

## Accepted Manuscript

Title: Multi-technique study of a ceramic archaeological artifact and its content

Authors: S. Legnaioli, F. Anabitarte Garcia, A. Andreotti, E. Bramanti, D. Diaz Pace, S. Formola, G. Lorenzetti, M. Martini, L. Pardini, E. Ribechini, E. Sibilìa, R. Spiniello, V. Palleschi



PII: S1386-1425(12)00361-7  
DOI: doi:10.1016/j.saa.2012.04.009  
Reference: SAA 9289

To appear in: *Spectrochimica Acta Part A*

Received date: 30-11-2011  
Revised date: 11-3-2012  
Accepted date: 3-4-2012

Please cite this article as: S. Legnaioli, F.A. Garcia, A. Andreotti, E. Bramanti, D.D. Pace, S. Formola, G. Lorenzetti, M. Martini, L. Pardini, E. Ribechini, E. Sibilìa, R. Spiniello, V. Palleschi, Multi-technique study of a ceramic archaeological artifact and its content, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2010), doi:10.1016/j.saa.2012.04.009

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



- We studied an ancient ceramic vase using several chemical and physical techniques
- FTIR and LIBS allowed to determine the vase material composition
- Thermoluminescence and typological and stylistic analysis, allowed dating the vase
- FTIR and Py-GC/MS allowed to formulate hypotheses on the vase original content

Accepted Manuscript

# MULTI-TECHNIQUE STUDY OF A CERAMIC ARCHAEOLOGICAL ARTIFACT AND ITS CONTENT

S.Legnaioli<sup>a</sup>, F.Anabitarte Garcia<sup>b</sup>, A.Andreotti<sup>c</sup>, E.Bramanti<sup>a</sup>, D.Diaz Pace<sup>d</sup>,  
S.Formola<sup>e</sup>, G.Lorenzetti<sup>a</sup>, M.Martini<sup>f</sup>, L.Pardini<sup>a</sup>, E.Ribechini<sup>c</sup>, E.Sibilia<sup>f</sup>, R.Spiniello<sup>a</sup>,  
V.Palleschi<sup>a,g</sup>

<sup>a</sup>*ICCOM-CNR, Research Area of Pisa, Via G. Moruzzi 1, 56124 Pisa – Italy*

<sup>b</sup>*Photonics Engineering Group, University of Cantabria, Santander (Spain)*

<sup>c</sup>*University of Pisa, Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa – Italy*

<sup>d</sup>*Institute of Physics 'Arroyo Seco', Faculty of Science, Tandil (Argentina)*

<sup>e</sup>*University of Naples "L'Orientale", Department of Classics and Ancient Mediterranean Studies, Piazza S. Domenico Maggiore, 12 - Palazzo Corigliano, Napoli - Italy*

<sup>f</sup>*INFN and University of Milano-Bicocca, Materials Science Department, Via Cozzi 53, 20125 Milano – Italy*

<sup>g</sup>*Department of Archaeological Sciences, University of Pisa, Via Galvani 1, 56126 Pisa - Italy*

\* Corresponding author: vincenzo.palleschi@cnr.it , Tel: +39 050 3152224

## Abstract

In this paper we report the results of a study performed with different physical and chemical methods on a ceramic vase originally attributed to the I century CE. The joint use of infrared spectroscopic analysis and laser techniques, as well as pyrolysis-gas chromatography coupled with mass spectrometry and thermoluminescence, allowed us to characterize the vase material and its content. The chemical data were combined with morphological and stylistic examinations of the object and helped in defining its actual geographical and chronological pertinence.

**Keywords:** *Archaeometry, Ceramics, FT-IR, LIBS, Thermoluminescence, Pyrolysis GC-MS.*

## 1. Introduction

At the beginning of year 2007, an Italian antique collector bought in a on-line auction a small vase from a north-American seller. Attached to the vase there was an handwritten label, which described, in Italian, the history of the object. According to the label, the vase was discovered in Herculaneum and it was given to a relative of the owner in 1929; brought to the United States as a family heritage, it was forgotten and then re-discovered by the seller only in recent times.

