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Sample preparation for X-ray analysis

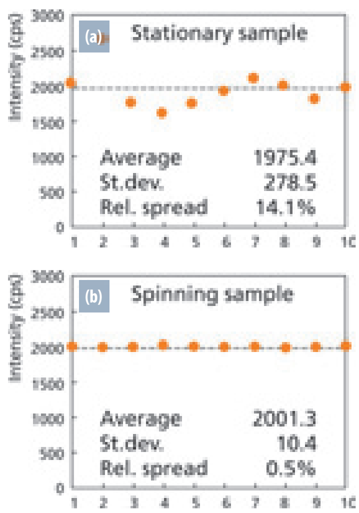
the critical first step

One of the many benefits of X-ray fluorescence (XRF) spectrometry and X-ray diffraction (XRD) is simple sample preparation. However, even though it is straightforward, it is still vitally important to get it right. In this article PANalytical demonstrates that good sample preparation is the critical first step to consistent and reliable X-ray analysis.

Figure 1, right: Particle statistics effects.
(a) Good statistics: all diffraction peaks within the diffractogram produced by a similar number of crystallites (true pattern).
(b) Bad statistics: diffraction peaks produced by different numbers of crystallites (false pattern).

Figure 2, bottom: Mica thin layer sample: dusted vs. pressed.

Figure 3, below: Effect of sample spinning.



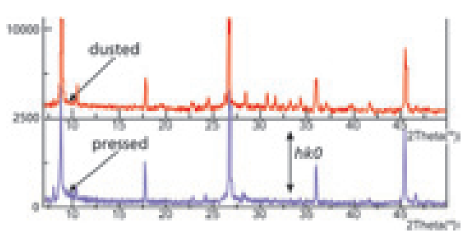
The use of X-ray analysis in the cement industry has increased considerably in recent years. While X-ray fluorescence (XRF) is the universally accepted standard method for raw material control, X-ray diffraction (XRD) is now also proving to be an essential technology in this rapidly evolving industry. The increased use of XRD has been helped by the development of advanced instrumentation, enabling the method to replace traditional calibration, wet chemical or Bogue methods for quantitative clinker and cement crystalline phase analysis.

X-ray analysis enables optimised use of raw materials, reduces the energy costs of production and controls product quality, while also providing the necessary level of analysis for alternative raw fuels, such as hazardous waste fuels. These attributes are vital in today's climate of stringent environmental legislation and rising energy costs.

Simple to learn, easy to use

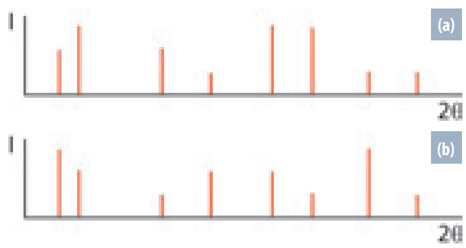
The key requirements of sample preparation for both XRF and XRD are that samples are homogenous and representative of the source material. Additionally, the composition of the sample should not be altered before or during the preparation process.

Fortunately, X-ray analysis usually requires only very simple, inexpensive, sample preparation work. Methods are both easy to learn and easy to use. Therefore, even when the need for good sample preparation is taken into account, X-ray analysis is a much easier and quicker process than almost all other chemical analysis techniques.



Sample preparation for XRF

For high quality XRF analysis in cement production, reproducible sample preparation and a good calibration of the XRF spectrometer are essential.



However, this can be difficult as there are few suitable reference materials available. Furthermore, available standards may not have the same mineralogy as local samples, which can lead to inaccurate data.

Preparing samples as pressed pellets is widely regarded as the most effective and economical way of preparing samples for routine control in cement production. Good sample preparation can minimise two of the major effects that can lead to bad data—particle size and mineralogical effects:

Particle size effects

These arise due to the penetration depth of X-rays. If large, unrepresentative particles are analyzed in the top layer of a sample, X-ray data will provide information about the composition of these large particles, not the overall sample composition.

Mineralogical effects

These happen when a single element is present in different phases, a sample that has silicon present as both silica and silicate, for example. To prevent problems, it is important that when pressed powder samples are measured, the standards and samples have the same mineralogical composition.

Sample preparation for XRD

XRD is a powerful tool for the analysis of the phase properties of samples. As with XRF, good sample preparation helps minimise errors and ensures good statistical representation. A measurement on a single sample must give

Expertise from sample preparation to analysis result

As world leaders in X-ray analysis systems, with over 50 years of experience, PANalytical is at the forefront of X-ray analysis sample preparation methods. The company's comprehensive range of manual and automatic, advanced sample preparation systems helps users create perfectly prepared samples.

The range includes the compact, bench-top MiniMill 2, which grinds samples at low cost with a high degree of reproducibility; and the MiniFuse 2 and Perl'X 3 instruments which offer, respectively, semi- and fully-automatic high quality fused bead preparation.

From left: Bench-top MiniMill 2, Perl'X and MiniFuse 2.

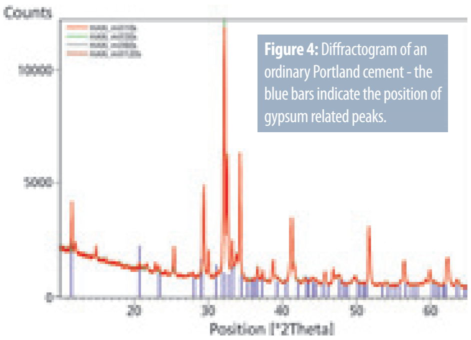


Figure 4: Diffractogram of an ordinary Portland cement - the blue bars indicate the position of gypsum related peaks.

