High-throughput, high accuracy pellet prep for XRF

In this issue: Preparation is key to success

In busy laboratories that are working constantly to make samples for XRF and other elemental analyses, pellet preparation is essential for quick turnover of samples and ease of sample handling. Different sample preparations also yield results that are both quantitatively and qualitatively different: but how different?

Read on to discover how pressed pellet sample preparation even improves the quality of your XRF spectra and enables accurate quantification to be obtained.

Part 1 - Advantages of Pressing Pellets for XRF

The analytical signal in XRF spectroscopy contains two major components: 1) X-rays emitted at characteristic wavelengths corresponding to electron transitions within the sample atoms; superimposed over 2) a continuous background of X-rays scattered by the outer electrons.

The characteristic X-rays generally emerge from depths on the order of 1-1000 µm below the surface of the sample, with the depth dependent on atomic weight; lighter elements are harder to detect than heavier ones.

Particle size, mineral composition, or density can all affect the intensity of the characteristic emission peaks and increase background scattering. These effects rule out reliable quantification of sample composition (1).

Grinding sample powders to a fine particle size and pressing them into a smooth, flat pellet should reduce scattering and improve the detection of light elements.

Here we investigate how the XRF signals produced from pressed pellets differs from the uncompressed powder.

Experimental

Samples of Type 1 Ordinary Portland Cement (Dragon Alfa, UK) were used as-purchased.

Loose powder preparation

10 g of sample was placed into an open-ended sample cup and covered with a 6 µm Mylar® film window.

Pressed pellet preparation

The sample was milled and homogenized with 20wt% of cellulose binder (SpectroBlend®) using a planetary ball mill. Pellets were pressed in aluminium sample cups at 20 tonnes using a 25 T Specac Autotouch Press.

Spectral acquisition

Spectra were recorded on a high-throughput wavelength dispersive XRF instrument with vacuum capability.

Results & Discussion

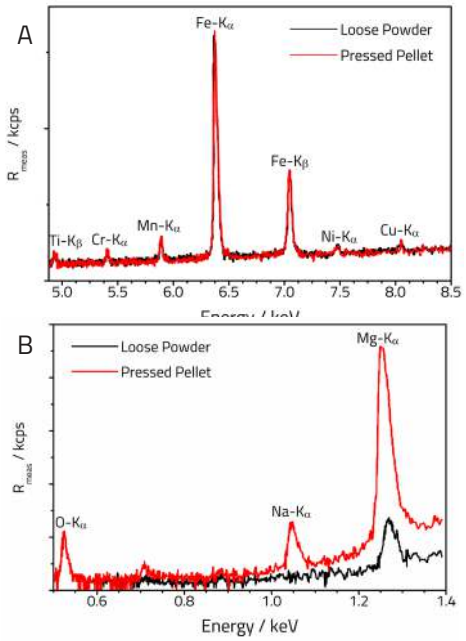


Figure 1. Spectral comparison for (A) heavy elements and (B) light elements in cement samples

Heavy and light elements

XRF spectra for the loose powders and pressed pellets show clear differences (Figure 1). The lightest element Na is undetectable in the powders, while the signals from Mg, Al, and Si are much reduced. As expected, the signal from the heavier elements such as Fe is not affected.

The samples prepared as pellets show higher signal-to-noise and allow the lightest elements to be detected easily above the background. The detection of light elements is further improved by avoiding the use of thin film coverings, which allows measurement under a vacuum.

Quantification of composition

The ability to clearly detect all the elements in the sample becomes critical for accurate quantification, as can be seen in Table 1. In the powder samples, underestimation of the lighter Al, Mg, and Na elements leads to overestimation of Fe and Ca in the cement. The pellet samples result in a quantification which is within the range established by averaged laboratory experiments.

Conclusions

Loose powder sample preparation is a low-intensity method for the detection of heavy elements; however, quantification is unreliable due to the inability to detect lighter elements.

Therefore, pellet preparation is essential for accurate quantification of sample composition. It allows detection of the lightest elements and prevents underestimation of the other light elements.

Part 2 - Optimising workflows for pellet preparation

The preparation procedure for XRF testing has three main steps once the samples arrive at the lab.

First, samples need to be crushed, ground, or milled into a fine powder using various kinds of milling machine. Then they ought to be sieved to ensure an even particle size distribution.

