

## COULOMETRY FOR THE DETECTION OF WATER CONTENT IN ARCHAEOLOGICAL FINDINGS

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**ABSTRACT.** In the present work, we performed coulometric measurements to detect the water content in archaeological pottery in order to get information on the manufacture technique. The samples under study were the so-called “Ionian Cups” coming from various archaeological sites in eastern Sicily (South-Italy). In particular, we tentatively achieved the estimation of firing temperatures of the archaeological samples by comparing the coulometric results with those obtained in the case of raw materials fired under controlled conditions. The results were in good agreement with those previously obtained on the same samples by Small Angle Neutron Scattering (SANS). It is worth underlying that for the first time, the detection of water content as revealed by this analytical technique was related to archaeometric issues.

### 1. Introduction

Archaeometric research represents a modern and innovative field of interchanges between scientific and humanistic areas thanks to a multidisciplinary methodological approach requiring several qualified expertise ranging from physics to chemistry, from biology to geology (Lo Russo and Schippa 1992). Hence, the scientific analyses permit to obtain a characterization of the used materials as well as provide useful information for understanding of our past, including the manufacture techniques, the production sites and the historical age of the artifact. Among the various ancient objects dated back to the past, pottery certainly represents the most abundant and stable product found in many archaeological excavations. The archaeometric study of pottery finds is a fundamental issue to enlighten the history of human. Pottery findings are challenging systems; they combine the physical complexity that originates from the coexistence of amorphous and crystalline phase in the same sample, with the charming richness of the historical information delivered if properly interrogated (Barilaro, Crupi, *et al.* 2005). In order to highlight on the manufacture technique, the knowledge of the firing procedure is a fundamental issue. In fact, as is

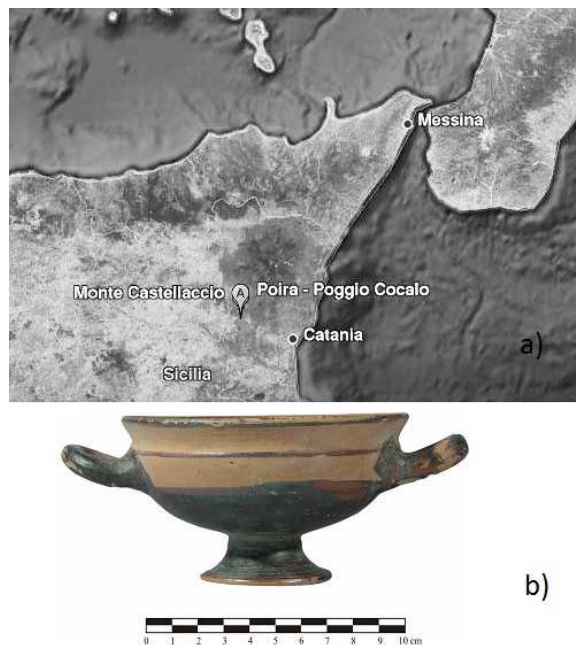


FIGURE 1. a) Sketch-map of Eastern Sicily with the indication of the archaeological sites; b) example of “Ionian Cup”.

well known, raw materials transform in new crystalline and amorphous compounds during the firing procedure. In particular, the detection of many new formed minerals (Barilaro, Barone, *et al.* 2005), including gehlenite, wollastonite, anorthite and diopside, can be used as indicators for an approximated estimation of firing temperature. Hence, in many studies the compositional characterization of pottery has been often connected to the estimation of firing temperature (Barone, Crupi, Longo, *et al.* 2011; Barone *et al.* 2004; Capel, Huertas, and Linares 1985; Riccardi, Messiga, and Duminuco 1999). Here, a new approach to evaluate this fundamental parameter is reported. Indeed firstly, we detected the water content in ancient potteries through a coulometric analysis, and then we related the obtained water amount to the firing temperature of the analysed ceramic fragments. In particular, the samples were shards of “Ionian Cups”, a ceramic typology widely diffused in the Mediterranean Area in archaic age (VI–V century B.C.). The investigated samples came from different archaeological sites in the province of Catania (Sicily, Italy): Poirà, Poggio Cocalo and Monte Castellaccio. A sketch-map of eastern Sicily with the locations of the investigated archaeological sites, together with an example of Ionian Cup are shown in Fig. 1. The production of “Ionian Cups” started in about 580 B.C. in eastern areas of Greece and was then continued in Magna Graecia until about 540 BC. The presence of various production centres in the Greek colonies have been hypothesised and it represents a hotly debated question (Barone, Crupi, Longo, *et al.* 2011; Barone, Crupi, Majolino, *et al.* 2011; Belfiore *et al.* 2010).

