

POTS WITH COLOURED POWDERS FROM THE FORUM OF POMPEII

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Abstract: *This paper presents the results of analytical research carried out on residues found inside some small ritual vessels from Pompeii. The ceramics were found in 1980/1981 excavations near the Temple of Apollo in the forum area. The residues of the original content consisted of powders of different colours: red, yellow and violet-pink. Analyses allowed to identify the precise nature of these compounds classifiable as hematite, goethite with Pb oxide, natrojarosite and purpurisum. The presence of these compounds in a religious context is scarcely attested in scientific literature and adds interesting data on rituals and religion in the classical world.*

Keywords: *pigments, votive offers, Pompeii, EDS, FTIR*

INTRODUCTION

In 1980/1981 stratigraphic excavations were carried out in the eastern side of the *forum* of Pompeii; here thirteen trenches were dug down into the rock-soil in an area comprised between the Capitolium, the Temple of Apollo, the Basilica and the Temple of Venus (cfr. *Arthur 1986*, Fig. 1). The excavations were among the first stratigraphic investigations of Pompeii and provided an overview through the civic, commercial and religious hearth of the settlement. The uncovered data threw considerable light on the history and urban development of Pompeii from the Archaic period to its final destruction in A.D. 79 (*Arthur 1986*).

Excavations brought into light several hundred boxes of ceramics and other archaeological objects. Most of the finds are still unedited and only in recent years the Superintendency at Pompeii, in co-operation with the University of Venice and Matera, has undertaken a complete study of the archaeological finds aimed at preparing the final publication (*Cottica 2007; Cottica & Curti 2008*).

While the study of the bulk of the ceramic material is in progress, an interesting group of six complete, or almost complete, vessels dating to the II century B.C. has been object of recent interdisciplinary research. The ceramics come from excavations carried out in area VII, located near the Temple of Apollo (cfr. *Arthur 1986*, Fig. 1 and *Cottica & Curti 2008* Fig. 2). They belong to layers interpreted by the excavator as fillings of two different pits and one cistern (cfr. **Table 1**), filled in when rebuilding activities were carried out in the temple area in the II century B.C. The pots still yielded part of their original content, consisting of coloured powders (similar to pigments in their aspect) either red, yellow or pink.



Fig. 1 Inventory n. 5665. Fragmentary terracotta figurine with traces of its original paint.

Five vessels (cfr. samples nos. 3821, 4146, 1728, 6964, 3270 in **Table 1**) are miniature versions, either in plain or in black glazed ware, of morphological types well known in Pompeii and the Campanian region, typologically datable between the III and II century B.C. (cfr. *Mazzocchin et al. 2008*, Fig. 19). A further pot is a complete jug in plain ware (cfr. n. 7238 in **Table 1**; *Mazzocchin et al. 2008*, Fig. 19).

For reason of completeness, authors included in the analytical programme a sample of powdery brownish-yellow residue that excavators separated from its original container: the vessel is now missing from the deposits in Pompeii (cfr. n. 24 in **Table 1**).

Table 1. Synoptic table of the analysed samples from the forum of Pompeii

Sample no.	Item description	Layer	Colour of analysed powdery residue	Nature of powder
7238	Powdery residue inside a ceramic jar in coarse ware comparable to type Chiaramonte Trerè 1984, tav. 107, 7-8 (II century B.C.).	VII B 38 filling of cistern 39	Red	Hematite, Cinnabar
3821	Powdery residue inside a black glazed miniature bowl comparable to type Morel F2788c (first half of the II century B.C.).	VII B 47 filling of cistern 39	Gold-yellow	Goethite, Pb compound
5665	Pigment on a terracotta figurine: fragmentary female head.	VII B 47 filling of cistern 39	Yellow-red	Hematite and yellow ochre (goethite)
4146	Powdery residue inside a black glazed miniature bowl variant of type Morel F2784d 2 (the prototype is common in the second half of the II century B.C.).	VII B 74 filling of pit 73	Gold-yellow	Goethite, Pb compound
1728	Powdery residue inside a miniature dish in plain ware similar to Grasso 2004 Piat' II variante b (tav. 7, f) (ca. III and the II centuries B.C.).	VII 40 interpreted as part of the filling of pit 25	Violet-pink	<i>Purpurissum</i> - Alizarine
6964	Powdery residue inside a miniature dish in plain ware similar to Grasso 2004 Piat' II variante b (tav. 7, f) (ca. III and the II centuries B.C.).	VII 40 interpreted as part of the filling of pit 25	Violet-pink	<i>Purpurissum</i> - Alizarine
3270	Powdery residue inside a black glazed miniature bowl comparable to type Morel F2788c (first half of the II century B.C.).	VII 40 interpreted as part of the filling of pit 25	Violet-pink	<i>Purpurissum</i> - Alizarine
24	Powdery residue inside a vessel (now missing).	VII 40 interpreted as part of the filling of pit 25	Browinsh-yellow	Natrojarosite

