Quantitative evaluation of XANES Spectra of the system CuO-Al_2O_3-SiO_2 at temperatures from 850°C-1150°C using a principal component analysis algorithm and linear combination analysis

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The motivation for our investigation of the system CuO-Al_2O_3-SiO_2 at temperatures from 850-1150°C has been the interest for the firing conditions and thus for information on the origin of some majolica ceramics (14^{th}-17^{th} century, Montelupo [1]). These ceramics were decorated either by so-called engobe-painting or by glaze-painting. Small amounts of CuO-engobes or CuO-glazes were applied onto the surface of the ceramic before firing and yielded a green coloured coating. In an attempt to copy the majolica technique, we prepared CuO-based engobes under defined conditions. The engobes were prepared by mixing kaolin with 1% CuO and 6% CuO, respectively, in a ball mill. The samples were then calcined in air at different temperatures [2,3]. Cu*K*-XAFS spectra of the samples were recorded at beamline X1 in transmission at 77K (DORIS III operating at 4.445 GeV, injection current 144 mA, Si(111)-double-crystal monochromator). The spectra were energy calibrated, background corrected and normalized [4]. The Cu*K*-XANES-spectra of the CuO-based engobes are compared to the reference compounds CuO, $CuAl_2O_4$ and a CuO-based glaze in Figure 1.

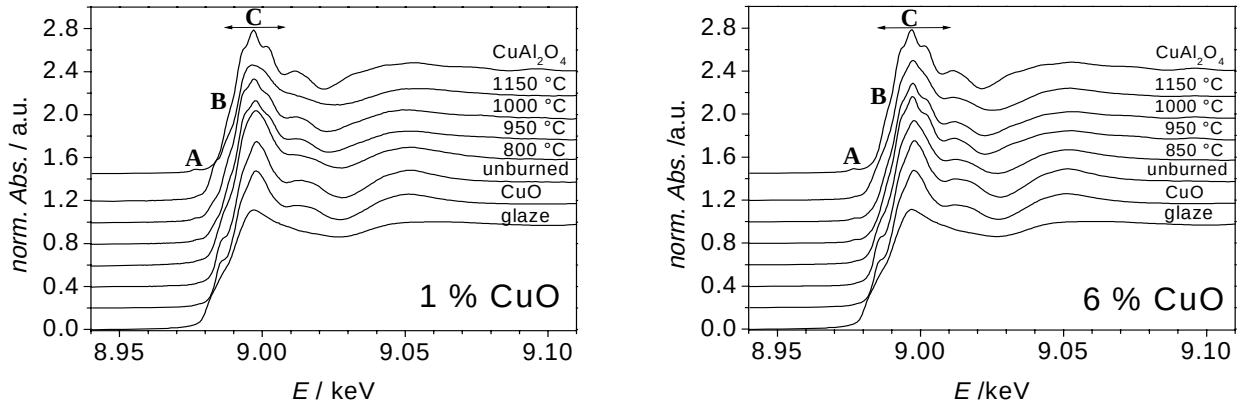

Figure 1: Cu*K*-XANES spectra of unburned and burned engobes with 1% CuO (left) and 6% CuO (right) in comparison to CuO, $CuAl_2O_4$ and a CuO-based glaze.

The pre-edge peak **A** and the area **C** are valuable diagnostic features to differentiate between the XANES spectra of $CuAl_2O_4$ and of CuO. The pre-edge peak **A** and the shape **C** of the spectra of the CuO-engobes burned at 950 °C and 1000 °C show some resemblance to the spectrum of the spinel $CuAl_2O_4$ whereas the spectra of the unburned engobe and of the engobes fired at 850 °C and 1150 °C are similar to the spectrum of CuO. These observations can be confirmed by first applying a principal component algorithm (PCA) analysis to determine the minimum number and type of probable components and then using a least squares fitting procedure to quantify the proportion of the components in the experimental XANES spectra [5]. The set of ten XANES spectra of the synthetic engobes can be reproduced by a minimum of three components. To determine these components, selected reference compounds were compared to their transformed spectra (Figure 2). Having identified CuO, $CuAl_2O_4$ and the CuO-based glaze as the three phases from which the spectra of the ten samples can be reconstructed (with a residual less than 0.6%), a least square fit of a linear combination of the three components was applied to quantify the amount of each phase in the engobes. An example of the fit can be seen in Figure 3. The results of the linear combination fits and thus the proportions of the three phases in the engobes are depicted in Figure 4. The error in the fit amounts to about 5%. It seems that only in the temperature range from 850 °C to 950 °C a considerable amount of $CuAl_2O_4$-spinel-type phase is formed. Furthermore, the proportion of the glaze-type phase is increasing with increasing temperatures. At the highest temperature, the proportion of the glaze phase in the engobe with 1% CuO is