In order to validate this “speculative” coulometric approach, for the first time applied to archaeometric field, we compared the results with previous Small Angle Neutron Scattering (SANS) (Barone, Crupi, Longo, *et al.* 2011)) analyses performed on the same samples. In this previous paper, we were able to establish a relation between the mesoscopic properties such as self-similarity, anisotropy and porosity and the manufacturing technology, i.e. the growth of the mineralogical aggregates and the maximum firing temperature. Finally, we also referred to the mineralogical composition, here obtained by Fourier Transform Infrared absorption (FT-IR) measurements.

## 2. Materials and methods

**2.1. Samples.** The studied archaeological samples included fragments of pottery from different Sicilian archaeological sites. In particular, we investigated fourteen fragments of B2-type Ionian Cups; those coming from Poirà necropolis were labelled POI 1, 2, 3, 4, 5, 13, 16, 17, 19, and 20, instead the shards from Poggio Cocalo were named PTPLCo 2, 3, and finally, the fragments from Monte Castellaccio were called PTPL 1 and PTPL 2. All samples were dated back VI–early-V centuries B.C.. In addition, we also analyzed two non-varnished local shards. POI 21 and 22, coming from Licodia Eubea facies, dated back VI–mid-V centuries B.C.

We used a group of test specimens of pottery as comparison samples in order to relate the water content to the firing temperature. These samples were properly produced in laboratory, using a clay sediment typical of the Tortonian Terravecchia Formation, close to the provenance archaeological sites of the investigated findings. In particular, the coulometric measurements were performed on these test specimens (labelled as TORT#) fired at known temperature, in a range from 700 °C to 900 °C.

**2.2. Coulometry measurements.** We performed the measurements of the water content in the investigated samples by means of “Sartorius Water Detection System 400” (WDS 400). This instrument combines three reference methods: oven drying, coulometry and the well-known phosphorous pentoxide principle (the reference method for determining moisture in gas (Keidel 1959)). WDS 400 is the ideal alternative to classic Karl-Fischer titration, because it eliminates the need for working with detection reagent, many of which are toxic and expensive. The combined use of the above-mentioned techniques gives rise to a high-resolution analytical direct method, easy to use that allows us to determine selectively the presence of water in solids and/or pasty. Furthermore, this apparatus permits a quantitative distinction among different “types” of water, namely surface water, capillary water and crystallization water. In order to get the water content in the analysed samples, we adopted a measurement procedure based on three main steps. In particular, as first step we performed a tare measurement for determining “extra unwanted” humidity (i.e.. residual moisture in the flow of carrier gas, moisture that enters the system when opening and closing the oven door, and moisture on the sample scoop). Then, the calibration with a standard sample of sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) containing a known water amount (1% of humidity in the T range 140 °C to 400 °C) was carried out. Finally, we performed the measurements on the samples, after a correct choice of the amount to be analysed, since we have had to take into account the total amount of expelled water in the appropriate temperature range.

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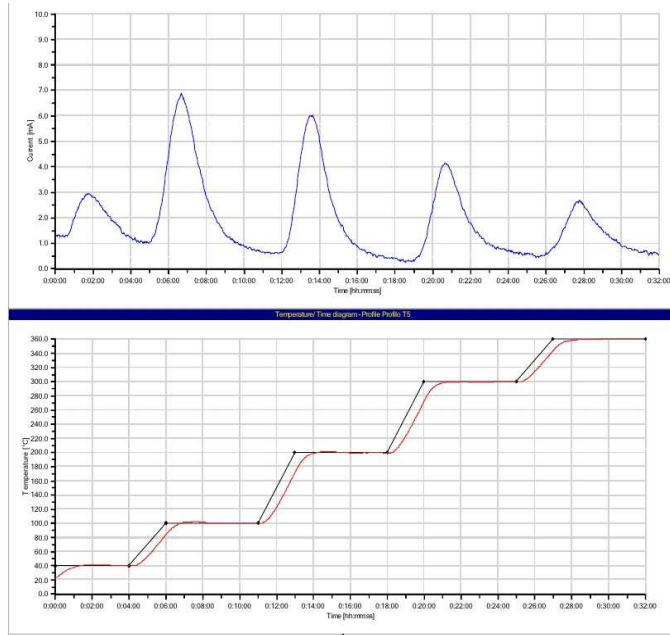


FIGURE 2. Coulometric measurement on TORT 700 sample, fired at 700°C. Top graph: current versus time. Bottom graph: temperature versus time.