This belonged to stratigraphic unit VII 40, interpreted as a dump of votive material in a pit (*Cottica & Curti 2008*, 31-35 and Fig. 9a-b); other three analysed samples come from the same stratum (cfr. nos. 3270, 1728 and 6964 in **Table 1**). The remaining specimens belong to three different layers, yielding abundant ceramics and other finds, including ritual objects such as terracotta statuettes. Some of the terracotta figurines still retained traces of yellowish paint therefore, for comparative purposes, samples of pigments were collected and analysed (cfr. n. 5665 in **Table 1** and **Fig. 1**). The figurines were manufactured in the Vesuvian area, as indicated by archaeometric analysis (*Daszkiewicz, Cottica & al. forthcoming*).

The presence of colourings in a votive context is rarely mentioned in scientific literature on Roman religious rituals, and there are no comparable finds from the numerous sanctuaries dedicated to Apollo known in the Mediterranean Greek and Roman world. The unicity of the assemblage reinforced the need to investigate the content of these votive vessels. As a start, the main aim of research was the definition by analytical approach of the precise nature of the retrieved colourings and their likely use/function: an account on results of research work is summarized below.

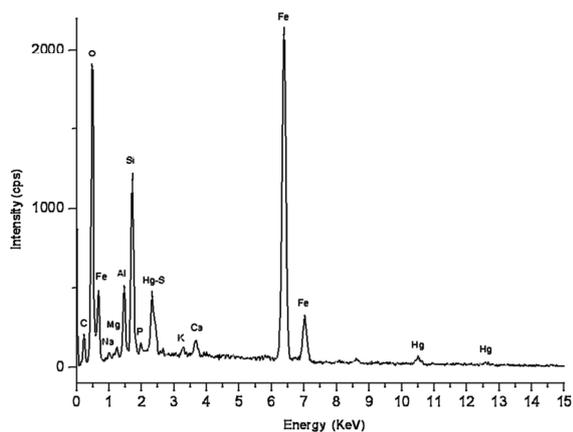


Fig. 2 EDS spectrum of sample 7238, Hematite – Cinnabar.

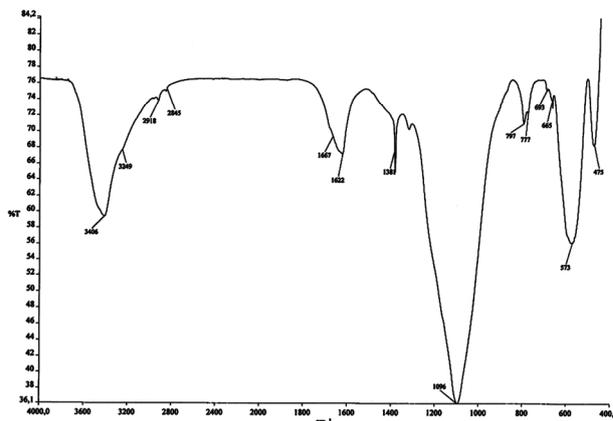


Fig. 3 FTIR spectrum of sample 7238, Hematite – Cinnabar

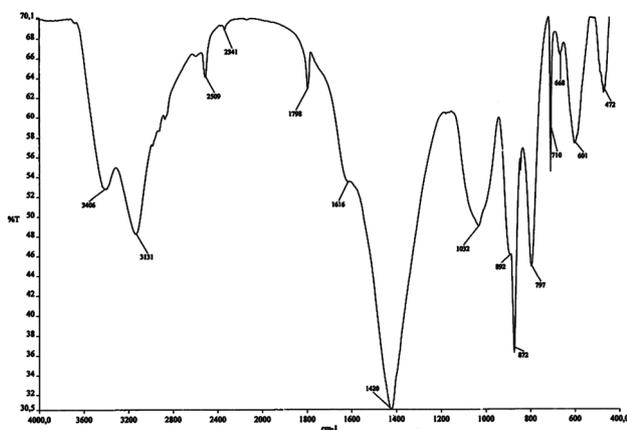


Fig. 4 FTIR spectrum of sample 3821, Goethite – Calcite – Pb compound.

