all its ingredients (colour, texture, protection, waterproofing, etc) in a similar effect to modern make-up.

IDENTIFICATION OF PLANT GUMS IN EGYPTIAN FUNERARY MASKS

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Abstract

The samples analyzed in the present study are collected from two funerary cartonnage masks coming from Museum of Egyptian Antiquity of Turin, discovered by Ernesto Schiapparelli in an excavation campaign performed between 1911 and 1913 in Assiut. Both objects can be dated at Late Period (600-300 B.C.) and are in bad conservation state. The masks were sampled before restoration and exposition. Results on the analysis of binding media with pyrolysis-silylation show that some polysaccharide may be contained in the paint layer, but not precise indications are obtained; therefore pyrolysis with thermally assisted hydrolysis and methylation was also performed.
In the pyrograms the marker compounds of monosaccharides could be identified, especially in the SIM at 129 m/z profile. Fatty acids were Also found, showing the presence of lipids, probably due to some material used from body embalming processes.
Comparison with standard plant gums analyses suggests that the masks samples may contain gum derived from fruit trees.

OINTMENTS JARS IN THE ROMAN WORLD: CONSIDERATIONS ON ANCIENT COSMETICS IN THE LIGHT OF SCIENTIFIC STUDIES

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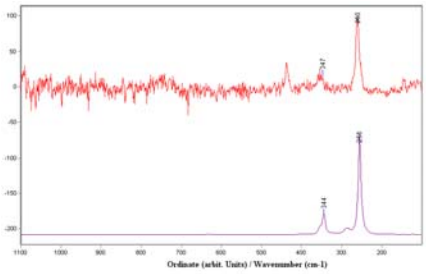
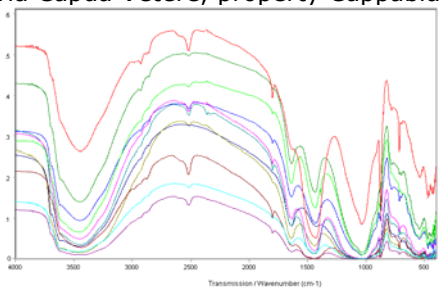
Abstract

My research has been to study the techniques of vibrational spectroscopy, the Raman and the infrared (IR), in order to study the content of balsams which are predominantly Hellenistic – Roman. These balsams have been found in the areas of Santa Maria Capua Vetere and Curti, specifically: the excavation of 1995 property Scrima (Patturelli Fund) and that of the excavation of 2007, ownership Delle Femmine (both in Curti), the excavation of 1984, Piazza Milbitz and lastly, the excavation of 2008, the property Cappabianca (both in Santa Maria Capua Vetere). Little information has been obtained about their discovery. Most of them comes from the worship area of the fund Patturelli and a Roman kiln found at Milbitz Square while others could not be traced to scientific reports. From the typological point of view they belong mostly to the types I, II, IV, V and VII of Forti's classification, following, according Camilli, a chronological range from the end of the fifth century BC to the first half of the first century BC. The pyriform type is from Roman times (about the first half of the first century AD).The construction and sale of perfumes were done by wealthy families because the equipment and raw materials were really expensive. The families used slaves to make their fortune by having them doing the hard work of making the perfumes while the Roman families collected the profits. The production of ceramics, oils, perfumes and the commercial activity inherent in producing them in Roman Capua was very robust: according to some sources they were producted in Seplasia, the area of the city that housed shops of perfumers that produce and sell perfumes. The fame of this area was so well known that the perfumers were known as "*seplasarii*" or "*unguentarii*". It is believed that there was a perfume called "*seplasium*" but its recipe is unknown. I have taken the content from 82 dirty containers, removing with a spatula also part of the walls of the clay ointments, after making the required photo documentation. Samples were stored in plastic containers that have been raised, well sealed, to the Department of Chemistry of Modena. The investigations were carried out by Professor Pietro Baraldi, one of the most prestigious experts in the field, which also led the analysis of balms of Pompeii and Oplontis. With these surveys we know the identity of the components, whose molecular groups react to radial stress issued. Infrared spectroscopy has led to the preparation of samples for analysis, with the production of tablets with potassium bromide (KBr) in a proportion of 1/100mg with 1mg of powder to be analyzed and 100 of KBr. The powders were mixed in a mortar with a pestle, both of agate, and entered into a matrix for tablets, which have made the pills. Each was analyzed with a spectrometer FT - IR Jasco, with the resolution of $2cm^{-1}$, equipped with

