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ESRF	**Experiment title:** **XAFS investigation on medieval glass of archaeological interest**	**Experiment number**: 08-01-608
Beamline: BM08	**Date of experiment**: from: 7/9/2002 to: 10/9/2002	**Date of report**: 14/02/2003
Shifts: 9	**Local contact(s)**: Chiara Maurizio	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Simona Quartieri*, Dipartimento di Scienze della Terra, Università di Messina (Italy)

Maria Pia Riccardi* and Bruno Messiga, Dipartimento di Scienze della Terra, Università di Pavia (Italy)

Federico Boscherini*, INFM and Dipartimento di Fisica, Università di Bologna (Italy)

Report:

It is known that various colors in glasses can be determined by the oxidation state and electronic configuration of the metal ions in them. They are usually elements belonging to the transition row of the periodic system, which absorb characteristic frequencies of visible region as a result of the d-d electronic transitions. Since the characterization of colorant components is important in understanding the manufacturing technique of the ancient glass samples, we applied synchrotron X-ray Absorption Spectroscopy to the study of ancient glass fragments from Val Gargassa. The glasswork of Val Gargassa (Genova, Italy) produced glass-wares (table glass and jug) during fourteenth century. The excavation gives back more than 3000 findings that allow characterising the whole productive cycle. In glass archaeology, the so-called "production indicators" are those remains which testify to specific operations carried out during the productive cycle, implying fritting, melting, flashing (mixing), boiling and working (Fig. 1). In other words, they allow us to reconstruct the processes and technological expedients used in the past to produce glass.

Figure 1. Production indicators found in the glasswork of Val Gargassa

The XANES experiments were performed at both Fe and Mn K-edges at Gilda beamline in fluorescence mode. The analysis of the pre-edge region was performed by least-square fitting of pseudo-Voigt functions to the pre-edge envelope and calculating its centroid position (Figs. 2-4).

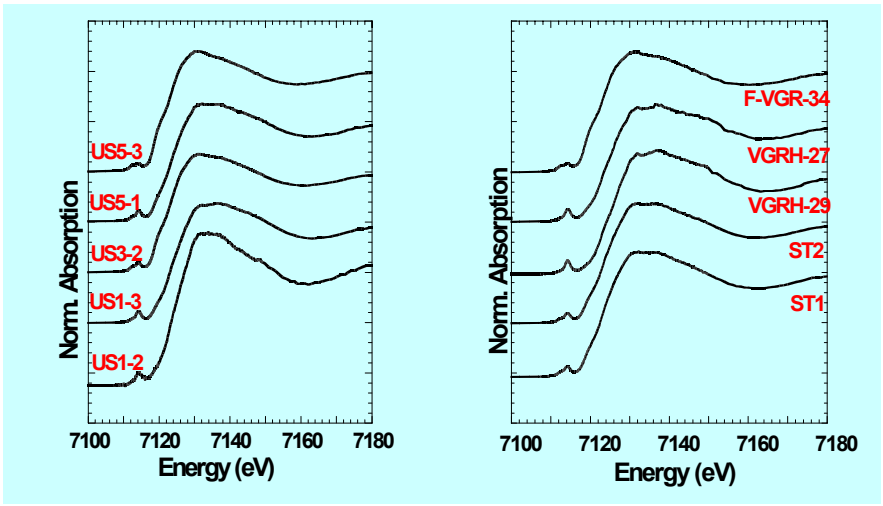

Fig. 2a Fe K-edge XANES spectra

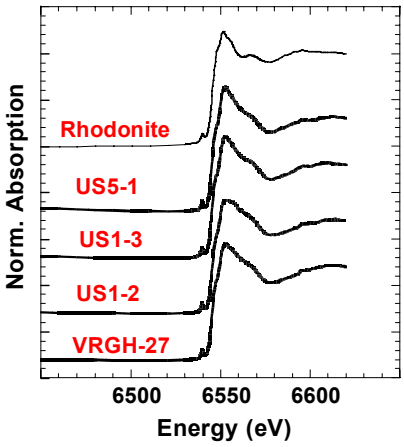

Fig. 2b Mn K-edge XANES spectra

Both production indicators and glass artifacts display very variable colour intensities and tonalities. In particular, while all the vitreous masses are bottle-green coloured and do not contain Mn, the drops are in general light-green or uncoloured. In addition, these production tests always contain Mn in its reduced 2^{+} oxidation state. These data suggest that the addition of MnO_2 as decolorant occured at a precise step of the production cycle (Fig. 3).

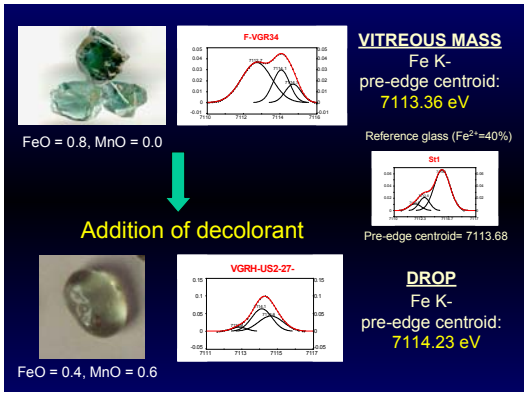

Figure 3. Fe K- pre-edge envelope of vitreous masses and drops

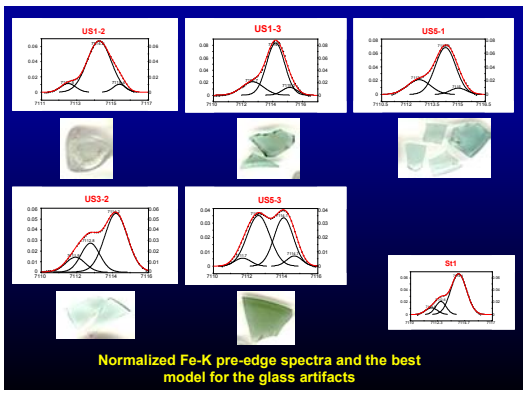

Figure 4. Fe K-pre-edge envelope of the manufacts.

The comparison among the chemical compositions of the original vitreous masses, of the intermediate test drops, and of the final glass products also suggests the use of chromium as a further colorant agent, present only in the final glass artifacts .