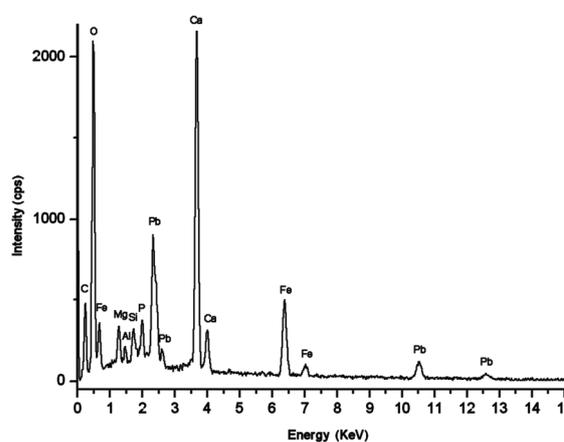


Fig. 5 EDS spectrum of sample 3821, Goethite – Calcite – Pb compound.

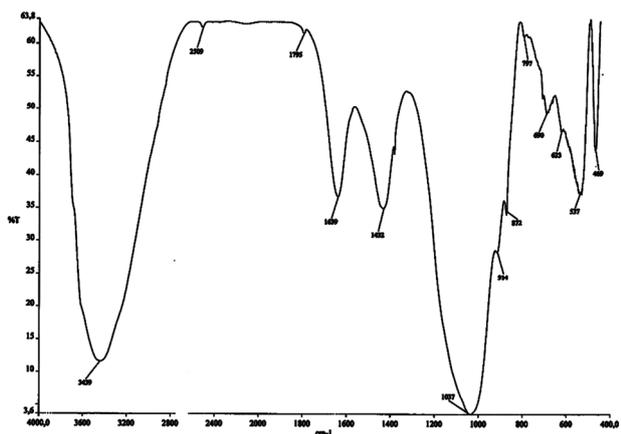


Fig. 6 FTIR spectrum of sample 3270, *purpurissum*.

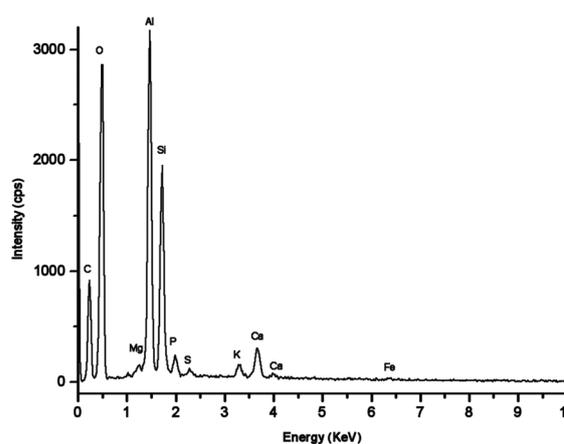


Fig. 7 EDS spectrum of sample 3270, *purpurissum*.

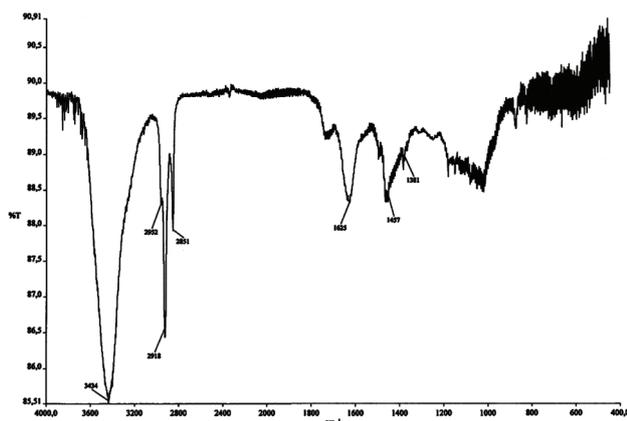
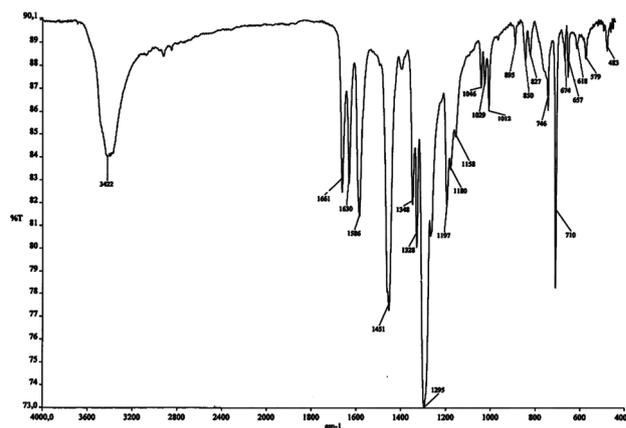


Fig. 8a: FTIR spectrum of sample 6964 (*purpurissum*) extracted in dichloromethane;



8b: FTIR spectrum of pure Alizarin Yellow extracted in dichloromethane.