The unusual circumstances associated to the purchase convinced the new owner to perform an authentication study on the object, which was committed to the authors of this paper.

We performed several non-destructive and micro-destructive analyses on the vase in order to determine the materials used for its manufacture, to investigate the possible use of modern pigments and to identify the amorphous organic residue adherent to the internal surface of the vase.

In particular, Laser-Induced Breakdown Spectroscopy (LIBS), Fourier Transform Infrared spectroscopy (FTIR) and Pyrolysis-Gas Chromatography Mass Spectrometry (PY-GC-MS) were used for the characterization of the elemental and molecular composition of the vase material and its organic content. This multi-technique compositional analysis was combined with a morphological and stylistic examination of the vase, which defined its possible chronological framework. A thermoluminescence study, performed at University of Milano-Bicocca, allowed us to give a definite answer concerning the authenticity of the vase and its dating.

## 2. Experimental

### 2.1. FTIR spectroscopy.

Fourier Transform Infrared (FTIR) [1] spectra were recorded between 4000 and 400  $\text{cm}^{-1}$  using a Perkin Elmer Spectrum 100 spectrometer. Disks were prepared by first mixing 1 mg of dried sample with 500 mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the resulting mixture at 5  $\text{tons/cm}^2$  for 5 min and at 10  $\text{tons/cm}^2$  for 5 min. The rinsing solution of the vase was analyzed by casting the solution on  $\text{BaF}_2$  windows. Thus, the FTIR spectra were recorded on the dried films.

## 2.2. LIBS spectroscopy.

Laser-Induced Breakdown Spectroscopy (LIBS) is used to determine the elemental composition of various solids, liquids and gases [2]. The range of LIBS applications utilising in Cultural Heritage and Archaeology is rapidly growing [3-5, 7]. The LIBS analysis was performed using the Modì LIBS instrument, developed at ALS Lab. with the collaboration of Marwan Technology s.r.l. (Pisa). More information on the LIBS instrument and the experimental parameters can be found in ref. [6]. Because of its minimal destructivity (the micro-crater produced by the laser at the object surface is practically invisible at the naked eye), LIBS is a technique particularly suited for the study of archaeological artifacts, in particular bronzes [3,5] and ceramics [7]. A typical analysis on archaeological samples can take between one and five minutes, according to the complexity of the LIBS spectrum produced. LIBS analysis was performed in various parts of the vase, without any preparation.

## 2.3. Thermoluminescence analysis.

The privileged technique for settling authenticity issues on ceramic artifacts is definitely the thermoluminescence analysis (TL) [8]. Its principles are based on the fact that some of the components of clays (quartz and feldspars) are thermoluminescent, i.e., they emit light under the effect of high temperature (hundreds of degrees Celsius). These materials in fact are able to accumulate in stable traps the electrons produced by the environmental natural radioactivity. The trapped energy is released in form of light when the material is heated at high temperature. At the moment of firing of the clay, the thermoluminescence accumulated during the geological existence is 'zeroed'. Since that time, it starts to rebuild steadily (depending on the environment and on the characteristics of the material itself). Therefore, the measurement of the residual thermoluminescence is also a measurement of the time elapsed since the last high temperature event in the history of the object. The determination of the age of the object can be rather precise ( $\pm 5\%$ ) provided both the internal and environmental radiation levels are known. The thermoluminescence analysis was performed on a few mg of ceramic materials taken from three different points on the base of the vase.

## 2.4. Py-GC/MS analysis.

The pyrolysis GC-MS (Py-GC/MS) [9] data were obtained by using the CDS 5000 Pyroprobe (CDS Analytical, Inc., Oxford, USA), coupled on-line with the injection port of the gas chromatograph 6890N GC system gas chromatograph, (Agilent Technologies), with a 5973 mass selective detector (Agilent Technologies) single quadrupole mass spectrometer equipped with Split-Splitless injector.

The Pyroprobe conditions were:

Pyroprobe temperature: 50 °C, 20 °C/ms up to 500°C and isothermal for 20 sec.

Interface temperature: 180 °C. Transfer Line: 300 °C. Valve Oven: 290 °C.