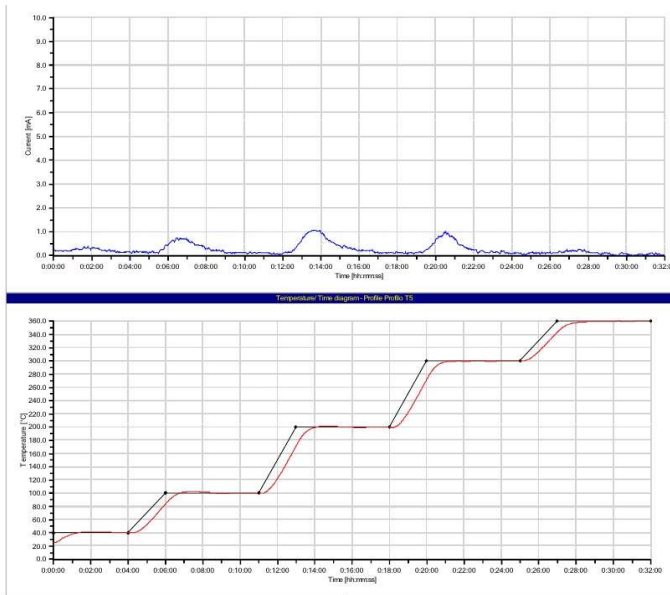


FIGURE 3. Coulometric measurement on TORT 900 sample, fired at 900°C. Top graph: current versus time. Bottom graph: temperature versus time.

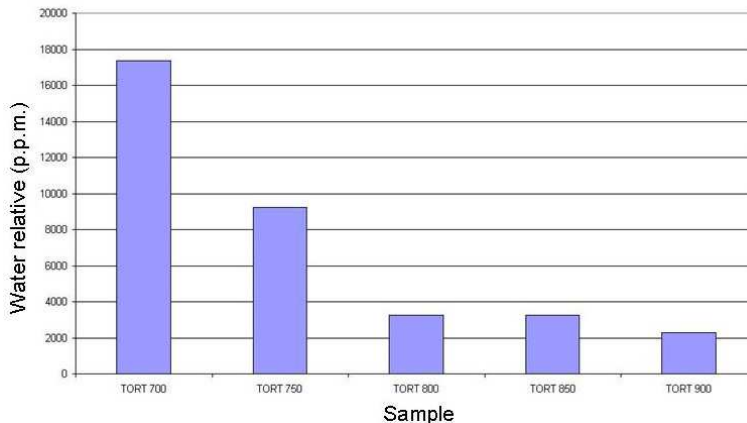


FIGURE 4. Histogram profile of the relative water content for test specimens (TORT#).

**2.3. FT-IR Absorbance measurements.** We collected FT-IR absorbance spectra using a BOMEM DA8 FT-IR spectrometer, equipped with a Globar lamp as source, a KBr beam-splitter and a DTGS/MIR detector with the aim to identify the mineralogical composition characterizing the ceramic bulk. In such a configuration, it was possible to collect the spectra from  $450$  to  $4000\text{ cm}^{-1}$ , with a resolution of  $4\text{ cm}^{-1}$ . The investigated samples were prepared in pellets, about  $0.5\text{ mm}$  thick, using small quantities (about  $2\text{ mg}$ ) of bulk sample dispersed in  $200\text{ mg}$  of powdered CsI that is transparent in the investigated IR frequency range. We performed the measurements in dry atmosphere to avoid any unwanted humidity contribution, 32 repetitive scans were automatically added to obtain a good signal-to noise ratio (SNR) and, a reproducibility of high quality spectra. In order to characterize the mineralogical phases present in the pottery samples unambiguously, we compared the experimental FT-IR profiles with those from the Sadtler 'Minerals and Clays' database (Sadtler Database for FT-IR, BioRad Laboratories) and with data reported in authoritative papers (De Benedetto *et al.* 2002; Griffith 1987).