EXPERIMENTAL

The following methodologies have been employed in order to define the nature of the retrieved powdery compounds.

Scanning Electronic Microscopy (SEM) with Energy Dispersion Probe (EDS).

SEM images were taken using a Jeol (Tokyo, Japan) JSM 5600 LV equipped with an Oxford Instruments 6587 EDS microanalysis detector. Images were taken under low vacuum conditions where samples did not show charging effects; in this way, it was possible to avoid the coating of the samples with a high conductance thin film (gold or graphite).

X-Ray Diffraction (XRD)

Powder X ray diffraction was used to identify the different crystalline phases present in the pigments. A Philips X'Pert vertical goniometer with Bragg-Brentano geometry, connected to a highly stabilised generator, was used for XRD analysis. Cu $K\alpha$ Ni filtered radiation, a graphite monochromator on the diffracted beam and a proportional counter with pulse height discriminator were used. Measurements in a $5\text{-}60^\circ$ range were taken with a step size of 0.05° and 2 seconds by point.

Infrared Spectroscopy (FT-IR)

Absorption spectra in the IR region were collected using a FT-IR Perkin Elmer Spectrum One spectrometer. Few milligrams of each sample were added to KBr (IR grade, Merck) and pellets of a diameter of about 13 millimetres were prepared. Thirty-two signal-averaged spectra were acquired on the samples.

RESULTS

The EDS spectrum of sample 7238 present inside a jar in coarse ware, reported in **Fig. 2**, reveals the main presence of iron together with small amounts of cinnabar, as indicated by the peaks of mercury and sulphur. Also traces of calcium, potassium, phosphorous, sodium and magnesium are present together with silicon and aluminium. In **Fig. 3** the FTIR spectrum of the same sample is reported. The bands of hydroxyl ions at 3406 and 1622 cm^{-1} , together with a large band of silicates and quartz at 1096 and $797 - 777\text{ cm}^{-1}$ appear together with a large band of haematite at 573 cm^{-1} confirming the results of EDS data.

In **Fig. 4** the FTIR spectrum of the yellow sample 3821 is reported. The bands of hydroxyl ions at 3406 , 3131 and 1616 cm^{-1} are evident, suggesting the presence of goethite; the carbonate bands appear at 1420 , 872 and 710 cm^{-1} . At 797 and 892 cm^{-1} come out the bands of iron hydrated oxides together with the bands at 601 and 668 cm^{-1} (*Edreira 2001*). In **Fig. 5** the EDS of sample 3821 is reported. As it can be seen the main peaks are those of calcium and of iron together with three peaks of lead. The presence of lead is quite unexpected in a sample containing goethite. It cannot be excluded that the small amount of lead belong to white lead, $2[\text{PbCO}_3 \text{ Pb}(\text{OH})_2]$ or to yellow lead oxide. The results of sample no. 4146 are identical to those discussed above.

The violet-pink samples 1728, 6964 and 3270 show FTIR spectra similar to that reported in **Fig. 6** (sample 6964), where the broad important bands of hydroxyl ions are present at 3439 cm^{-1} ; a weak band of carbonate is present at 1432 cm^{-1} together with the band at 872 cm^{-1} . Important bands of silicates at 1034 cm^{-1} are also present. In **Fig. 7** the EDS spectrum of the violet sample 6964 is reported; from this spectrum it can be deduced the presence of an alumino-silicate with traces of iron, potassium, calcium, phosphorous, sulphur and magnesium.

To verify if the violet colour was due to small amounts of organic substance adsorbed in a solid alumino-silicate compound, the organic substance was extracted from all samples using the procedures adopted for the extraction from coloured yarn in dichloromethane (Cibin 2007). The yellow dried extract shows the FTIR spectrum reported in **Fig. 8a** (samples 6964, 3270 and 1728). The bands due to the hydrogen-carbon stretching are now well pronounced at 2952, 2918 and 2881 cm^{-1} . Important bands are present also at 1625, 1457, 1437 and 1381 cm^{-1} . In **Fig. 8b** the FTIR spectrum of pure yellow alizarine extracted in dichloromethane is reported (evidence from Pompeii is reported in Barbet *et al.* 1999, 78-79). As it can be seen the two spectra are similar, indicating that the light violet colour can be attributed to a Garance Lacquer adsorbed on “*creta argentaria*” in presence also of “*creta calcarea*”, added to dilute the intensity of the colour (Augusti 1967, 76).