The chromatographic oven was programmed as follows:

30 °C, isothermal for 10 min, 10 °C/min up to 280 °C, isothermal for 10 min, 20 °C/min up to 300 °C and isothermal for 20 min. The carrier gas was used in constant flow mode at 0.8 ml/min.

A few mg of the content of the vase, admixed with 4 µl of a solution of hexamethyldisilazane, were inserted into a quartz tube and then pyrolysed.

## 3. Results and Discussion

### 3.1. Sample description

Figure 1 shows the vase studied; it was manufactured in black ceramics. It is 192 mm high with an annular foot, with rounded external profile (diameter 76 mm, height 8.5 mm), ovoid body (diameter 119 mm) and a cylindrical neck 64 mm high with a diameter of 56 mm. The lip is trilobate, the frontal lobe is 86 x 33 mm, while the two lateral lobes are 82x41 mm both, pointing down towards the outside. The handle is rather thick (15 mm), 20 mm wide and is attached to the main body of the vase 96 mm from the foot and in correspondence of the upper extremity of the neck.

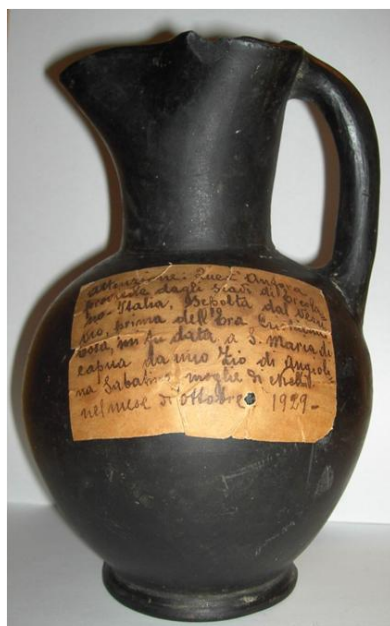


Fig.1 – The vase under study

Furthermore, a handwritten piece of paper is glued to the body, carrying some information about the alleged provenience of the vase as a gift from the excavations of Herculaneum, destroyed by the Mount Vesuvius eruption in 79 CE.

### 3.2. Material Analysis

The study on the vase was performed using a series of physical and chemical techniques [1, 10], with the purpose of determining the origin of the material used and confirming or disproving its identification as a I century CE ceramic object.

#### 3.2.1 FTIR and LIBS

The most striking characteristic of the object under study is its solid black color, typical of the *bucchero* ceramics [11, 12]. It is commonly accepted that in the antiquity this color was obtained through firing of the clay in reducing atmosphere. Therefore, if the elemental analysis of the clay would have revealed the presence of black pigments (e.g. manganese oxide), it would have raised serious concerns on the authenticity of the vase [13].

As a first method, we performed the FT-IR analysis on the clay micro-sampled from three points on the foot (1 mg in KBr pellet). It was found the presence of silicates,



quartz, iron oxides (Fe-O stretching bands at  $463\text{ cm}^{-1}$ ) and aluminum oxides as expected in natural clays (Figure 2) [14, 15].

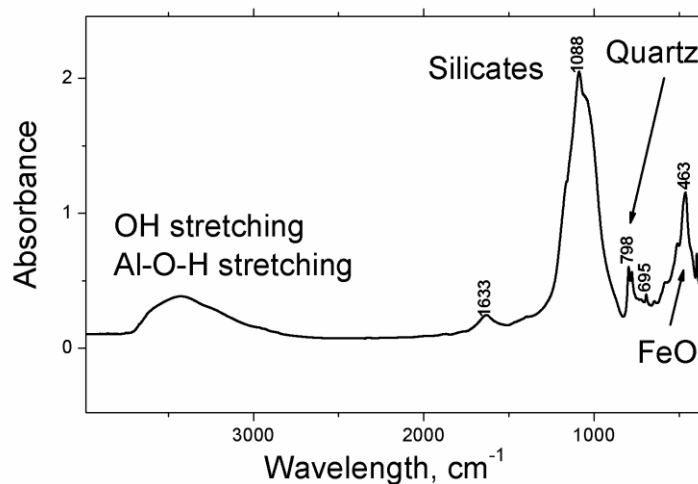


Fig. 2 – FTIR spectrum of the black ceramics

Laser-Induced Breakdown Spectroscopy technique [2] was used for the determination of the elemental composition of the vase material. Figure 3 shows the LIBS spectrum of the vase clay.