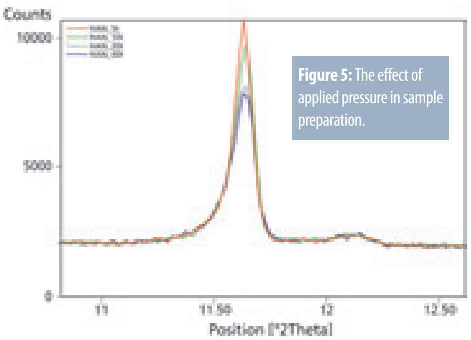


Figure 5: The effect of applied pressure in sample preparation.

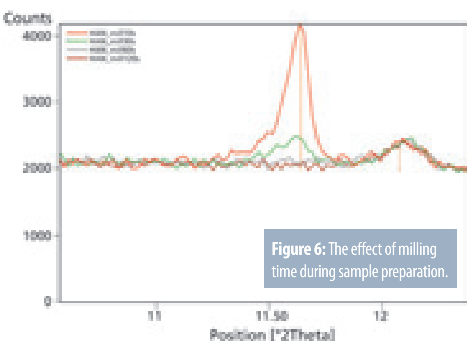


Figure 6: The effect of milling time during sample preparation.

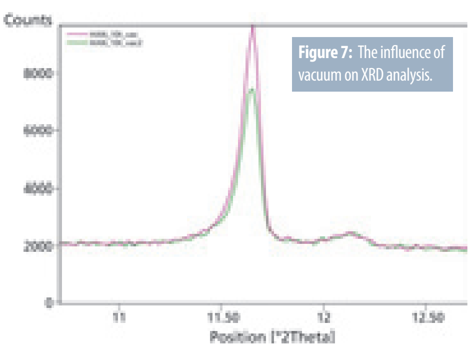


Figure 7: The influence of vacuum on XRD analysis.

the same result as an average measurement on a number of the same samples. Inadequate sample preparation can lead to significant variation, which is difficult to correct following analysis.

Particle size

Particle size is an important aspect in sample preparation for XRD. The particle should not be too big, because of particle statistics (also known as crystal statistics) effects. Crystal statistics cause incorrectly measured intensities. In severe cases, these effects also influence the shape of the peaks. In this instance, peak shapes are not smooth but show a jagged outline, which affects peak intensities (see Figure 1).

Equally, the particle should not be too small. This can cause damage to the crystal structure or alteration of phases, making it difficult to identify or quantify the actual phases present in the sample.

Orientation effects

Additionally, preferred orientation effects, which can be induced merely by touching a sample, play an important role for the analysis of, for example, gypsum and calcite samples. Figure 2 shows comparison between dusted (random orientation) and pressed (preferred orientation) samples. Reflections of type hk0 disappear in the pressed sample.

Instrumental parameters and sample preparation solutions

For good crystal statistics, a large number of crystallites should contribute to the diffraction process. This can be achieved by grinding samples to reduce the average particle size. A range of grinders is available for this process, many of which are optimised for specific powder types. It is important to identify the optimum level of sample grinding, or broadening of peaks can still occur if particles are too small or if lattice damage occurs. Therefore, thorough investigation of different grinding methods is essential.

There are many sample preparation techniques that address the problem of preferred orientation effects, including back- or side-loading, surface roughening, use of amorphous filler or isostatic pressing. Additionally, modern X-ray analysis instruments are equipped with spinning sample holders, greatly reducing the influence of sample orientation (see Figure 3).

Influences of sample preparation parameters

A very important aspect of sample preparation, particularly for cementitious materials, is ensuring that a sample's physical properties are not altered during preparation. This is achieved by monitoring the effects of certain parameters, such as applied pressure and milling time, prior to actual sample measurement.

Figures 4-7 show data from studies to determine the influence of various parameters on sample preparation. The data underline the importance of monitoring and controlling influential parameters during the sample preparation process. These results cannot, however, be used to extrapolate a trend to other samples because cements differ widely in composition.

Influence of pressure

The Portland cement analysed in the diffractogram in Figure 4 was used to study the effects of applied pressure when samples are pressed as part of the preparation method. The results on peak intensity are clearly visible in Figure 5. The higher the applied pressure, the lower the intensity of the peak. This effect is caused by the loss of crystal water, which alters the physical property of the cement.

Influence of milling time

Various milling times were applied to samples of the Portland cement. The results are shown in Figure 6. It can be concluded that the longer the milling time, the lower intensity of the peak.

Measurements under vacuum

Once milling time and pressure parameters have been optimised, the selection of the right measurement sequence must also be considered. With XRD technology becoming increasingly commonplace in the cement industry, a manufacturer may have the option to perform both XRD and XRF analysis. However, with XRF analysis, cement samples are usually measured under a vacuum, which has an effect on subsequent XRD measurement.

Figure 7 shows the influence of a vacuum on cement samples. Here, an XRF measurement has been conducted under vacuum, followed by XRD analysis. This results in reduced peak intensity. In this example, the reduced intensity of the gypsum peak occurs because the gypsum phase is partly transformed into a semi-hydrate phase.

Conclusion

For many years, XRF has been at the heart of production control in every modern cement works. Now, to keep pace with industry needs, advanced XRD technologies are also becoming increasingly commonplace. Both are used routinely—as the principal means of controlling composition of raw materials, raw feed, clinker and cement.

As reliance on X-ray analysis increases, so too does the importance of good sample preparation. This, and the correct measurement sequence, ensures the highest possible accuracy and precision.