The size, colour and cubical shape of sample 3270 (cfr. **Fig. 9**) are identical to those described by Augusti and attributed to “*purpurissum*” obtained adding an organic colouring (extracted from the *Murex brandaris*) to “*creta calcarea*” and “*creta argentaria*” (Augusti 1967, 76 and Table VII). According to literary sources (Pliny, *Nat. Hist.* XXXV, 6) a special high quality *purpurissum* was made at Puteoli: in addition to the usual ingredients it contained a fraction of Garance Lacquer (Augusti 1967, 75-76). The bromine atoms of *purpurissum* were not revealed by EDS analysis, but this can be due to the decomposition of the original organic red compound. *Purpurissum* at Pompeii was used in wall painting, in ceramic decoration and in cosmetics (as cheek powder cfr. Augusti 1967, 76).



Fig. 9 Inventory n. 1728. Miniature dish still yielding part of its original content identified as *purpurissum*, manufactured and traded in cubical shape.

As far as Garance Lacquer is concerned, in the Roman world it was used in medicine, cosmetics (Mazzocchin *et al.* 2003) and was employed for dyeing textiles and painting statues (cfr. Stage *et al.* 2004; Santamaria & Morresi 2004).

The FTIR spectrum of sample 24 reported in **Fig. 10** shows intense bands due to OH stretching and strong bands of sulphate group at 1093 and 1009 cm^{-1} . The EDS spectrum of this sample shows the presence of iron and sulphur in similar amounts (**Fig. 11**), together with sodium and traces of aluminium and silica. These data suggest the presence of hydrated iron sulphate. The XRD spectrum of this material (**Fig. 12**) confirms the above suggestions, indicating that sample 24 in **Table I** is sodium natrojarosite, a sodium iron(III) sulphate hydroxide ($\text{Na Fe}_3(\text{SO}_4)_2(\text{OH})_6$).

Finally, the authors analysed samples of yellow-red pigments still visible on a fragmentary terracotta figurine (sample 5665), found in the same context as sample 3821 (*i.e.* miniature bowl with yellow pigment inside, cfr. **Table I**). **Fig. 13** reports the FTIR spectrum recorded on the pigments: as it can be observed small peaks at 3691 and 3619 cm^{-1} appear, attributed to the coarse ware, and broad peaks at 3428 and 1633 due to OH stretching. The small bands at 1426, 827 and 710 cm^{-1} indicate the presence of small amounts of calcite. The bands at 1034 and 911 cm^{-1} are related to the presence of silicates and quartz. The bands at 800 and 910 cm^{-1} are indicative of the presence of yellow ochre and iron hydrate oxide as goethite. The band at 539 cm^{-1} can be attributed to the red hematite pigment, present together with the yellow goethite. In **Fig. 14** the EDS spectrum of the same red-yellow powder (sample n. 5665) is reported. High silicon, aluminium, iron and calcium peaks are present together with traces of potassium, sodium, magnesium, titanium and phosphorous. These data confirm the IR data indicating the presence of red hematite and yellow ochre as the pigments used to paint the terracotta figurine in **Fig. 1**.

DISCUSSION

Data in **Table 1** indicate that the powders found inside the ceramic vessels of this study are selected natural colourings of good quality: hematite, goethite and natrojarosite can be classified as pigments frequently used for painting and wall painting, known at Pompeii as elsewhere in the Roman world. We may observe that some pigments well in use for wall painting such as yellow and red ochre, Egyptian blue and green earths are absent. Among the identified colourings it is of interest to note the presence of natrojarosite and *purpurissum*.

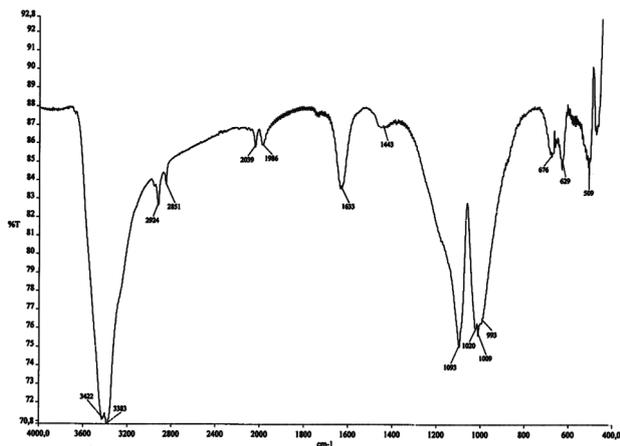


Fig. 10 FTIR spectrum of sample 24 (natrojarosite).