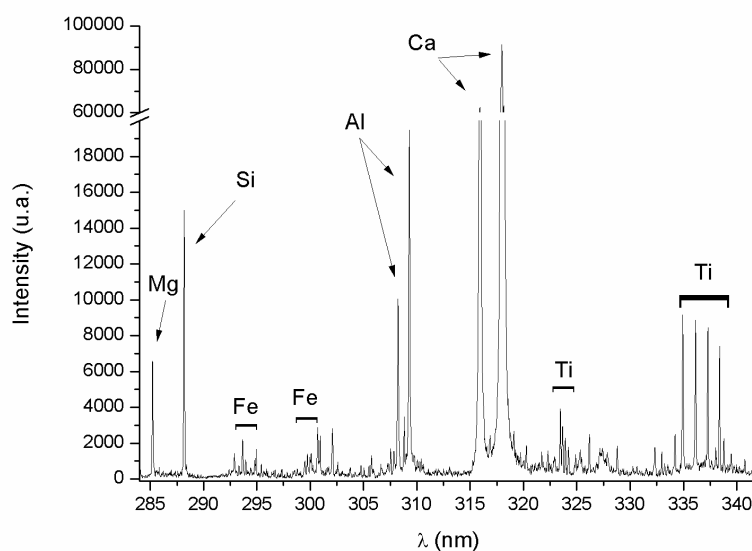


Figure 3 – LIBS spectrum of the vase clay

The qualitative analysis of the spectrum, performed through the identification of the main emission peaks, excludes that natural or artificial black pigments were added to the clay. Instead, all the expected elements of natural clay (iron, magnesium, silicon,

aluminum, calcium, titanium) are clearly identified. Therefore, the LIBS analysis does not disprove the authenticity of the vase.

In summary, the black color of the vase under study can be associated with the presence of Fe-O stretching bands at  $463\text{ cm}^{-1}$  in the FTIR spectrum, confirmed by the evidence of intense Fe lines in LIBS spectrum. Therefore, we can deduce that material and the realization technique of the artifact is coherent with that of an original *bucchero*.

### 3.2.2 Age - TL analysis

The identification of the vase as a *bucchero* would rise to serious concerns about its authenticity or, at least, its dating. Indeed, this kind of black terracotta is well documented in the Campania region, near Herculaneum, from the beginning of VI century BCE to the end of V century CE. However, in 79 CE, at the time of the Mount Vesuvius eruption which destroyed Pompei and Herculaneum, this kind of vase was not used anymore [16, 17].

In order to obtain a definite answer on the authenticity of the vase, a thermoluminescence study was performed at University of Milano-Bicocca.

When, as in our case, there is no precise information about the site where the object was found and the internal radioactivity cannot be measured (to preserve the integrity of the object), the technique cannot provide a precise estimation of the age of the object, but just a check for its authenticity.

The thermoluminescence analysis was carried out by means of the *fine-grain* technique [18]. It was determined that the natural TL signal is quite high, with a broad peak around  $300^{\circ}\text{C}$ . A linear growth as a function of the calibration dose was observed, and a total absorbed dose of  $16,8 \pm 0,7$  Gy was measured. Assuming the radioactivity parameters typical for the *bucchero* production area and taking into account their possible natural variations (3-6 ppm  $^{238}\text{U}$ ; 10-25 ppm  $^{232}\text{Th}$ , 1.0-2.0 %  $\text{K}_2\text{O}$ ), the fabrication of the vase can be placed between VII century BCE and I century CE. The vase is thus authentic and, although the dating obtained by thermoluminescence is marginally compatible with the I century CE, there are strong indications that it could be much older, as suggested by the typological and stylistic analysis.

