Determination of amorphous matter in industrial minerals with X-ray diffraction using Rietveld refinement

G. E. Christidis[1], K. Paipoutlidi[1], I. Marantos[2], V. Perdikatsis[1]

(1)Technical University of Crete, School of Mineral Resources Engineering, 73100 Chania, Greece
(2) Institute of Geology and Mineral Exploration (IGME), Spyrou Loui 1, 13677 Acharnes, Greece. christid@mred.tuc.gr

The presence of amorphous matter in industrial minerals and rocks during the quantitative analysis with X-Ray diffraction (XRD) is not always visible and its exact quantification may be difficult. This results to an overestimation of the remaining crystalline phases, because the quantitative analysis is normalized to 100 % for the crystalline phases, thus rendering the analysed sample not representative. Therefore, determination of the amorphous matter is an important task for complete assessment of industrial minerals. In this work we applied Rietveld refinement to determine and quantify the amorphous matter in a series of synthetic samples. The samples were examined on a Bruker D8 Advance Diffractometer equipped with a Lynx Eye strip silicon detector, using Ni-filtered CuKα radiation (35 kV, 35 mA). Data were collected in the range 3–70° 2θ with a step size of 0.02° and counting time 1 s per strip step (total time 63.6 s per step). The XRD traces were analyzed and interpreted with the Diffract Plus software package from Bruker and the Powder Diffraction File (PDF). The quantitative analysis was performed on random powder samples (side loading mounting) emplaced in Al-holders, by the Rietveld method using the BGMN computer code. The code performs quantitative analysis by varying the particle size and preferred orientation parameters.

Two series of experiments were performed. The first series included mixtures of synthetic quartz and calcite at 1:1 ratio containing 5, 10, 20, 25, 30, 40, 50 and 80% amorphous material. The second series included natural calcite and quartz at the same ratio and the same proportion of glass. In both experimental series corundum (α-Al2O3) internal standard with particle size <1 μm was added. The main difference between the two series of the experiments was particle size. The synthetic quartz and calcite had comparable particle size as the internal standard, whereas their natural counterparts were considerably coarser, being derived from a quartzite and a coarse grained marble respectively. Consequently they were ground with an agate pestle and mortar. The natural samples were free of impurities, within the accuracy of the XRD method. The aims of the work were to determine the accuracy in the determination of the amorphous matter, to evaluate the influence of particle size in the accuracy of the measurements and to identify the amount of glass at which the presence of the hump at 18-30 °2θ, the criterion to identify amorphous matter, becomes visible.

The accuracy of the quantitative determinations depends on the particle size of the minerals present in the mixtures (quartz and calcite) due to the microabsorption effect, and the difference between the particle size of the internal standard and the minerals. In the experiments with synthetic quartz and calcite without glass, the amounts of the minerals determined by quantitative analysis were comparable to the calculated values of the mixtures assuming particle size <1 μm (error ± 1-2%). In the mixtures with natural quartz and calcite similar error values between the experimental and the calculated abundances were observed for particle size <10 μm. In the synthetic samples good agreement between the calculated and the actual content was observed for assuming preferred orientation for calcite. By in contrast, in the natural samples good agreement between the calculated and the actual contents (error ± -2%) was observed for assuming preferred orientation for both minerals. In all cases increasing particle size led to increase of the calcite content and decrease of the quartz and the corundum (internal standard) contents.
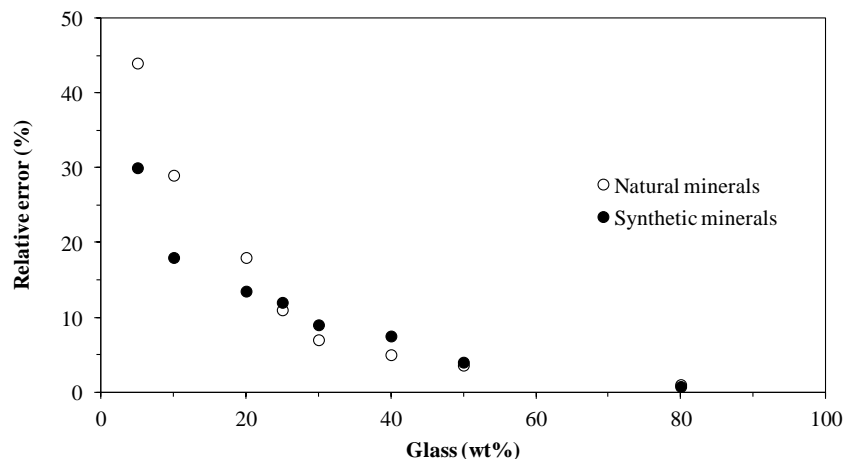

Figure 1. Relative error of determination of amorphous matter in mixtures natural and synthetic minerals.

The mixtures containing glass also showed similar trends in the mixtures of both the synthetic and natural minerals. In the experiments with synthetic quartz and calcite minimum errors were observed in experiments assuming particle size <1 μm, whereas in the experiments with natural quartz and calcite minimum errors were obtained assuming particle size <10 μm. In addition, particle size affects the absolute error of determination of amorphous matter. The relative error in natural samples was higher for amorphous matter contents lower than 20% (Figure 1). As expected, for higher amorphous matter contents the relative error decreased due to decreased uncertainty and it was comparable in the two sets of experiments (Fig. 1).

The XRD traces of the mixtures of both the synthetic and natural minerals showed the existence of a hump in the range 18-30 °2θ characteristic of the amorphous matter in mixtures containing more than 25% glass. For lower glass contents the hump was hot visible. The only indication for the presence of an additional phase undetected by X-rays was the gradual decrease of the intensities of the diffraction maxima of both calcite and quartz, with increasing amorphous matter content. This indicates that the lack of the hump is not a safe criterion for the recognition amorphous matter at low amorphous matter contents and that the presence of amorphous matter should be verified and quantified by the use of an internal standard. Rietveld refinement is a very promising technique in this aspect. Nevertheless, particle size should be carefully controlled for optimum results. It is suggested that particle size for more accurate determinations of amorphous matter should be lower than 10μm, preferably less than 5μm and that sample preparation should be carefully made to avoid preferred orientation of mineral phases.