### 3. Results and discussion

Firstly, we performed measurements on test specimens (TORT#). Figures 2 and 3 show, as examples, the coulometry analyses in the case of TORT 700 and TORT 900, fired at  $700^\circ\text{C}$  and  $900^\circ\text{C}$ , respectively. In particular at the top, the graphs display the current profile versus time of the analyzed specimens while at the bottom, the graphs show the corresponding chosen temperature profile, again versus time. The area of the current peaks represents the total water content in the analyzed sample. Hence, the height of the current peaks produced during the measurement depends on the quantity of water released at a given temperature, which in turn is dependent on the quantity of the tested sample material. Figure 4 plots the histogram profile of the relative water content for the test specimens, as obtained by the coulometric analysis. As can be seen, it deeply changes versus the firing temperature, indeed in the case of TORT 700 and TORT 750 the corresponding amount of

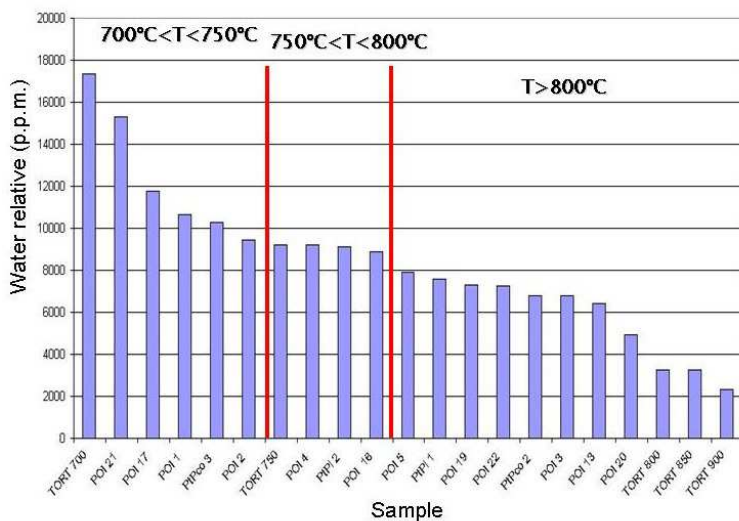


FIGURE 5. Histogram profile of relative water content for archaeological and test samples.

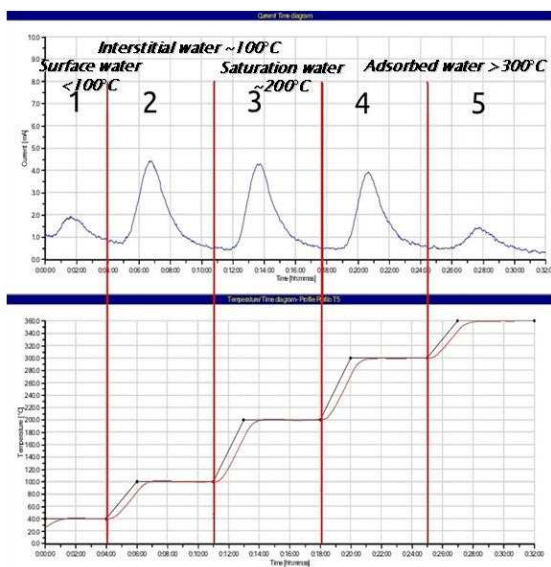


FIGURE 6. Coulometric measurement on POI 17 sample; each peak was associated to different types of water. See text for details.

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TABLE 1. Coulometric data of archaeological samples: sample weight (mg), absolute ( $\mu\text{g}$ ) and relative (% and p.p.m.) water content. The uncertainty was estimated equal to 0.001%.