TGS detector, operating with a range between 4000 and 400cm^{-1}. There are no preparations for investigations with Raman spectroscopy, it is analyzed with a small portion of material, so we proceed to a selective analysis of different areas, for samples of not of homogenous composition. Part of the dust removed from each container was laced on a metal shelf and observed with a optical microscope; each grain has appeared as a crystal of different shape, color and brightness. To register does not meet a specific spectral range, which depends on the type of compound: the range has varied about from 200 to 1800 cm^{-1}, in some cases has risen between 3500 cm^{-1} and 500 cm^{-1}. For each peak corresponded to a particular compound, identified by intensity, shape and position. The recording time varied spectrum: with a weak signal could be a few minutes. The table containing the results of the analysis shows that there were no organic substances, but there has been a predominance of minerals related to the earth and clay of the ointments: feldspars such as microcline, analcime and the orthoclase, are minerals belonging to the group tectosilicates, present in small amounts in rocks, clay, and calcium carbonate are contained in the calcite, dolomite, diopside and in aragonite. Very common are iron oxides such as ilmenite, hematite and magnetite, while other types of oxides are present in the corundum (aluminium oxide) and quartz (silicon oxide), a prominent inert, which comes in the form granules of red, pink or gray. Of all the minerals mentioned, hematite acts as a red-brown ceramic to high degrees of temperature (about 750° C and more) when well-oxidized, in the presence of a lot of air, it could be ground and used to brighten the face (Raman spectrum 21601 of sample 3). The same function could be also taken up by mica, coming from the furnace (in this case not used as a cosmetic). Another iron oxide capable of giving a dark coloration to the ceramic, in environments lacking oxygen, during the same firing, is magnetite: it can be present by itself or with hematite. The cosmetic use can be attributed to coal (present in plant form because apatite does not appear) resulting from the charring wood, seeds and kernels and used for eye makeup (Raman spectrum 21640 of sample 6). An alternative to white lead and less pernicious was the chalk, found in two ointments (seen more clearly in the Raman spectrum 21621 of sample 17); it was used to give pallor's effect to the face by who could not afford more expensive tricks. For this reason it was called "the cosmetic of the poor". Feature is the presence of the pigments cinnabar and Egyptian blue (Raman spectrum 21651 of sample 5), the first of which is also used for coloring the perfumes; it is not clear the presence of the blue. We can suppose the possibility of reuse of the fusiform type balsamar with shoulder high (corresponding to type VII Forti); about the context of excavation we don't know anything. The IR spectra are essentially identical (as is clear in the spectra of some samples stacked). It observes the presence of calcite and silicates in various proportions, (evident in the IR spectrum of the sample 33), rarely (in samples 54 and 78) are found traces of KNO3, saltpeter, usually used with white lead to give the effect rosy face, which, in this case, for the area of origin of the container, a furnace, is attributable to clay or to the land of discovery.



Raman spectrum 21651 of sample 5: cinnabar and Egyptian blue (band at 430 cm-1), from Santa Maria Capua Vetere, property Cappabianca



IR Spectra: From top to bottom samples 9, 12, 6, 14, 17, 3, 4, 47, 54, 57, 33

HPLC-APCI-MS ANALYSIS OF TRIGLYCERIDES IN ANCIENT COSMETIC AND PHARMACEUTICAL FORMULATIONS

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Abstract

The lipid fraction of pottery jar residues from the ancient apothecary of the Aboca museum (XVIII century AD), the monastery "Real Cartuja de Valldemossa" (1722-1929 AD) and the Schiaparelli excavation in Egypt (2100-1900 BC) were analyzed by reversed-phase liquid chromatography (RP-HPLC) coupled to mass spectrometry detection (MS) with atmospheric pressure chemical ionization (APCI).

A comparative study, based on triglycerides (TAG'S) composition detected in raw natural materials and reference ointments prepared as described in ancient bibliographic sources, was also performed. Furthermore, these reference materials were subjected to artificial ageing in order to evaluate the kind of chemical modification in which lipids were occurred during the ageing process.

TAG's were successfully detected even in "up to ten ingredients" recipes, after harsh treatments such as saponification and ozone oxidation, and in archaeological samples.

The identification of residual TAG's in the samples of the Aboca museum collection showed a predominant use of olive oil and pig adipose material as emollient and moisturizing agent. The detection of high level of tripalmitin (PPP) and trilinolein (LLL) in some samples indicated that other vegetable oils were employed. Moreover, the contamination of two sample with tristearine (SSS) and myristin-palmitin- stearin glycerol (MPS) suggested the presence of a fatty material of ruminant origin.