The shape and the fabrication technique define the vase under study as an *oinochoe* (vase for serving wine) in heavy *bucchero*. *Oinochoai* were present in the Campania region since the first quarter of VI century BCE. In particular, the *oinochoe* under study corresponds to type 13b1 in the Pontecagnano classification [17] and is very similar to

other vases conserved in the Museo Campano in Capua and to other material from Campania necropolis. Thus, on the basis of these associations, the present *oinochoe* can be likely attributed to the phase IVc of Capua, in the first quarter of VI century BCE, probably realized by local handicrafts.

### 3.3. Analysis of vase content

Once confirmed the authenticity of the vase, we performed several measurements on the contents of the *oinochoe* under study. Several internal parts of the vase were sampled and analyzed by FTIR [1] and Pyrolysis coupled with GC-MS (Py-GC/MS) [9].

#### 3.3.1 FTIR and Py-GC/MS

Figure 4 shows the FTIR spectrum of the vase rinsing solution (see Experimental).

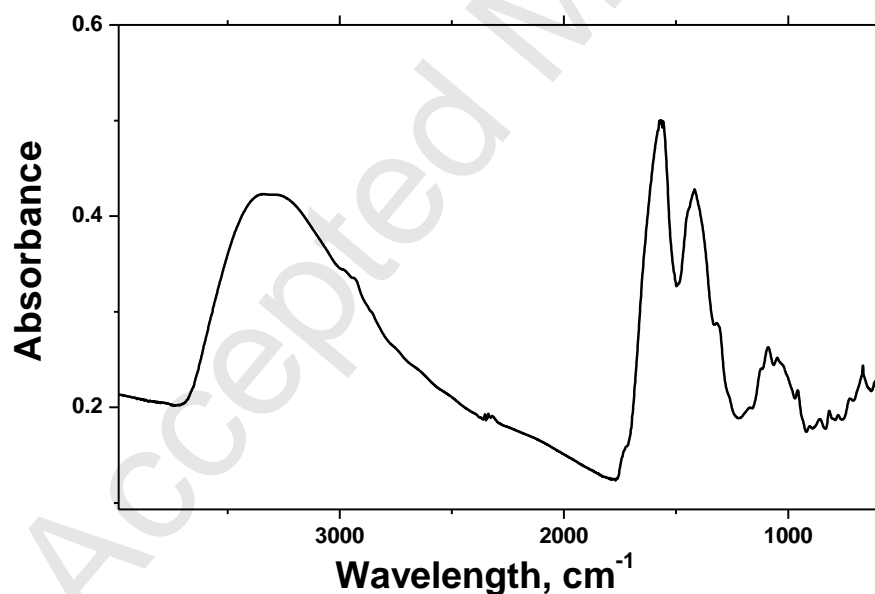


Fig. 4 - FTIR spectrum of the vase rinsing solution

Given the nature of the vase, it appeared useful to compare this FTIR spectrum with FTIR spectra of common fermented liquid like wine and beer (Figure 5a and b, respectively).

Moreover, it is known that in the Mediterranean and Central Europe area a honey fermented beverage called hydromel (mead or honey wine) was also diffused [19]. In the absence of an existing reference standard for hydromel, we analyzed a hydromel solution fermented in the laboratory according to a modern recipe<sup>1</sup>. The FTIR spectrum of hydromel is reported in Figure 5c.

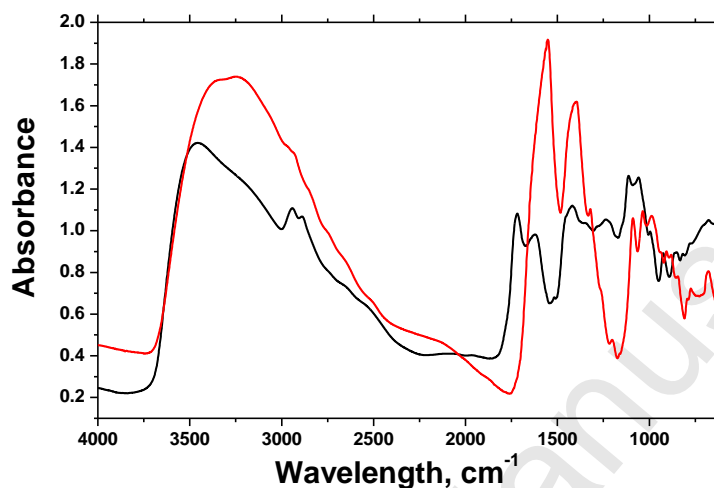


Fig. 5a – FTIR spectrum of wine (in red, the FTIR spectrum of the vase rinsing solution)