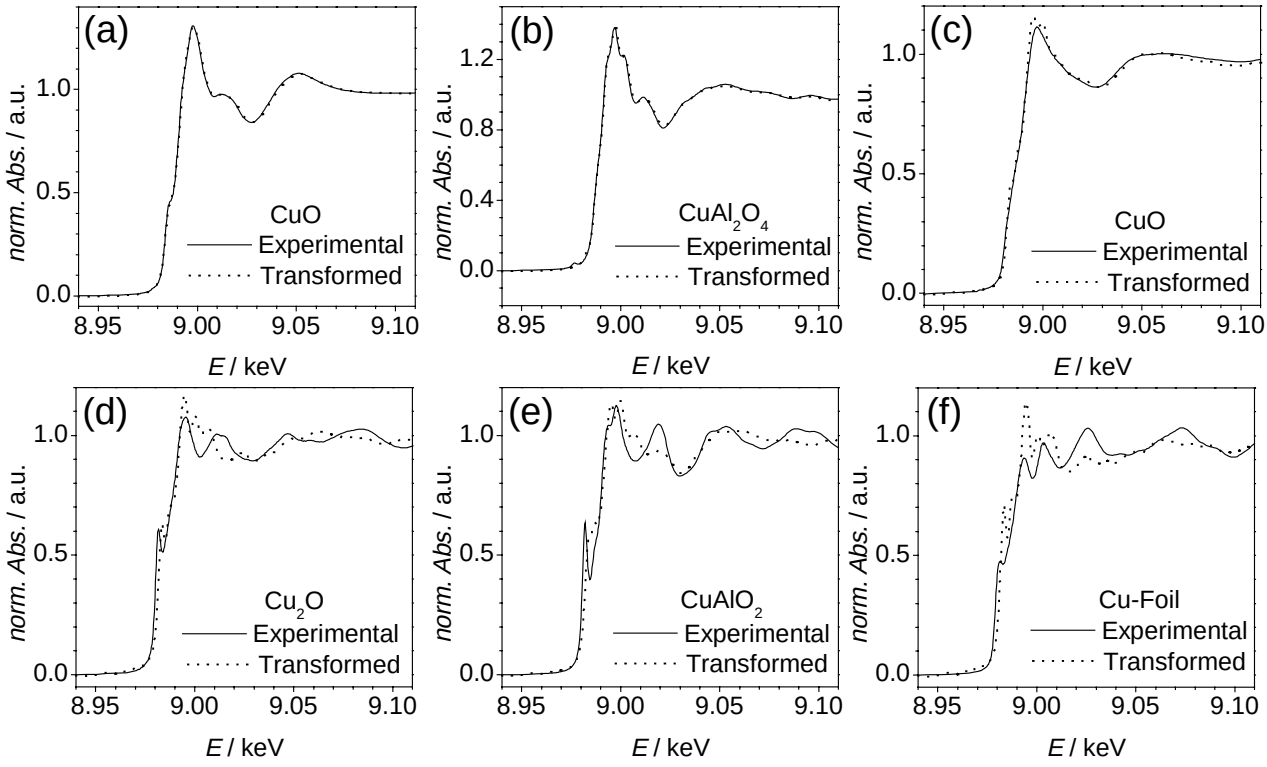

Figure 2: Target transformation results (dashed lines) for (a) CuO, (b) $CuAl_2O_4$, (c) CuO-based glaze, (d) Cu_2O, (e) $CuAlO_2$ and (f) Cu-foil. Solid curves are the corresponding experimental XANES spectra.

significantly larger than in the engobe with 6% CuO. The described procedure can be applied to the Majolica ceramics to evaluate the firing conditions used during preparation in medieval times**.**

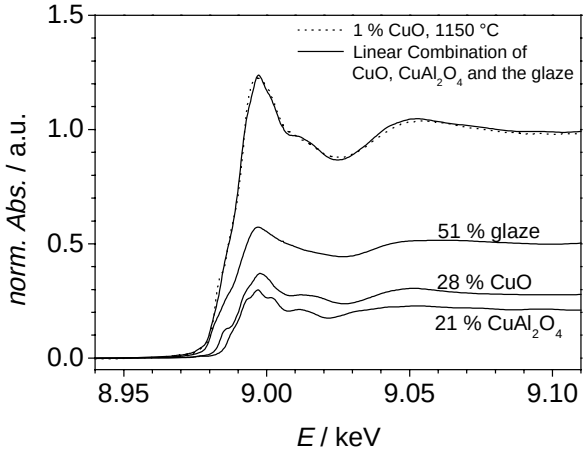

Figure 3: Linear combination of the XANES spectra of CuO, $CuAl_2O_4$ and of the CuO-based glaze to the spectra of the engobes.

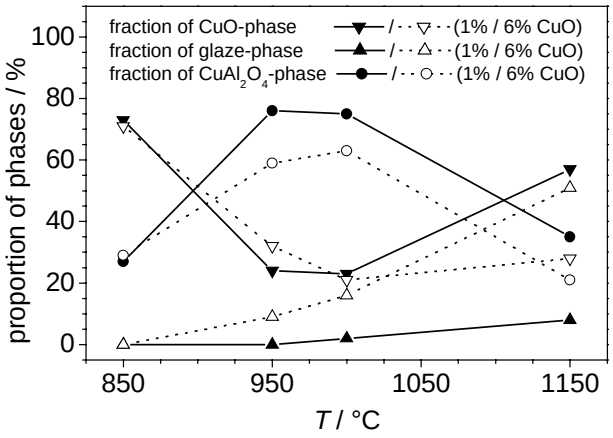

Figure 4: Results of the quantitative determination of phases in the engobes with 1% CuO (black symbols) and with 6% CuO (white symbols).

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References

[1] F. Berti, *Montelupo Ceramics, From Sixtheenth to Eighteenth Centuries*, Ed. Electra-Milano, 1986.
[2] H.-J. Wölk et al., Jahrestagung der Archäometrie u. Denkmalpflege, Dresden 2000.
[3] M. Hartl, B. Spandl, H.-J. Wölk, P. Behrens, H. Hartl, R. Schlögl, Hasylab Annual Report 2000.
[4] T. Ressler, J. Synch. Rad. 5, 118 (1998).
[5] T. Ressler, et al., Environmental Science & Technology 34, 950 (2000).