Sample	Weight (mg)	Absolute water content ( $\mu\text{g}$ )	Relative water content (%)
POI 1	21.19	225.630	1.065
POI 2	21.14	201.810	0.945
POI 3	21.00	142.194	0.677
POI 4	21.40	197.303	0.922
POI 5	21.37	169.121	0.791
POI 13	21.14	135.481	0.641
POI 16	21.11	187.115	0.886
POI 17	21.31	272.097	1.277
POI 19	21.35	155.759	0.730
POI 20	21.38	105.820	0.495
POI 21	21.32	400.074	1.877
POI 22	21.08	152.998	0.726
PTPCo 2	21.37	144.866	0.678
PTPCo 3	21.00	221.112	1.029
PTPL 1	21.12	160.302	0.759
PTPL 2	21.18	193.213	0.912

released water is clearly different from that of the specimens fired at higher temperature, namely TORT 800, 850 and 900. In principle, we could relate this experimental evidence to the occurrence that during the firing procedure, at different temperature ranges, some chemical reactions with releasing of water can occur. In particular, as is well known, the raw materials that compose the pottery in the course of the firing process undergo chemical transformations that lead to the disappearance of certain compounds and the formation of newly formed minerals, at temperatures higher than  $750^\circ\text{C}$  (Campanella *et al.* 2007). The results of coulometric measurements performed on the archaeological samples are reported in Table 1. Figure 5 displays the relative water content sorted by descending order together with the results obtained for the test specimens. By a first inspection of the histogram profile, on the basis of the comparison with the relative water amount released by TORT# samples, fired at known temperature, we tentatively grouped the archaeological samples hypothesizing their firing temperature. Indeed, for the fragments labelled POI 21, POI 17, POI 1, PtPco 3 and POI 2 we suggested a firing temperature  $T$  in the range  $700^\circ\text{C} - 750^\circ\text{C}$ , for POI 4, PtPco 2 and POI 16 we identified a  $T$  range from  $750^\circ\text{C}$  to  $800^\circ\text{C}$  and, finally the remaining investigated samples were supposed to be fired at  $T > 800^\circ\text{C}$ .

In addition, we studied in detail the “different” types of water ascribable to the current peaks observed during the coulometric measurements. For all the analyzed samples, we clearly revealed 5 well distinct peaks in the current profile. As previously mentioned, we associated each peak to the different types of water released by the sample, during the temperature treatment, as displayed in Fig. 6 in the case of POI 15, as an example.

TABLE 2. Contributions of relative water content expressed as a percentage associated to each current peak.

Sample	1	2	3	4	5
TORT 700	15.48	29.77	23.13	18.17	13.45
TORT 750	12.54	26.74	27.25	21.24	12.24
TORT 800	17.74	28.01	27.37	14.67	12.21
TORT 850	16.08	17.78	22.45	27.71	15.99
TORT 900	12.80	23.22	32.55	24.61	6.81
POI 1	9.15	16.52	27.31	34.49	12.53
POI 2	18.47	26.48	21.36	22.87	10.82
POI 3	14.61	23.91	29.01	27.31	5.17
POI 4	11.27	22.04	33.31	27.87	5.51
POI 5	12.60	23.01	29.52	27.33	7.54
POI 13	9.22	19.22	29.36	32.13	10.06
POI 16	11.48	24.50	27.10	26.68	10.23
POI 17	15.31	29.37	27.54	16.65	11.13
POI 19	9.22	24.45	35.22	26.63	4.47
POI 20	12.65	25.58	33.83	22.73	5.21
POI 21	16.98	32.79	27.65	15.73	6.84
POI 22	12.57	27.28	26.91	25.96	7.29
PtPco 2	9.75	17.56	32.40	32.50	7.79
PtPco 3	10.67	19.97	28.06	29.63	11.68
PtPl 1	6.40	12.55	38.28	35.75	7.01
PtPl 2	3.64	10.73	36.11	38.16	11.37

In particular, the first peak (peak 1) was ascribed to superficial water related to residual humidity covering the surface of clayey materials, essentially due to the air humidity and easily removable at  $T < 100^\circ\text{C}$ . The second peak (peak 2), instead, can be associated to interstitial water located inside the pores of the clayey material, released at about  $100^\circ\text{C}$ . Going on, the third peak (peak 3) can be connected to saturation water that surrounds particles with a thickness between 20 and 200 molecules, and that can be released at  $T$  about  $200^\circ\text{C}$ . Finally, the fourth and fifth peak (peaks 4 and 5), revealed at  $T > 300^\circ\text{C}$ , can be assigned to the so-called adsorbed water that directly surrounds the single particle, forming layers with a thickness of about  $100\text{\AA}$ . Table 2 reports the corresponding contributions of percentage relative water content associated to each current peak. At it is evident, for all the samples peaks labelled 2, 3 and 4 correspond to the highest percentage contribution of total expelled water. In order to quantitatively interpret the behaviour versus  $T$  of the released water content, in the case of TORT# specimen we summed the corresponding contributions associated to the current peaks area observed at temperature lower than  $300^\circ\text{C}$  ( $A_1 + A_2 + A_3$ ). After that, we also summed those contributions related to the last two peaks ( $A_4 + A_5$ ) corresponding to  $T > 300^\circ\text{C}$ . The results are displayed in Fig. 7, as a function of the firing temperature  $T$ . From an inspection of the figure, we revealed a clear