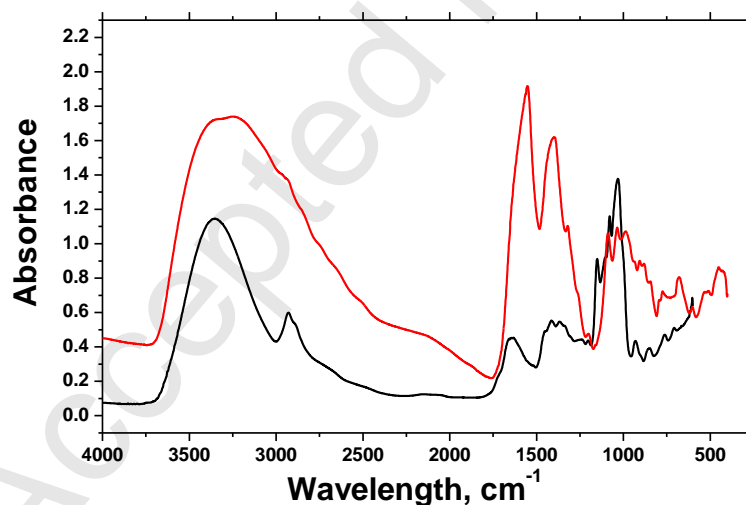


Fig. 5b – FTIR spectrum of beer (in red, the FTIR spectrum of the vase rinsing solution)

<sup>1</sup> The hydromel was obtained in the laboratory by fermenting 58 g of honey, 87 ml of boiled water and 725 mg of baker yeast. The FTIR spectrum was acquired after 2 weeks of fermentation, using the same procedure used for the rinsing solution of the vase.

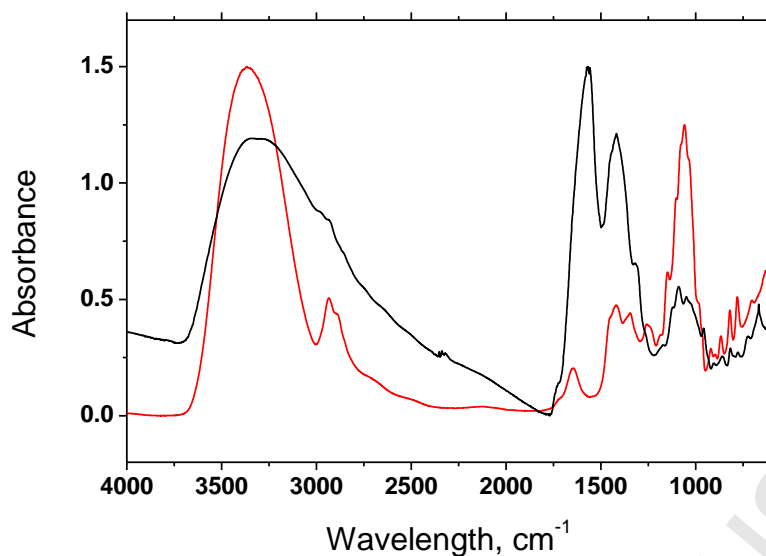


Fig. 5c – FTIR spectrum of hydromel (in red, the FTIR spectrum of the vase rinsing solution)

The comparison of the FTIR spectra with the vase rinsing solution shows that the content of the vase is an alcoholic substance obtained from fermentation. However, the technique does not allow a clear discrimination between wine, beer or hydromel, since the characteristic peaks of the FTIR spectrum are present in all the samples and their relative intensity is not useful for discrimination, because of the probable degradation of the vase content.

On the other hand, the analysis of particles micro-sampled inside the vase by pyrolysis coupled to GC-MS (Figure 6) evidenced the pyrolysis products characteristic of polysaccharide materials [20,21], derived from fruit or vegetables fermentation.

