Sample Preparation for X-Ray Diffraction Analysis

The XRD-Mill McCrone preserves the crystal lattice structure of the sample

With resources becoming increasingly scarce, innovative technologies allowing for sustainable use of raw materials are much sought after. The mineralogist Dr. Robert Moeckel is researching mineral and metallic raw materials at the Helmholtz-Institute for Technology of Resources in Freiburg, Germany which is part of the Helmholtz-Center Dresden-Rossendorf.

Dr. Moeckel´s research projects involve pulverization and homogenization of mineral samples prior to x-ray diffraction (XRD) analysis. This analytical method uses the fact that the wavelength of x-rays is similar to the atomic spacing in a crystal. The x-rays are diffracted at the atomic structures in specific angles (Bragg´s Law) which provide information on the atomic spaces in the crystals.
XRD allows to determine the order of different atoms towards each other which makes it possible to distinguish, for example, between coal and diamond which both consist of pure carbon. The main difference lies in their crystal lattice. The samples are pulverized to homogeneous powder before XRD analysis, and the individual crystalline phases are identified with the help of a data base. Quantification is done, for example, by Rietveld-Analysis which matches theoretical diffraction diagrams to the measured data. In recent years, XRD has been more widely used for research and development and quality control in industries like construction materials, minerals, cement or mining.

Sample homogenization in the XRD-Mill McCrone

RETSCH´s XRD-Mill McCrone was specifically designed for X-ray diffraction and is mainly used for applications related to mineralogy, cement industry, chemistry, geology, or material sciences, both in R&D and quality control. The unique grinding principle uses cylindric grinding elements and homogenizes the sample gently with friction while the crystal structure is preserved, an important premise for obtaining reliable X-ray diffractograms. The McCrone Micronizing Mill, which is the previous version of the XRD-Mill McCrone, is mentioned in many publications [e. g. 1-4]. The 125-ml polypropylene grinding jar is filled with 48 identical grinding elements, made of agate, zirconium oxide or corundum. After 3 to 30 minutes of grinding

volumes of typically 2 to 4 ml, the sample is perfectly homogeneous. Dr. Moeckel tested different types of mills for sample preparation to XRD analysis. He used a mixture of fluorite, barite, and quartz in a known ratio for the tests. The best results were achieved with the XRD-Mill McCrone (Table 1).

Testing sample mixtures for comparison of mills

The XRD-Mill McCrone is characterized by a gentle grinding mechanism with low energy input based on friction. In contrast, the Planetary Ball Mill PM 100 or the Mixer Mill MM 400 (both RETSCH mills) work with friction and impact, thus generating a higher energy input. The particle size distribution of samples ground in the XRD-Mill McCrone is very narrow and their crystal lattice structure remains intact which is ideal for x-ray diffraction. A mixture of minerals with 50 % fluorite, 43 % barite and 7 % quartz (w/w) with particle sizes suitable for the XRD-Mill McCrone (barite and quartz: 100 - 200 µm, fluorite < 400 µm) was ground to a fineness < 10 µm with the XRD-Mill McCrone, the Planetary Ball Mill PM 100 and the Mixer Mill MM 400. The samples were then analyzed (*Rietveld analysis*) with the x-ray diffractometer *PANalytical Empyrean* (Co-Kα-rays; Detector: PIXcel3D-Medipix3 1x1, 35kV/35mA, angle 5-80°2θ, increment 0.0131°2θ, total time of measurement 2.5h). Due to the high contrast difference for the applied x- rays between barite with high absorption and quartz or fluorite with low absorption, the particle size and particle size distribution have great influence on the results. Consequently, ingredients with higher absorption are underrated if the particle size is too big. Moreover, some sample materials react with partial glass formation on the particle surface if too much energy is applied during grinding. Hence, those parts cannot be detected by x-ray diffraction and are consequently underrated (like quartz in this case). As shown in figure 2, the height and the width of the peaks of those samples vary greatly due to the described physical effects. On the one hand, the particle sizes are too large for analysis by x-ray diffraction; on the other hand, glass formation has started on the surfaces (Table 1). The analysis results of the samples ground in different mills under different conditions show variations as well.