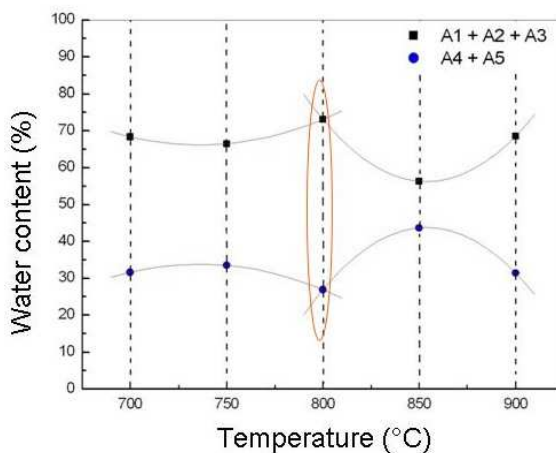


FIGURE 7. Sum of current peaks area plotted versus temperature for TORT# specimen. See text for details.

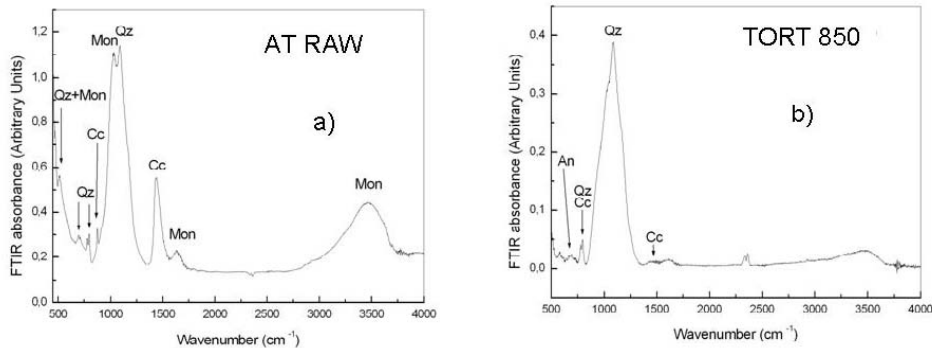


FIGURE 8. FT-IR spectra collected on (a) raw material and (b) TORT 850. Qz = Quartz; Cc = Calcite; Mont = Montmorillonite. An = Anorthite

change in the behaviour of the various contributions at  $T = 800^{\circ}\text{C}$ . This occurrence is in full agreement with the decreasing of the water content in the T range  $750^{\circ}\text{C} - 800^{\circ}\text{C}$ , already observed and evidenced in the histogram profile of Fig. 5. Hence, once again, we can ascribe this trend to mineralogical transformations (new-formation minerals) occurring just at about  $800^{\circ}\text{C}$ , as above mentioned. In addition, this latter result was supported by FT-IR absorbance measurements performed on the same samples. In Fig. 8 we report the FT-IR profiles collected on the raw material (a) and on TORT 850 specimen (b), as examples. The mineralogical composition obtained by the analysis of FT-IR spectra is summarized

TABLE 3. Mineralogical composition obtained by FT-IR measurements for raw clay and test specimens (TORT#). Qz = quartz; Cc = calcite; Mont = Montmorillonite. An = anorthite. “+” symbol stands for the relative abundance of the compounds in each sample; “tr” and “-” symbols stand for trace and absent, respectively.

