

ROMAN AND BYZANTINE GLASSES FROM NORTHERN TUNISIA: A TECHNOLOGICAL STUDY

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The analysed roman and byzantine glasses belong to the archaeological small finds collected during survey and excavation campaigns of Trento University (director *Prof. M. de Vos*) around the ancient city of Thugga in northern Tunisia [1,2]. Between 1994 and 2008, 641 sites have been discovered in an intensively surveyed area of about 371 km². Out of these sites the important Late Roman-Byzantine farm of Aïn Ouassel was excavated as settlement model, to understand lifestyle, activities and trades of this rural area in antiquity, the.

Around 80 fragmentary glass forms have been collected during the fieldwork: walls, rims, bases and feet, stems, handles and some ornamental objects. Their colours differ sensibly, ranging from different hues of blue to green and yellow.

The samples were analysed by means of pXRF (portable X-Ray Fluorescence) to study the glass matrix elemental composition and to identify the components responsible for the colour. SEM analyses were carried out to investigate both composition and corrosion effects, too.

The chemical nature of chromophores was investigated by means of UV-vis-NIR (Ultraviolet -Visible - Near Infrared) reflectance spectroscopy both in reflectance and transmission set up (depending on the sample colour and transparency); in particular, the spectra have been acquired by FORS (fibre optic reflectance spectroscopy). The study of the element oxidation state by XPS (X-ray Photoelectron Spectroscopy) has then allowed the acquisition of information on the production technology.

Glasses were first of all examined by microscope to identify manufacturing details on surface and to define a list of visual glass colorations. SEM-EDX (scanning electron microscopy coupled with X-ray photoelectron spectroscopy) has evidenced surface alteration because of the post-depositional conditions. This is also attested by the presence of iridescent effects due to formation of new products on the glasses surface. Taking into account that with pXRF elements with Z less than 13 (such as Na and Mg) cannot be detected, the glass matrix mainly contains Si, Fe, Al, Ca, K, Rb, Sr; Na and Mg were put in evidence by SEM-EDX.

From the CaO/K₂O ratio [2] has been possible to make some hypotheses about the flux added to the glass matrix: only for one sample natron could have been used as flux while for all the other samples we can hypothesize an intermediate situation with the use of a mixture of natron and plant ash (as attested in the literature) [3]. As concerns the colour, the chemical elements responsible for the different shades are generally Fe for the green shades, Cu and Co for the blue ones, Mn (used as discoloring agent) for the transparent samples.

From the comparison of SiO₂ against CaO content between samples from Thugga area and a control group of samples from another area in Northern Tunisia [4], a common provenance of

sand for most of Thugga and the control samples can be hypothesized (Fig. 1a). Since Fe and Ti are normal sand impurities, a different sand has been instead probably selected for the production of olive green glasses (as evidenced in Fig. 1b).

