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Accuracy improvement by means of porosity assessment and standards optimization in SEM-EDS elemental analyses on archaeological and historical pottery and porcelain

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SEM-EDS analyses of pellets produced with powdery clay and ceramic standards and fired at increasing temperatures showed a systematic overestimation of the abundance of heavier detected elements (K, Ca, Ti and Fe) using the conventional procedure of calibration with massive mineral certified materials followed by normalization of the detected values. Errors were particularly noticeable for samples fired in the typical range of temperatures of archaeological and historical pottery (600-900 °C) and for unfired samples, and were attributed to material porosity. An extremely simple method based on the SEM-BSE image analysis is proposed for the semi-quantitative evaluation of porosity. A remarkable increase of accuracy was evidenced when the calibration is performed using a standard with porosity comparable to the samples, with regard to the pottery temperature range.

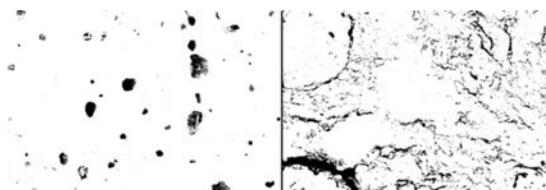
Sample name	Raw material	Preparation procedure	Firing temperature
CL1	Clay standard	Hydraulic press	-
CL2	Clay standard	Hydraulic press	600 C°
CL3	Clay standard	Hydraulic press	900 C°
CL4	Clay standard	Hydraulic press	1200 C°
CL1k	Clay standard	Kneading moistened clay	400 C°
CL2k	Clay standard	Kneading moistened clay	600 C°
CL3k	Clay standard	Kneading moistened clay	900 C°
CL4k	Clay standard	Kneading moistened clay	1200 C°
CE1	Ceramic standard	Hydraulic press	-
CE2	Ceramic standard	Hydraulic press	600 C°
CE3	Ceramic standard	Hydraulic press	900 C°
CE4	Ceramic standard	Hydraulic press	1200 C°

Two commercial Standard/Certified Reference Materials, a clay (CL) and a ceramic (CE) powder, were subjected to different preparation procedures and to firing at diverse temperatures to obtain series of simulated samples of historical pottery (600 and 900 °C) and porcelain (1200 °C).

EDS analyses on these samples gave detected compositions quite different with respect to the certified composition, showing an apparent composition change vs. firing temperature.

Analyses were performed by using two different instruments, an EVO-50 Zeiss and a Cambridge S-360 SEM equipped with an Oxford Instruments INCA Energy 200 EDS spectrometer and a X-Act3 SDD-EDS detector, respectively. All measurements were performed on polished section. All these variations are quite comparable for the two instruments. The good reproducibility indicates that the observed difference should be a matter of accuracy.

Errors are ascribed to the different path in the sample with respect to a non-porous material; a semi-quantitative evaluation of the porosity of these materials was hence carried out to correlate these results with the compositional data obtained by SEM-EDS. BSE images was employed to obtain a binary image, the porosity calculation was carried out by simply dividing the number of black pixels (voids on surface) of this image by the total number of pixels. The results show a general increasing trend up in porosity to 900 °C for all CL, CLk and CE series and then an abrupt decrease at higher temperatures. The porosity was also estimated on historical (a fragment of porcelain, picture below, left) and on archaeological (a ceramic sherd, picture below, right) respectively, demonstrating that the obtained standards are representative for real materials, as far as the porosity is concerned.



Therefore, the ceramic standard samples were used as calibration standards in the analyses of the clay standard samples, in order to check for an accuracy improvement when the calibration is performed using a standard with comparable porosity with respect to the analysed sample. RMS (Root Mean Square) differences between the certified compositions and the values obtained ana-

lyzing samples CL1, CL2, CL3, CL4 and CL4k using massive mineral standards and CE1, CE2, CE3, and CE4 as calibration standards showed an evident tendency of the RMS differences to decrease the more the estimated porosity of the sample and of the calibration standard are similar.

The results clearly showed that the use of a standard characterized by a porosity similar to the porosity of the samples is advisable for the determination of chemical composition of ceramic materials, considerably increasing data accuracy. This observation is particularly essential in the temperature interval (600-900 °C) of the typical firing step of ancient pottery, which usually shows a porosity of even few tens percent in volume. The influence of the porosity is definitely less important in the case of high temperature fired samples, such as porcelain, since porosity is low and its effect is negligible. The proposed method for a semi-quantitative evaluation of ceramic and porcelain materials porosity is extremely simple and rapid and it is suitable for calibration optimization.

The proposed calibration method seems particularly suitable for studies on production technologies or in the SEM-EDS examination of multilayer ceramics, where trends in the composition of each layer (i.e. body, slip, glaze) need to be evaluated. Moreover, it seems seminal in the case of characterization studies.

The full discussion, including analogous considerations about XRF technique, is available in Turco et al. *Journal of Archaeological Science: Reports*, 2017, 12, 54-65.

Topography and nanomechanical properties of cellulose fibers: application to ancient paper

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Cellulose is the main component of paper since the beginning of its production in the Far East in the first century A.D. and in the Western world in the Middle Ages. The remarkable properties of this material are due to the specific hierarchical structure that this polysaccharide assume within each fiber. The micro-fibrils that are stacked in the

different layers are in fact composed by distinct regions where cellulose polymers are arranged either in crystalline or in amorphous domains. The different and opposite mechanical properties of these regions impart most of the mechanical properties to the fibers and thus to the paper sheets. Paper plays also an important role in cultural heritage due to the large number of precious artefacts, however the many degradation processes that take place within its structure might affect its preservation.¹⁻³

In this frame studying in the less invasive way the morphology and the mechanical properties of cellulose fibers open the way to novel diagnostic tools to monitor the degradation processes of these artefacts.

We have applied two different techniques, atomic force microscopy (AFM) and optical profilometry, to measure over different lengthscales the three dimensional (3D) morphology of paper from the whole sheet to the sub-fiber constituents. Moreover, we have explored³ the possibility to measure the mechanical properties of a single fiber down to the nanometer scale to map it as a function of the aging of the sample.

Profilometric measurements were performed using a Smart-WLI 3D Prime Optical Non-contact Profilometer (GBS-Ilmenau GmbH); images were collected at five different position in each sheet, near each corner and in the center.

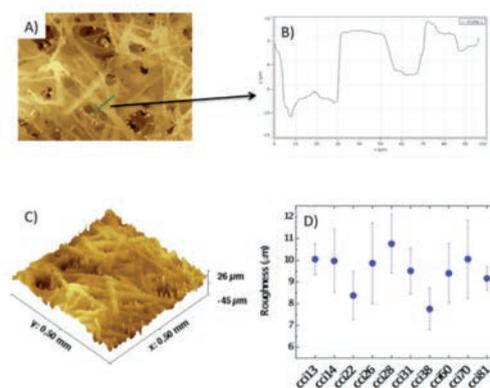


Figure 1. Profilometric image of an ancient paper sheet. A) The top view with the cross section (green line). B) The profile corresponding to the cross section of A. C) A 3D rendering of the image where the z-scale can be appreciated. D) The roughness measured onto different sheets of the *Corpus Cartarum Italicarum*.

AFM experiments were performed as described in ref. 3; briefly a single cellulose fiber was extracted from each sheet and positioned on a OH enriched glass slide that was then placed under