

Quantitative analysis by the Rietveld Method of Makeup Powders from the Ancient Egypt

This exercise has as aim the quantitative analysis of a makeup powder dated from the Egypt of pharaohs. It emphasizes the difficulties we can find when analyzing an archaeological sample: very small available volume, complex mixture (at least five mineral phases of which some in very small amounts and not well crystallized). Non-destructive analyses have been performed in a laboratory in order to identify the major constituents: optical microscopy, X-ray microanalysis coupled to scanning electron microscope and X-ray powder diffraction. Synchrotron X-ray powder diffraction has finally been used for quantitative analysis by Rietveld refinement. The makeup recipe corresponding to the mixture can be then described and compared with those described in medical papyri. Appropriate references concerning this problem are:

Walter P., Martinetto P., Tsoucaris G., Bréniaux R., Lefebvre M.A., Richard G., Talabot J., Dooryhée E. (1999) *Making make-up in Ancient Egypt*, *Nature*, **397**, 483-484.
Ungár T., Martinetto P., Ribárik G., Dooryhée E., Walter P., Anne M. (2002) *Revealing the powdering methods of black makeup in Ancient Egypt by fitting microstructure based Fourier coefficients to the whole x-ray diffraction profiles of galena*, *Journal of Applied Physics*, **91** (4), 2455-2465.

1. With the aid of the program WinPLOTR, visualise the powder diffraction patterns taken at a synchrotron radiation facility.
Conditions of data collection:
Synchrotron: DW22 beam line of the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE, Orsay), Debye-Scherrer geometry (capillary), $\lambda = 0.96270 \text{ \AA}$, data file **EgyptMakeUp.xys** (INS = 10).
You may remark that the quality of the synchrotron data allows a good detection of the minor phases and a better resolution improving the peak overlap in crucial d-spacing regions (for instance, close to $d=2 \text{ \AA}$)
2. The five major phases identified in the qualitative analyses are: laurionite PbOHCl , phosgenite $\text{Pb}_2\text{Cl}_2\text{CO}_3$, cerusite PbCO_3 , galena PbS and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. From the provided CIF files for the five phases (in the subdirectory ICSD), create five PCR files and do a calculation of structure factors for each phase using $\text{HKL}=5$. See note of 9 February 2007 in the file fp2k.inf.
3. From the CIF files provided for the five phases create a single PCR file able to treat the data file **EgyptMakeUp.xys**. Do the quantitative analysis using the Rietveld method, fixing the structural parameters. Use a different B_{ov} for each phase for empirically taking into account the absence of absorption correction.
4. Use the hkl-files generated in 2 for making a quantitative analysis without entering atoms in the PCR file. For details see the notes of 9 February 2007 and 3 July 2004 in the file fp2k.inf
5. What is the recipe for preparing this makeup powder (fractional mass of each component)?

Remark: The refinement can be improved significantly by adding the very minor phases: calcite CaCO_3 and dolomite $\text{MgCa}(\text{CO}_3)_2$. No absorption or Brindley correction is taken into account.