***Figure 1**: XRD-Mill McCrone oo RETSCH*

Table 1: Results of grinding tests with a sample 50 % fluorite, 43 % barite and 7 % quartz (w/w)

Mill	Sample amount	Parameter	Final fineness d_{90}	Fluorite, weight per cent %	Barite, weight per cent %	Quartz, weight per cent %
XRD-Mill McCrone	2.5 ml + 10 ml Ethanol	48 x grinding elements zirconium oxide; 12 min; step 4	9.51 µm	50.5 ± 0.4	42.7 ± 0.3	6.8 ± 0.2
MM 400	15 g + 6 ml Ethanol	Grinding jar zirconium oxide 25 ml; 40 g grinding balls zirconium oxide 2 mm; 30 min; 30 Hz	4.37 µm	51.7 ± 0.3	40.4 ± 0.3	7.9 ± 0.2
MM 400	10 g + 4 ml Ethanol	Grinding jar zirconium oxide 25 ml; 9 x grinding balls zirconium oxide 10 mm; 30 min; 30 Hz	11.42 µm	52.4 ± 0.3	42.5 ± 0.4	5.1 ± 0.2
PM 100	28 g + 9 ml Ethanol	Grinding jar zirconium oxide 50 ml; 110 g grinding balls zirconium oxide 2 mm; 5 min; 650 rpm	4.47 µm	49.0 ± 0.3	45.8 ± 0.3	5.2 ± 0.1

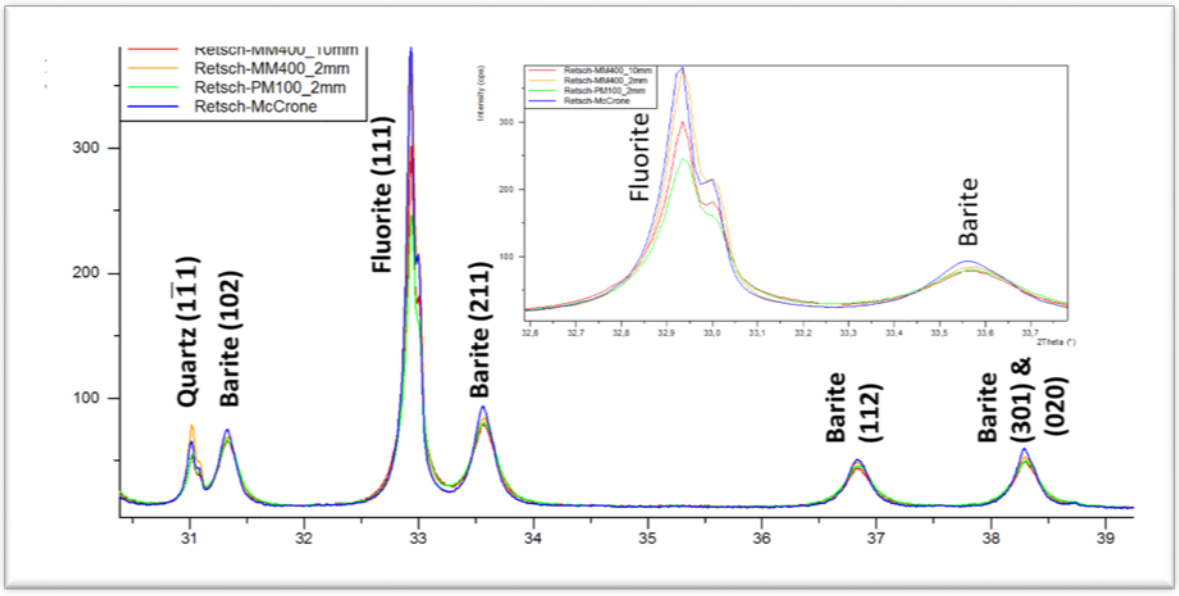

Figure 2: *Partial result of the diffraction analysis of the test mixture. The height and the width of the peaks differ clearly, depending on the previous sample preparation. Also, the integral intensities, which are used for quantification, vary.*

Conclusion

The gentle homogenization of samples which are analyzed by XRD, is an important prerequisite to ensure accurate results. RETSCH's XRD-Mill McCrone has been used for many decades for sample preparation to x-ray diffraction analysis. The unique grinding principle helps to preserve the crystal lattice of the sample much better than that of other mills, for example ball mills.

Application reports which mention the McCrone Micronizing Mill:

[1] Srodon *et al.* 2001, Clays and Clay Minerals, Vol. 49, No. 6, 514-528

[2] Weight *et al.* 2011, Mudstone Sedimentology, Vol. 81 No. 6, 743-764

[3] Kleeberg *et al.* 2008, Clays and Clay Minerals, Vol 56, 404-415

[4] Armitage *et al.* 2013, Journal of the Geological Society, Vol 170, 119-132

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