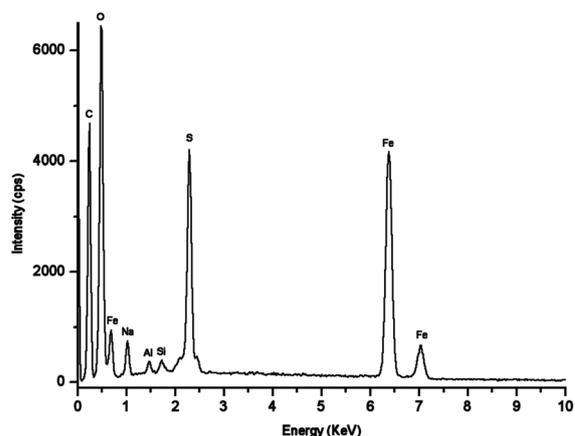


Fig. 11 EDS spectrum of sample 24 (natrojarosite).

The former is a brownish-yellow pigment that can be found in Greece at Laurion, or in some Italian regions such as in Tuscany, Sardinia and Emilia Romagna but not in the Vesuvian area. The use of this pigment is attested in wall paintings at Pompeii (Fagnano et al. 2003; Siddall 2006) as well as in Egypt. Interestingly, yellow potassium jarosite, that could be extracted from the Vesuvius Mount near Pompeii, is not among the analysed compounds. Moreover, analyses revealed the presence of an expensive and good quality colouring, identified as a special variety of *purpurissum* made,

according to literary sources, in Puteoli and characterized by the presence of a fraction of Garance Lacquer, added to strengthen the intensity of its colour (Augusti 1967, 75-76).

Bowls in coarse ware yielding pigments as part of their original content are well known at Pompeii: numerous similar containers were found buried under the ashes of the eruption of 79 A.D. in merchant outlets, fabricant shops and private houses (on these finds, their morphology, contexts and content cfr. Truffreau-Libre 1999; Barbet et al. 1999).

Sample ident.:

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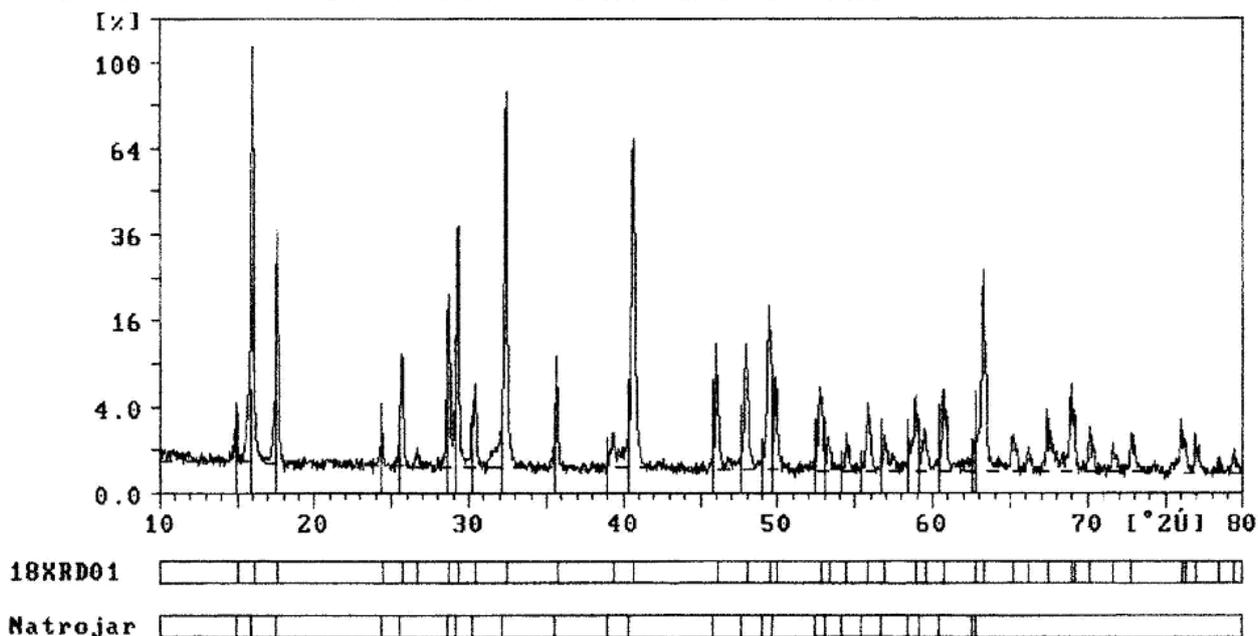


Fig. 12 XRD spectrum of sample 24 (natrojarosite).