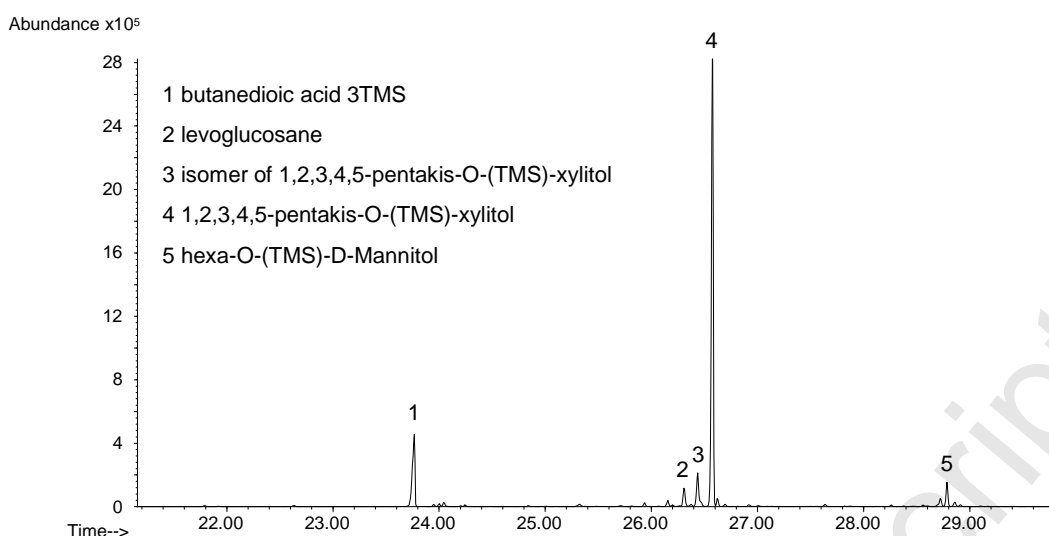


Fig. 6 – Pyrogram of the vase rinsing solution

It is known from the Homeric poems that around the VI century BCE the word ‘wine’ defined a broad range of fermented products from grape to fruits [22]. The pyrolysis pattern observed is compatible with the presence of fruit or vegetable matter in the alcoholic beverage contained in the vase. It should be noted that, although the presence of alcoholic residuals in archaeological vases has been scientifically confirmed in many circumstances [23-27] (the earliest chemically confirmed archaeological beer dates ca. 3400-3000 BCE, while the earliest wine remains date back to ca. 5400 BCE (Early Neolithic Period)), there is no way of knowing, at least with the techniques used in this paper, at what time in its long life the beverage was actually contained in the vase [27].

#### 4. Conclusion

The multi-technique analysis performed in this work, together with the stylistic and typological study of the vase, allowed us to establish its authentication and to make hypothesis on its content. The joint use of physical and chemical techniques demonstrates that the vase studied, originally attributed to the I century CE on the basis only of its label, is authentic but much older (VI century BCE). The reference to the Herculaneum excavations was probably given at the time of the ‘gift’ (October 1929, according to the paper label glued on the vase body) to increase its value, considering that just a couple of years before the Italian king Vittorio Emanuele III inaugurated the new excavations in Herculaneum, thus bringing the site to the popular attention.