SPEZIERIA OF SANTA FINA IN SAN GIMIGNANO: SPECTROSCOPIC AND GASCHROMATOGRAPHIC STUDY OF SOME ANCIENT MEDICINES

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Abstract

Recently, we became interested into a diagnostic study concerning ancient medicines stored in ceramic and glass pots in the Spezieria of Santa Fina, that is part of the museum located in the Conservatorio of Santa Chiara in San Gimignano.

The story of the Spezieria is strongly related to that of the homonymous Hospital, built in the 14th century in San Gimignano, but in the 16th century it became an independent structure, formed by a shop and a 'kitchen', active up to the end of the 19th century.

The scope of this research was the development of analytical methods suitable to allow the chemical characterization of organic materials present in the different medicines as well as the evaluation of their conservation status.

Spectroscopic and gaschromatographic techniques have been widely exploited in the study of materials used in different artistic works,[1] while the characterization of ancient medicinal samples has been less developed. On this basis, the application of these methodologies to disclose the chemical composition of some ancient 'pharmaceutical' mixtures was investigated.

As reported in the old 'Ricettario Senese' by Jacinto Marchi, traditional medicines are classified as '*Semplici*' or '*Composti*'. Natural materials belonged to the first class while the mixture of different natural compounds by 'human industry' gave rise to medicines of the second type.

Following this classification, some simple and composed materials were analyzed. Infrared and nuclear magnetic resonance spectroscopies were applied to different extracts obtained by treatment of the ancient samples with deuterated solvents of various polarity. Then, the spectral studies, in conjunction with gaschromatographic analyses, allowed the characterization of fractions of different solubility.

Commercial samples of natural compounds were also analyzed with the aforesaid techniques to build a database useful for the chemical characterization of the ancient samples and also to evaluate their conservation status.

The results obtained in this new preliminary study will be properly discussed to evidence the limits and the potentials of the different analytical approaches.

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THE PIETRALBA ARCHEOLOGICAL SITE (PIEVE S.STEFANO, AREZZO, ITALY): A MINERALOGICAL AND BIOCHEMICAL STUDY OF ANCIENT MANIFACTURED STONES

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Abstract

A mineralogical and biochemical study of some manufactured rocky block found in the archeological site of Pietralba (Pieve S.Stefano, AR, ITALY) has been carried out aiming to clarify the use of these enigmatic objects. According to the pottery found nearby the structures, these latter could be attributed to the Middle Age. Even though similar manufactured rocks have wide diffusion (e.g. Vicchio, Massa Marittima, Montefeltro; Cherici, 1989, 1990), their use and their age are still unclear though several hypotheses have been put forward. The most credited ones concern uses as water places, as plant-mills or for tanning.

This research represents the first work trying to shed light on this "mystery" by using both traditional and innovative chemical methodologies.

The Pietralba site is located on the right slope of the deeply incised valley of the Tignana Creek, a tributary of the Tiber River. Along this slope several blocks of sandstone (Fig. 1) occur as the product of ancient rockfalls. Some of these blocks are carved and despite they are highly weathered, the chisel signs are still visible. The blocks, clearly worked "*in situ*", display different shapes resembling, for instance, a *tub*, the *letter L*, a *throne*, a *pyramid*, and were probably used for different purposes.

In this work we focused on the *tub* and on the adjacent *L*-shaped carved block and report the chemical results obtained on the *tub* block).

The *tub* (Fig. 2), characterised by an open side downslope, has a depth of few decimetres; this feature suggests that only small volumes of unknown substances were temporarily stored in the *tub*. Beside this volume limitation, we argue that any stored substance may have had a significant economic value to justify its manipulation in a so remote location. Furthermore, the absence of any source of water at a suitable distance suggests that any treatment would be possible with few or no water solution. The location of the two handicrafts along the slope, with the *L*-shaped carved block resting downslope the *tub*, suggests that the hypothetical productive process exploited the morphologic gradient to drain fluid phases eventually extracted and accumulated in the *tub*. The present

lack of physical connection between the two blocks may have provided during the productive operation by mobile and perishable (wood) linking artifacts.

Rock samples collected in the *tub* were analysed in order to obtain the sandstone mineralogical (XRD analyses) and chemical composition (XRF analyses). Successively, analytical instruments such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS) were used with the aim of investigating

the possible organic components. Very interestingly, oily organic substances have been found and, in particular, vegetable lipids, both diterpenic and triterpenic molecules which are often contained in the bark of plants. These results are in agreement with the hypothesis that the *tub* was used for maceration or beaten of cortex or berries, acorns and/or leaves of oak or chestnut. Furthermore, according to this hypothesis, is possible to comprehend the importance of both the topographic position and morphology and the vegetable cover and to understand the characteristics of the handicrafts: resistant water tight tanks, located in a dry place, and capable of withstanding the weight of such a type of working.