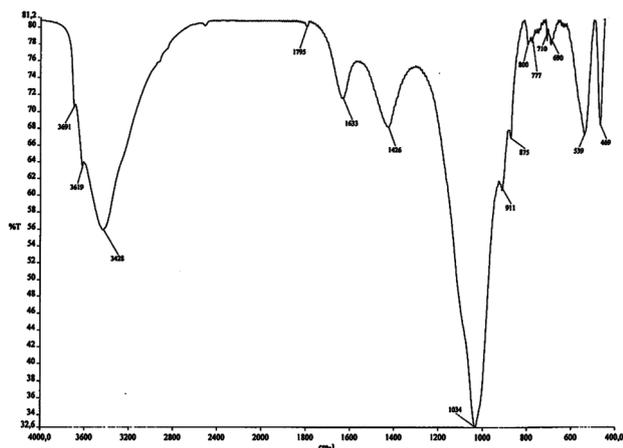


Fig. 13 FTIR spectrum of sample 5665 (pigment on painted terracotta figurine: hematite and yellow ochre).

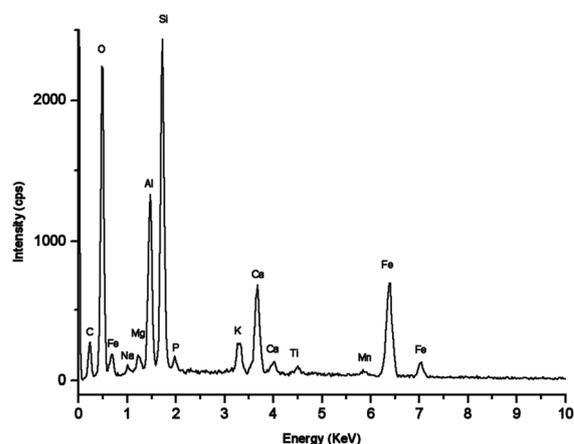


Fig. 14 EDS spectrum of sample 5665 (pigment on painted terracotta figurine: hematite and yellow ochre).

Interestingly, in the assemblage object of this paper five vessels are miniature pots which do not have morphological *comparanda* among the published pigment ceramic containers. On the other hand, these are common finds in religious contexts, where they usually contained an offer dedicated to the god. These vessels were found in the filling of pits containing abundant re-deposited votive material, cleaned and sealed when the Sanctuary of Apollo was restructured in the 2nd century B.C.

It seems therefore plausible to suggest that at least some, if not all, of the ceramic vessels containing colour powders originally were votive offers deposited as part of a religious ritual. However, the absence of available comparative data does not allow to fully understand the association between content, container and context, and consequently the symbolic meaning of the finds presented here. In the present state of knowledge only working hypotheses can be put forward. An interesting possibility is that the colourings were connected with the presence of painters: perhaps some of them may have been involved in the manufacture of the numerous votive statuettes retrieved in the temple area (Cottica & Curti 2008, 35 and Fig. 6d). These artifacts were locally manufactured for the sanctuary's needs and demand (Daszkiewicz, Cottica & Al. forthcoming; Cottica & Toniolo forthcoming) and some moulds have been found together with the finished products (cfr. Cottica & Curti 2008, Fig. 6 d). Analyses undertaken on samples of the original paint found on some terracotta statuettes (Biancofiore 2007 and Figs. 13-14 in this paper) revealed that at least two of the identified powdery pigments, hematite and

goethite, could have been used for painting the votive figurines. However, so far no traces of violet-pink pigment have been found on these objects, although we know that at Pompeii *purpurissum* could be used for painting ceramics (Augusti 1967, 76).

CONCLUSIONS

The combined archaeometric and archaeological data here presented testify for the existence of ritual offers consisting of coloured powders in the sanctuary of Apollo at Pompeii. Before the beginning of research, the powders had been provisionally interpreted and termed as pigments similar to those frequently used in Roman wall paintings at Pompeii. However, in addition to some widely used pigments (hematite and goethite), data revealed the puzzling presence of less common colourings such as natrjarosite and a variety of *purpurissum*. According to Pliny, the latter was made at Puteoli (not far from Pompeii): this colouring in Antiquity was used in cosmetics and for ceramic decoration. In the available literature the association colouring, context and container has generally led to interpret the evidence as related to a painter kit, concluding that the pigments were used for wall painting. Therefore, the presence of colourings as votive offers is quite exceptional in the archaeological record and it proves that results of interdisciplinary analysis may bring forward new and unexpected evidence on ancient society, its rituals and habits.