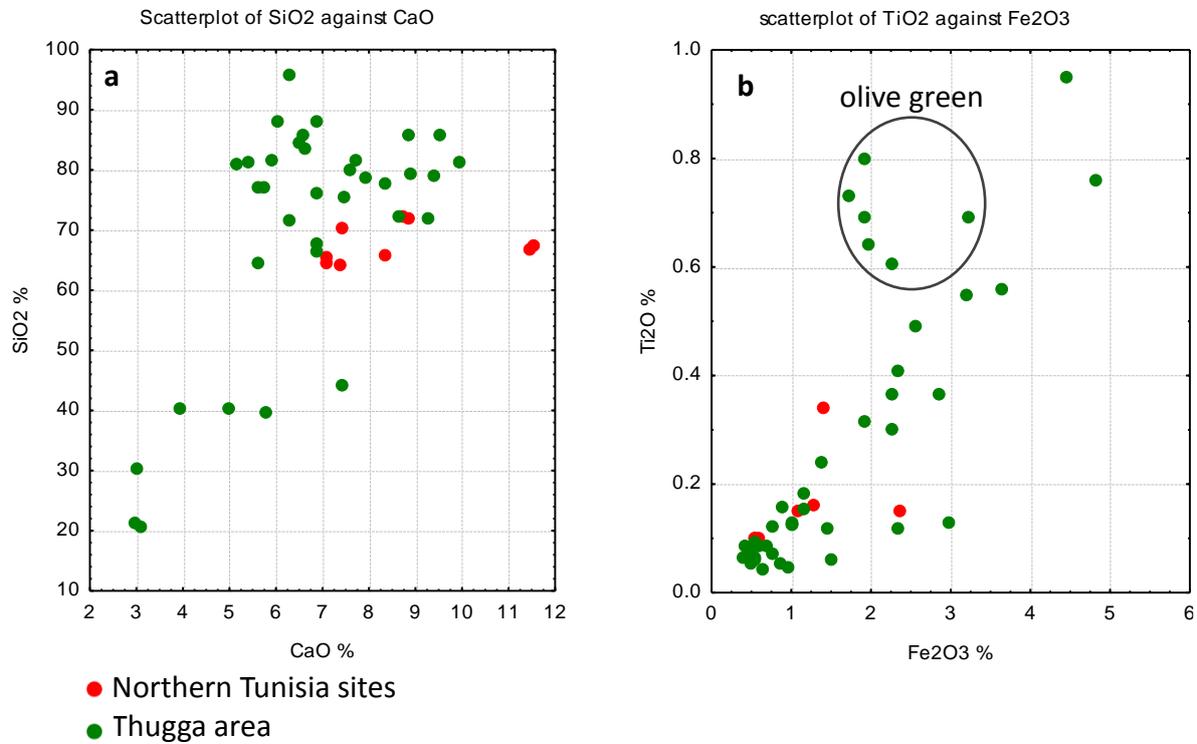


Fig. 1. (a) Scatter plot for SiO₂/CaO: comparison between glass samples from Thugga area and a control group from other sites in Northern Tunisia; (b) scatter plot for TiO₂/Fe₂O₃: comparison between glass samples from Thugga and the control; olive green samples are evidenced.

As demonstrated by FORS spectra [5], for the deep blue colours Co has been added as chromophore, while in the case of light blue a mixture of Fe²⁺ and Fe³⁺ with the addition of Mn has been evidenced (in this case Mn compensates the green due to Fe). Also for the green and yellow samples, a variety in the composition has been observed as concerns both Fe oxidation states and Mn content. Indeed Iron is the major colouring impurity present in natural sands and it is well known that melting conditions (namely, temperature and oxygen partial pressure of the atmosphere and batch) should be carefully controlled in order to define Fe²⁺/Fe³⁺ equilibrium and green, blue, and yellow/amber hues can be obtained using similar sands controlling the firing conditions [6]. Finally, violet was obtained by manganese addition. On the base of these considerations, we can hypothesize that these ancient artisans had deep knowledge of glass technology production.

References

- [1] de Vos, M., 2000. *Rus Africum. Terra acqua olio nell'Africa settentrionale. Scavo e ricognizione nei dintorni di Dougga (Alto Tell tunisino)*. Trento.
- [2] Raaijmakers de Vos, M., & R. Attoui, 2013. *Rus Africum: tome I. Le paysage rural antique autour de Dougga et Téboursouk: cartographie, relevés et chronologie des établissements*, Bari.

[3] Schalm O., Janssens K., Wouters H., Caluwé D., 2007. Composition of 12-18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings. *Spectrochimica Acta Part B*, 62:663-668.

[4] Foy D., 2003. *Le verre en Tunisie: l'apport de fouilles récentes tuniso- francaises*. *Journal of Glass Science*, 90: 45-59.

[5] Gallo F., Silvestri A., Molin G., 2013. *Glass from the Archaeological Museum of Adrai (Noth-East Italy): new insights into Early Roman production technologies*. *Journal of Archaeological Science*, 40: 2589-2605.

[6] Mirti P., Davit P., Gulmini M., 2002. *Colurant and opafiers in seventh and eighth century glass investigated by spectroscopic techniques*. *Anal. Bioanal. Chem.*, 372:221-229.