Sample	Qz	Cc	Mont	An
Raw clay	+++	+++	+++	-
TORT 700	+++	++	++	-
TORT 750	+++	++	+	-
TORT 800	++	+	+	+
TORT 850	++	+	tr	+
TORT 900	++	+	tr	+

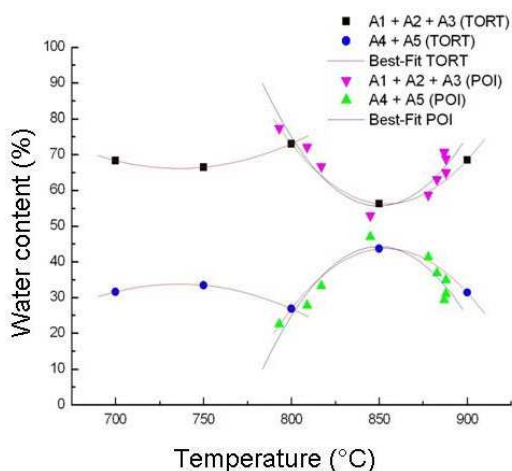


FIGURE 9. Sum of current peaks area plotted versus the firing temperature for TORT# (squares and circles) and for archaeological samples (up and down triangles), along with polynomial best-fit (continuous lines). See text for details.

in Table 3. From the comparison of the experimental spectra with those of the database and of literature, we were able to identify the presence of some main mineralogical phases, namely quartz, calcite and montmorillonite in all the fragments. In particular, we observed that calcite and montmorillonite tend to decrease with increasing firing temperature and, on the contrary, starting from 800 °C we also detected the typical bands of anorthite, which is a newly formed mineral. Actually, the presence of anorthite was previously revealed in Ionian cups shards, coming from Poirra again by FT-IR absorbance measurements (Barone *et al.* 2004). In order to have a deeper characterization of the mineralogical phases present, other

TABLE 4. Firing temperatures estimated by coulometric and SANS measurements for the archaeological samples; the error for the calculated T values ( $^{\circ}\text{C}$ ) is of the order of 6% and 7%, respectively.

Sample	Firing temperature (coulometric data)	Firing temperature (SANS data)
POI 2	907	887
POI 5	896	888
POI 16	892	883
POI 17	799	809
POI 19	903	888
POI 21	792	793
POI 22	809	817
PtPco 2	883	917
PtPco3	880	878

analyses, namely X-ray diffraction (XRD) and/or Neutron diffraction (ND), are planned. Going on, we also reported the percentage water contributions (A1 + A2 + A3 and A4 + A5) as a function of firing temperature in the case of archaeological samples together with the results obtained for the test specimens, as shown in Fig. 9. In the same figure, the continuous lines represent the polynomial best-fit. Actually, since the firing temperatures of archaeological samples were unknown, we used the T values obtained by previous small angle neutron scattering (SANS) measurements performed on the same samples (Barone, Crupi, Longo, *et al.* 2011). As can be seen, looking at Fig. 9, the graph displays the results of a smaller number of archaeological samples than the analyzed ones, since for some of these pottery fragments the firing temperature estimated by SANS measurements was higher than  $900^{\circ}\text{C}$ . Therefore, it was not included in the T range of the polynomial fit performed on the test specimen. However, we observed that the behavior followed by the archaeological samples was in good agreement with that of TORT# specimen, indicating that the contribution of each current peak to the whole water content follows the same trend of TORT# specimen. Hence, using the parabolic curves of the best-fit relative to the test specimen fired at  $T > 800^{\circ}\text{C}$ , we were able to estimate the firing temperatures of the archaeological findings, reported in Table 4 along with the firing temperatures estimated by SANS measurements (Barone, Crupi, Longo, *et al.* 2011). By looking at the table, the agreement of the order of 3% among the T values obtained by the coulometric investigation and those from SANS experiments results clear. This latter occurrence, once more, supports the validity of this new approach in archaeometric research.

#### 4. Conclusions

In the present paper, we performed a coulometric investigation on a group of ancient potteries, the so-called “Ionian Cups” with the aim of obtaining useful information in estimating the firing temperature, crucial information for the reconstruction of the manufacturing process. In particular, we were able to connect the water content released by the archaeological pottery in an opportune time interval to the firing temperature. In addition,

we ascribed “different types of water” to the current peaks revealed during the coulometry experiments. The whole of the results highlighted how this analytical technique, even in comparison with other more usual methodologies, can represent a suitable new approach in the archaeometry field.

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Communicated 15 June 2015; manuscript received 12 November 2016; published online 20 June 2016;  
amended version published online XX July 2016.

EDITOR'S NOTE: Due to a mere typographical oversight the name of Monica Interdonato was missing from the authors' list in the electronic version of the article published online on June 20, 2016.



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