

The successful use of spectrometers in the analytical laboratory requires an understanding of the method and profound practical experience. Everyday routine often does not leave the users enough time to develop and optimise the methods. Some analysis technologies require elaborate external trainings of the laboratory workers which delays the use of the instruments and reduces their acceptance among the users.

X-Ray Fluorescent Analysis is an exception as the sample is analysed in solid form and the measurements are easily carried out. Therefore, this method is well established in areas where quick results are essential, e.g. for quality checks during production.

As XRF measurements are so simple to carry out, the importance of reliable sample preparation is often neglected. This can lead to insufficient reproducibility and even to wrong analysis results.

For XRF analysis, the laboratory sample consisting of a few grams often has to represent a total amount of several tons. Beside the quality of the spectrometer, the quality of the sample preparation has a decisive influence on the precision and reproducibility of the analysis results.



Figure 1. From laboratory sample to pellet

The “art of milling” consists in turning a laboratory sample into a representative part sample with homogeneous analytical fineness

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REPRESENTATIVE SAMPLE PREPARATION FOR XRF ANALYSIS

PREPARING HOMOGENEOUS SAMPLES BY MILLING

The “art of milling” consists in turning a laboratory sample into a representative part sample with homogeneous analytical fineness (Figure 1). When selecting a suitable mill and grinding tools it should be taken into account that the material properties to be determined (e.g. heavy metal traces by XRF analysis) are not altered in any way during the sample preparation process. This not only requires a thorough knowledge of the instruments but also some experience in the preparation of different materials. Finally, care should be taken that possible abrasion from the grinding tools does not interfere with the analysis results.

XRF ANALYSIS OF DOLOMITE

The deeper the x-ray enters the sample, the more it interacts with atoms. This means that the part which is absorbed by the sample is increasing so that from a defined thickness onwards, the x-ray light can no longer penetrate the sample. In turn this also applies to the fluorescent light which needs to leave the sample in order to be detected.

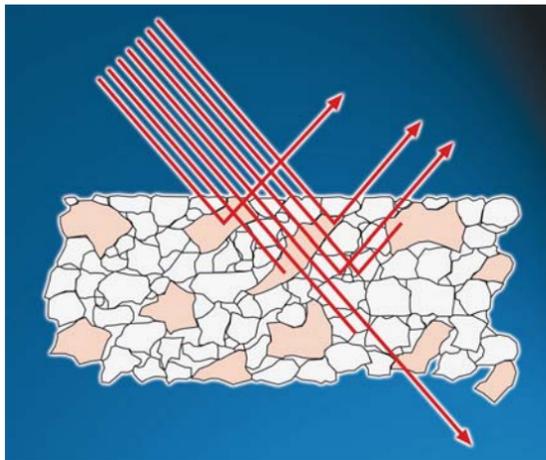


Figure 2. Saturation depth. Only a part of the fluorescent light leaves the sample

The lowest detectable sample layer is called saturation depth (Figure 2). It depends on the intensity of the x-rays, the wave length (i.e. the type of detected atom) and the density of the sample's surroundings (the matrix). If different elements are analysed in the same surroundings, the saturation depth increases with increasing atomic number of the element in question. Table 1 shows this correlation for dolomite.

Table 1. x-ray saturation depth of different elements in a dolomite sample.

Element	Atomic number	Saturation depth
Fe	26	170 µm
Mn	25	140 µm
Ca	20	100 µm
K	19	80 µm
S	16	30 µm
Al	13	10 µm

The general rule says that the saturation depth decreases with the atomic number which means that the element becomes more difficult to detect and with less reproducibility. That is the reason why elements such as carbon and boron emit very weak fluorescent signals.

PREPARING SAMPLES FOR XRF ANALYSIS

When preparing samples for XRF analysis, care should be taken that the size of the particles to be examined lies within the saturation depth of the x-rays to obtain a representative analysis result. This means for the dolomite sample that a fineness of 80 microns is only necessary if elements lighter than potassium have to be analysed.

Otherwise, a grind size of 100 microns, which can be obtained with any suitable laboratory mill quickly and easily, is sufficient.

Frequently, sample materials come in large amounts and great feed sizes which makes a preliminary size reduction necessary. After preliminary size reduction a part of the sample is subjected to fine grinding. This part sample must be representative, i.e. have the same properties as the total amount in order to obtain reliable information about the composition of the complete sample. Dry, pourable bulk samples can be fed to rotating dividers via vibratory feeders whereas sample splitters are suitable for heavily flowing materials.

The part sample thus obtained is then subjected to pulverisation. The most frequently used mill for the size reduction of hard and brittle sample materials for subsequent XRF analysis is the Vibratory Disc Mill (Figure 3). Inside the grinding jar the grinding tools, usually a puck and a ring, are moved in such a way that the sample is crushed by impact and friction effects. With this size reduction principle the required reproducible analytical fineness is achieved after very short grinding times. This is a decisive advantage when the analysis results are needed quickly, e.g. for a product approval.



Figure 3. Retsch Vibratory Disc Mill RS 200

Small sample volumes can also be processed in a Mixer Mill (Figure 4). Here, the grinding jars perform radial oscillations in a horizontal position. The inertia of the grinding balls causes them to impact with high energy on the sample material at the rounded ends of the grinding jars.



Figure 4. Retsch Mixer Mill MM 400

PRODUCTION OF PELLETS

For most XRF applications pellets with a plane surface are used. In contrast to loose powder, a pellet has the advantage that the element concentration detected by the x-ray is higher because the material is more compact. In addition, a smooth surface is preferable to a rough one from an optical point of view. Usually, pellets are either produced by fusion of the sample with salt or by pressing the sample.

Fusion of the sample with lithiumtetraborate is a very effective method of producing a bead.

The sample is weighed together with the flux in a platinum crucible, then the crucible is heated up in a fusion machine to more than 1000 °C. This process destroys the original matrix and creates a homogeneous borate glass. This method yields highly reproducible results, regardless of the original material.

However, this method also has a few disadvantages. Volatile elements such as thallium or cadmium tend to escape during the fusion process and therefore cannot be detected. Moreover, the sample is heavily diluted with lithium salt (factor 10 - 50) which impairs the detection limit compared to pellets. Certain elements (e.g. boron, iron, carbides) could even damage the very expensive platinum crucible. Finally, it takes much more time to produce a bead than a pellet (15 minutes compared to approx. 2 minutes).

Therefore, pressing a pellet is the most common procedure for many applications – even though calibration of the spectrometer is more elaborate due to the sample matrix. A pressed pellet should basically fulfil the following quality criteria:

1. it must be homogeneous
2. the pellet must be absolutely solid as loose particles pollute the x-ray tube
3. the pellet should be stable (and storable)

Pressing the sample can be carried out with or without auxiliary materials. The most frequently used materials are cellulose-based or paraffin-based. Cellulose has the advantage of acting as grinding aid at the same time thus avoiding caking of the sample inside the grinding jar. Cellulose can be used in vibratory disc mills as well as mixer mills.

Wax is added after the sample has been ground, either manually or by mixing it with the help of polyamide balls in a plastic jar in the mixer mill. The addition of wax makes the pellet's surface indelible. Moreover, wax is more inexpensive than cellulose and not hygroscopic which is important if the pellets are to be stored. To stabilise the pellets either steel rings or aluminium cups are used (*Figure 5*). The cups can be labelled on the reverse side and are useful for storing the pellets.



Figure 5. Retsch Pellet Press PP 40