Second, a cellulose or boric acid binder is added to help the powder grains adhere under high pressure and form a solid pellet. The binders must be composed of light elements like B, C, N, and O to avoid detection by the XRF. The mixture is homogenised by ball milling for several minutes.

Third, the homogenised powders are pelletised using a press and a pellet die.

Often, all three stages are operated by one person, moving successively between them. Simplifying or removing steps involved in any one of them can speed up the overall workflow.

Manual pressing operation

The simplest hydraulic press systems use a separate, multi-piece pellet die. It consists of a body with a cylindrical bore, a plunger of matching diameter, a base, and two polished internal discs which are in direct contact with the powder material.

Pellet die components disassembled

These parts are assembled into a die which is axially compressed using a hydraulic press. The powders trapped between the two polished discs will cause the powders to compact and coalesce into a solid, circular pellet the same diameter as the die bore.

Assembled pellet die

The pellet cannot be easily removed from the die bore due to residual strain created by the relaxation of the die itself and a slight expansion of the pellet. To remove it, the base of the die is removed and replaced with a hollow extraction sleeve or cap. This allows us to remove the pellet by forcing the plunger through the die body under load from the press.

Schematic of the workflow for pressing with manual dies

All these steps require time consuming handling of the dies and samples. The cycle time for the pressing procedure is typically 3-4 minutes per sample with additional time for milling and homogenising. 10-15 samples per hour can typically be produced with these methods.

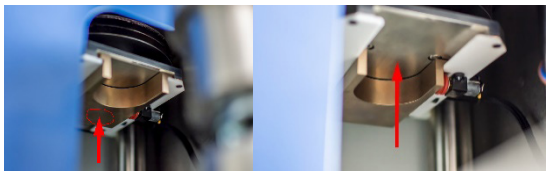
Automated pressing cycles

An alternative design of die uses a spring-loaded plunger acting from below the die body. The die is open at the top and contacts the press piston directly.

Spring-loaded pellet die

The procedure for forming the pellet is the same as before: add the powders, press to form the pellet, and then add an extractor cap to press the pellet out of the top of the die body.

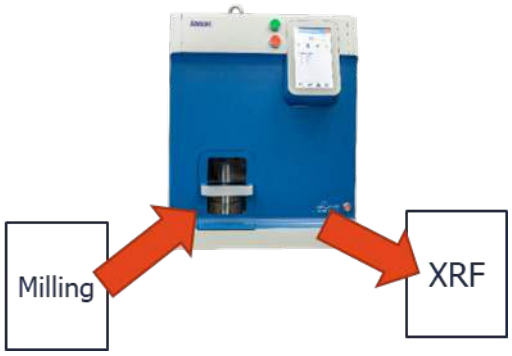
The difference is that we can fully integrate this kind of die with the press. Specac's APEX press features a motorised pressure plate attached to the piston ram, which can shift between pressing and releasing positions under control of the press programming. This is known as Quickshift Technology.



Pressing position (left) and extraction position (right)

We still require two activations of the press, one to compress the sample and a second to extract it, but now it is all being handled automatically. The die itself also stays with the press, meaning we are not handling it directly either.

With this method, the pressing time reduces to around 2-3 minutes per sample and can run automatically while lab staff return to milling or homogenising the next samples. The overall sample rate is around 20-25 per hour.



Schematic of the workflow for pressing with APEX

Pressing with steel supporting rings

The final common method of pressing samples is the supporting ring method.

A pellet die designed to accept rings has a recess which the ring fits into loosely enough to be removed by hand. The pellet will be captured inside the ring during compression.

Because it is loose fitting, the sample can be removed easily after a single activation of the press and sent directly for analysis.

The workflow involves having enough steel rings to produce a whole batch of samples. Once the samples have been analysed on the XRF instrument, they can be broken out of the steel rings with a mallet or other tools. The rings are then returned for reuse.

This process ends up being much faster overall due to the single-stage of pressing required. Cycle times for a single sample are usually in the vicinity of 60 seconds. Some time has to be allowed for the other workflow steps, including returning the used rings to the process, but it is still possible to make 40-45 samples per hour with this method.

Conclusions

Automations which reduce the amount of physical handling of dies and die parts can improve both the speed and physicality of making pellets for XRF sample analysis.

Forming pellets inside reusable steel rings is a significant improvement because they slot easily into the die by hand and do not require a second stage of pressing to remove. However, since samples are then analysed in the ring, a supply of several such rings is required to make a batch of samples for analysis.

References

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