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REFERENCES

- ARTHUR P. (1986): Problems in the urbanization of Pompeii: excavations 1980-1981. *The Antiquaries Journal* (LXVI, part 1): 29-44.
- AUGUSTI S., (1967): I colori pompeiani, De Luca Editore, Rome.
- BARBET A, TUFFREAU-LIBRE M. & COUPRY C. (1999): Un ensemble de pots à peinture à Pompéi. *Rivista di Studi Pompeiani* (X): 71-81.
- BIANCOFIOR M. (2007): Analisi di pigmenti e reperti archeologici dipinti provenienti dagli scavi del foro di Pompei. *Unpublished thesis* 2006/2007, University of Venice Ca' Foscari, Faculty of Science.
- CIBIN R. (2007): Studio delle interazioni metallo-legante in presenza di leganti ausiliari. Effetto della matrice proteica sul degrado fotochimico dei coloranti naturali. *Unpublished PhD thesis in Chemical Sciences*, 2006-2007, University of Rome La Sapienza.
- CHIARAMONTE TRERÈ (1984): Ceramica grezza e depurata, in: M. BONGHI JOVINO (ed.) *Ricerche a Pompei. L'insula 5 della Regio VI dalle origini al 79 d.C.*, Roma, 140-192.
- COTTICA D. (2007): Il progetto di recupero e studio dei reperti relativi agli scavi I.E. (Impianto Elettrico) 1980-1981. *Rivista di Studi Pompeiani* (XVII, 2006): 65.
- COTTICA D. & CURTI E. (2008): Il progetto di recupero ed edizione degli scavi I.E. (Impianto elettrico) 1980-1981 nel Foro di Pompei, in: P. G. GUZZO & M. P. GUIDOBALDI (eds.): Nuove Ricerche Archeologiche nell'area Vesuviana (scavi 2003-2006). *L'Erma* di Bretschneider, Roma, 25-36.
- COTTICA D. & TONIOLO L. (forthcoming.): Produzioni pompeiane e vesuviane dai saggi 1980-81 presso il foro di Pompei: le forme. *RCRF Acta* (41).
- DE CARO S. (1986): Saggi nell'area del tempio di Apollo a Pompei: scavi stratigrafici di A. Maiuri nel 1931-32 e 1942-43. *Annali dell'Istituto Universitario Orientale*, Sezione di archeologia e storia antica, Quaderno n. 3.
- DASZKIEWICZ M., COTTICA D., BOBRYK E. & SCHNEIDER G. (forthcoming). Pompeii as a production centre: an archaeometric approach. *RCRF Acta* (41).
- EDREIRA M.C., FELIU M.J. & FERNANDEZ-LORENZO C. & MARTÍN J. (2001): Roman wall paintings characterization from Cripta del Museo and Alcazaba in Mérida (Spain): chromatic, energy dispersive X-ray fluorescence spectroscopic, X-ray diffraction and Fourier transform infrared spectroscopic analysis. *Analytica Chimica Acta* (434): 331-345.
- FOGNANO C., TINTI A. & BARALDI P. (2003) La tavolozza dei colori negli affreschi di Pompeii, in ricordo di Alessandro Bertoluzza. *Clueb*, Bologna, 125-137.
- GRASSO L. (2004): Ceramica miniaturistica da Pompei. *Quaderni di Ostraka* 9, Loffredo, Napoli.
- GRASSO L., (2005): La ceramica miniaturistica votiva di Pompei. In: A. COMELLA & S. MELE (eds.): Depositi votivi e culti dell'Italia antica dall'età arcaica a quella tardo-repubblicana. *Atti del Convegno di Studi Perugia*, 1-4 giugno 2000. Edipuglia, Bari, 545-554.
- LIVERANI P. (2004) (ed.), I colori del bianco: policromia nella scultura antica, Luca editore, Rome.
- MAZZOCCHIN G.A., AGNOLI F. & MAZZOCCHIN S. (2003): Investigation of Roman age "bulk pigment" found in Vicenza. *Analytica Chimica Acta* (475): 181-190.
- MAZZOCCHIN G.A., ZACCARIA RUGGIU A. & COTTICA D. (2008): Ricerche archeometriche a Venezia applicate all'Archeologia Classica, in S. GELICHI (ed.) *Missioni Archeologiche e progetti di ricerca e scavo dell'Università Ca' Foscari-Venezia*, Venice, 133-144.
- SANTAMARIA U. & MORRESI F. (2004), Le indagini scientifiche per lo studio della cromia dell'Augusto di Prima Porta, in LIVERANI P. (ed.), I colori del bianco: policromia nella scultura antica, Luca editore, Rome, 243-248.
- SIDDALL R. (2006): Pigments and painting techniques of Roman artists. *Infocus - The Proceedings of the Royal Microscopical Society* (2): 19-31.
- STEGE H., FIEDLER I. & BAUMER U. (2004), L'indagine dei pigmenti e dei leganti nel rivestimento a colori del ritratto di Caligola, in LIVERANI P. (ed.), I colori del bianco: policromia nella scultura antica, Luca editore, Rome, 261-268.
- TUFFREAU-LIBRE M. (1999): Les pots à couleur de Pompéi: premier résultats. *Rivista di Studi Pompeiani* (X): 63-70.