Work is still in progress and the chemical analyses will be performed on several rock samples. Even though preliminary, our data seem to suggest that the treatment of berries and/or other vegetable substances could have been carried out in the *tub* to obtain particular medicated ointments.

Fig. 1 – Sandstone blocks in the Pietralba site

Fig. 2 – The *Tub*

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THE COMPOSITION OF SOME 17TH CENTURY PILLS RECOVERED FROM THE SALCOMBE BAY (UK) WRECK-SITE

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Abstract

In 1995 divers exploring Salcombe Bay off the coast of Devon in the south west of the UK discovered a collection of artefacts now known as the 'Salcombe Treasure'. Coins, ingots, jewellery and miscellaneous ceramic and metal objects were recovered and are thought to be associated with the wreck of a trading vessel sailing between England, the Low Countries and Morocco which sank some time in the late 1630s or 1640s. Amongst the objects was a lidded, brown glazed ceramic pharmacy jar containing *c*. 25 well-preserved pills.

Analysis was carried out on one of the pills in order identify the constituent ingredients with a view to determining the ailments they may have been intended to treat. The inorganic elemental constituents were determined using X-ray fluorescence spectroscopy (XRF). The organic constituents were characterised by gas chromatography-mass spectrometry (GC/MS) of both solvent-extractable fraction and volatile constituents by headspace analysis (the latter because a strong aroma was noted when samples were powdered in preparation for extraction).

The inorganic components detected by XRF analysis were found only at low levels and are almost certainly due to accidental contamination during pill manufacture (or possibly post-depositionally) rather than being intentional ingredients. The solvent-soluble organic fraction contained an abundance of diterpenoid resin components characteristic of a degraded conifer resin, most likely of the Pinaceae family. The presence of volatile constituents offered a rare opportunity to narrow this classification further and infer a *Pinus* sp. source for the resin. No organic ingredients other than resin were identified. The absence of sugar or plant gums is particularly surprising as these were typical ingredients in pills in the 17th century [1]. It does, however, account for their good preservation; although the jar appears to have been largely watertight ingress of even small amounts of water would have caused disintegration of gum or sugar bound pills.

Pine resin was used therapeutically in the 17th century for external treatments but this seems an unlikely application for small pills. Being virtually indigestible pine resin is not an obvious substrate for pills but it has strong anti-septic and antibacterial properties so could have some application as a slow release medicine, or perhaps was intended to be chewed, as a dental treatment or breath-freshener, or even to treat nausea

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STUDY OF ANCIENT PHOENICIAN REMAINS

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Abstract

The Mozia Museum conserves some funerary vessels coming from the isle's archaic necropolis, commercial Greek, Phoenician and Etruscan amphorae, a rich collection of black varnish jars with red images of Birgi necropolis and also materials coming from Mozia Tofet and houses. Also jewels and weapons, amulets, scarabs and objects with original captions engraved are found, as well as cosmetic and surgical instruments and fragments of inscribed stones coming from the Lilibeo necropolis.
From the collection of the Mozia Museum about 200 samples from the Unguentaria and Balsamaria were taken, some having large amount of residue, others a very small one. A preliminary spectroscopic analysis was carried out on these samples by using Micro-Raman and SERS techniques and the results of a first series are reported below:

Inventory Number	Description	Raman Results
482	White powder	Gy, Qz, Ca, HgS
805	Brown grains	Crocoite ($PbCrO_4$) Phoenicochroite ($PbCrO_4$*PbO)
807	Red fine powder	Qz, He, Mg, TiO_2, PbO, Oxalate, Fl
810	Brown powder with red and iridescent points	Qz, Mg, He, PbO, Cor
813	Red fine powder	He, Mg, Qz, PbO
816	Black powder	Pyr, Qz, Fl, He, Mg
1566	Grey fine powder and grains	Ca, PbO, C
3149	Grey fine powder	Ca, C, Ap, PbO, Qz, KNO_3
4519	White powder	Ce, PbO Fl, Qz, He, Mg, C, Ca
4754	White powder and flakes	PbO, Ce, KNO_3, Go, Ca
6158	Grey powder with red grains	C, Ca, organic red (with SERS)
6159	Grey powder	Qz, Ind

Gy=Gypsum; Qz=Quartz; Ca=Calcium; HgS=Cinabar; He=Hematite; Mg=Magnetite; TiO_2=Anatase; PbO=Massicot or litharge; Fl=Feldspar;

Cor=corundum (Al_2O_3); Pyr=pyrolusite (MnO_2); C=Charcoal; Ap=apatite; Go=goethite; Ce=Cerussite ($PbCO_3$); Ind=indigotin.