## References

- [1] E. Ciliberto, G. Spoto, *Modern analytical methods in art and Archaeology Chemical Analysis*, Vol 155, Wiley Inter Science, 2000.
- [2] A.W. Miziolek, V. Palleschi, I. Schechter, *Laser Induced Breakdown Spectroscopy*, Cambridge University Press, Cambridge (UK) 2006.
- [3] M. Ferretti, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, E. Console, P. Palaia, *Spectrochim. Acta B*, 62 (2007) 1512-1518.
- [4] S. Zanini, C. Riccardi, M. Orlandi, V. Fornaia, M.P. Colombini, D.I. Donato, S. Legnaioli, V. Palleschi, *Wood Sci. Technol.* (2008) DOI 10.1007/s00226-007-0160-7.
- [5] M. Corsi, G. Cristoforetti, M. Giuffrida, M. Hidalgo, S. Legnaioli, L. Masotti, V. Palleschi, A. Salvetti, E. Tognoni, C. Vallebona, A. Zanini, *Microchim. Acta* 152 (2005) 105-111.
- [6] A. Bertolini, G. Carelli, F. Francesconi, M. Francesconi, L. Marchesini, P. Marsili, F. Sorrentino, G. Cristoforetti, S. Legnaioli, V. Palleschi, L. Pardini, A. Salvetti, *Anal. Bioanal. Chem.* 385 (2006) 240-247.
- [7] A. Ramil, A. J. López, M. P. Mateo, A. Yáñez, in: Javier Ruiz, Roxana Radvan, Mohamed Oujja, Marta Castillejo and Pablo Moreno (Eds.), *Lasers in the Conservation of Artworks*, Proceedings of the International Conference Lacona VII, Madrid, Spain, 2007, pp. 121-125.
- [8] L. Campanella, G. Favero, P. Flamini, M. Tomassetti, *J. Therm. Anal. Calorim.* 73 (2003) 127-142.
- [9] T. Wampler, *Applied Pyrolysis Handbook*, CRC Press (UK), 1995.
- [10] D. Peacock, D. Williams, *J. Archaeolog. Sci.* 24 (1997) 1089-1091.
- [11] M. Bonamici, *I bucheri con raffigurazioni graffite*, Espera s.r.l. Firenze, 2004 (in Italian).
- [12] G. Pianu, *Gravisca, scavi nel santuario Greco: Il bucheri*, Bari, 2000 (in Italian).
- [13] L. Angeli, C. Arias, G. Cristoforetti, C. Fabbri, S. Legnaioli, V. Palleschi, G. Radi, A. Salvetti, E. Tognoni, *Laser Chem.* (2006) Article ID 61607, 7 pages doi:10.1155/2006/61607.
- [14] J. Madejova, *Vib. Spectrosc.* 31 (2003) 1-10.
- [15] P.S. Nayak, B.K. Singh, *Bull. Mater. Sci.* 30 (2007) 235-238.
- [16] W. Johannowsky, *Materiali di età arcaica dalla Campania*, Napoli, 1983 (in Italian).
- [17] M. Minoja in: N. Allegro (Ed.), *Il Museo Archeologico dell'Antica Capua*, Napoli, 1995, pp. 27-29 (in Italian).
- [18] M.J. Aitken, *Thermoluminescence dating*, Academic Press, Oxford (UK), 1985.
- [19] I. Hornsey, *A History of Beer and Brewing*, Royal Society of Chemistry, ISBN 0-85404-630-5, 2003.
- [20] C. Riedo, D. Scalarone, O. Chiantore, *Anal. Bioanal. Chem.* 396 (2010) 1559-1569.
- [21] A. Andreotti, I. Bonaduce, M. P. Colombini, F. Modugno, E. Ribechini, *Int. J. Mass Spectrom.* 284 (2009) 123-130.
- [22] F. Fedele in: O. Longo, P. Scarpi (Eds.), *Storie del vino. Homo Edens. Ragioni, miti e pratiche dell'alimentazione nella civiltà del Mediterraneo II*, Diapress, Milano, 1991, pp. 35-68 (in Italian).
- [23] P.E. McGovern, D.L. Glusker, L.J. Exner, M.M. Voigt, *Nature* 381 (1996) 480-481
- [24] R.H. Michel, P.E. McGovern, V.R. Badler, *Anal. Chem.* 65 (1993) 408A-413A

[25] P.E. McGovern, J.Z. Zhang, J.G. Tang, Z.Q. Zhang, G.R. Hall, R.A. Moreau, A. Nuñez, E. D. Butrym, M.P. Richards, C.S. Wang, G.H. Cheng, Z.J. Zhao, C.S. Wang, *Proceedings of the National Academy of Sciences* 101 (2004) 17593–17598.

[26] M. D. Petit-Domínguez, R. García-Giménez, M. I. Rucandio, *Microchim. Acta* 141 (2003) 63-68.

[27] A. C. Prieto, M. Avella, M. A. González, J. Jiménez, F. Romero, R. de Pablo, C. Górriz, C. Sanz, *Spectrosc. Lett.* 45 (2012) 141-145.

Accepted Manuscript