The preliminary analyses carried out with the Raman techniques have shown the presence of a variety of compounds.
The white powders, among the more abundant ones, present in lead pyxes, were made of Cerussite $PbCO_3$ coming from a complete carbonatation of hydrocerussite $PbCO_3*Pb(OH)_2$. This is compatible with the high chronology of the samples: instead, hydrocerussite has been identified in Pompeii samples. Its presence can be a clear indicator of cosmesis, since it is well known that its use in mural painting is not advisable. At the time, cerussa (lead white) was employed as a foundation.
Other white substances are calcite and aragonite: the first could come from the ground where the unguentaria were found, the second one could derive from ground sea shells.
Litharge, an oxide present in many containers, could derive from the alteration of cerussa, or from a proper addition, whether the yellow colour had a special meaning for the population of the site.
The container NI 3149 had a gray powder composed of Carbon mixed with calcium phosphate. This could have been a bone-black or could come from cinerary urn.
Among the red pigments found there are cinnabar and hematite: the latter can be found as a natural compound or as a thermodegradation product from goethite. The presence of red lead chromates crocoite and phoenicocroite, two rare minerals, in a particularly precious unguentary is a singular discovery.
With the SERS technique it has been possible to record spectra relative to red dyes. However, these spectra do not correpond to compounds coming from madder, purple and kermes. Other comparisons are outstanding.
In comparison with other sites, such as Pompeii, Herculaneum and Oplontis, this cosmetic powders exhibit a wider range of materials [1-3].

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ORGANIC RESIDUES IN COOKING WARES: AN EXPERIMENTAL APPROACH

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Abstract

The identification of organic residues preserved in archaeological ceramics is fundamental for the interpretation of their function and for the understanding of ancient activities, in particular food production, preparation, consumption and trade.

To study the residues produced by the cooking process of different foodstuff that played an important role in ancient times, experimental broths of chicken, pig, bovine and fish were prepared. In addition wine and oil were also cooked. Unglazed coarse ware ceramic pans were used for the experiment.

In this paper, we present the results of the gas chromatography-mass spectrometry analysis of the by-products of the experiments carried out. After the cooking, a fragment of each pan was experimentally aged in the laboratory and a half of each pan was buried, as part of a long-lasting experiment in order to observe the possible effect of postdepositional process on the residues.

This work was performed in the framework of the project Production, trade and consumption of food in Late Antiquity (PROFOLANT), founded by the Marie Curie Actions.

COLOR TRACES AND THEIR IDENTIFICATIONPAINTINGS, COSMETICS, WRITINGS.

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Abstract

During the last years of research carried out on the basis of a financial support by MIUR, many samples have been encountered of different nature, color, origin and physical state. In examining containers present in the Italian Archeological depositories and Museums, we have found or we were adviced of interesting colored materials and we were asked to identify them.
The identification is sometimes rich of information about the ancient technology for preparing elaborated formulates, such as cosmetics, drugs, ointments, perfumes, pigments, lakes, dyes. Thereby, their analysis enables important passages of the production to be understood and some literary sourced to be interpreted.
In examining some materials present on bones due to particular rituals of the first centuries after Christ in Aemilia, a particula identification of manganese based materials was encountered. The presence of manganese oxides can be related to the geology of the Aemilian territory. However, similar compounds are present in Etruscan tiles decorated with Egyptian blue and other pigments in Marzabotto. This fact supply information on the commerce of Egyptian blue far before Roman Empire times and the passage of manganese oxide treatment for painting to subsequent civilizations.
The necessity for ancient populations to paint testimonies of past religious or military chiefs lead to a search for materials coming from far countries, such as Baltic amber, Egyptian blue, indigo… In places with an always more ancient chronology, such as Verucchio in Aemilia, these materials are found in large amounts. It is not clear whether indigo was extracted from *Isatis tinctoria* or an *Indigofera*.
Traces of saffron and indigotine on fictile antefissae in Cuma testifies the use of re-painting the artifacts every while, as a sign of respect for the temples.
Ancient colored lipsticks contain pink ingredients, that may be *purpurissum*, but could be also the cheaper *purpurissum puteulanum*, as revealed by Sers analysis of Pompeiian samples.

Residuals of precious materials are found also in small containers of the Roman ages. Small traces of gold on a black preparation identify the knowledge of a gilding technique on alabaster, with the black assisa applied on small spots.
The ensemble of materials and their use enable an amount of knowledge to be supposed in ancient populations in order to make their life more confortable and elegant.

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