

X-ray diffraction (XRD) as a fast industrial analysis method for heavy mineral sands in process control and automation—Rietveld refinement and data clustering

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X-Ray diffraction (XRD) provides useful information about the composition of an ore sample in terms of quantification of crystalline phases and amorphous content. The use of new, fast detection systems in XRD creates the opportunity to use this technique in modern process control.

In the analysis of heavy mineral sands, XRD can identify the main mineral phases, such as ilmenite FeTiO_3 , rutile TiO_2 , Zircon ZrSiO_4 and quartz SiO_2 , and any other minor components present, such as anatase TiO_2 , magnetite Fe_3O_4 , haematite Fe_2O_3 or monazite $(\text{Ce, REE})\text{PO}_4$.

Quantitative analysis is possible by various classical methods such as straight line or polynomial calibration with standards, but modern quantification analysis techniques such as Rietveld analysis (Bish and Howard, 1988) are attractive alternatives, as they do not require any standards or monitors. These methods offer impressive accuracy and speed of analysis. The Rietveld method compares calculated versus experimentally derived X-ray powder diffraction patterns for the sum of all crystalline phases.

Another analysis technique offering great benefit to mining industries is cluster analysis. Enormous amounts of XRD measurement data are generated during the process control and material evaluation. New ways of handling such vast amounts of data are required to produce meaningful information for the end users. Cluster analysis greatly simplifies the analysis of a large amount of data from different processes or different raw materials, and automatically sorts closely related scans of an experiment into clusters and marks the most representative scan of each cluster as well as outlying patterns. The use of cluster analysis to evaluate the XRD data allows fast and reliable tracking of the process. It is the most economical procedure to have automatic data evaluation without involving any dedicated personnel in the process.

Details of the techniques used, sample optimization methodologies, results, data precision and limitations will be discussed. The approach has potential as a relatively inexpensive, reliable tool, useful in the characterization of heavy minerals sand materials.

Analytical methods

X-Ray powder diffraction

X-ray powder diffraction (XRD) is a versatile, non-destructive analytical method for the identification and quantitative determination of crystalline phases present in powder and solid samples. Identification of phases is achieved by comparing measured data to a reference database, the most comprehensive of which is maintained by the International Centre for Diffraction Data (ICDD). This decades old technique has been a standard technique for qualitative analysis of mineralogical phases, but quantitative methods were often difficult when the technique called for pure phase standards. The reference intensity ratio (RIR) method is a quantification method that can give a quick analysis, but is subject to inaccuracy due to preferred orientation of crystals in the sample.

Modern quantification analysis techniques such as the Rietveld analysis are attractive alternatives, as they do not require any standards or monitors. These methods offer

impressive accuracy and speed of analysis. Modern XRD equipment (Figure 1) is also capable of producing data of sufficient quality for Rietveld analysis in just minutes, instead of an hour or more with traditional detectors, making it more amenable to process control.

Rietveld analysis

The Rietveld method compares calculated vs. experimentally derived X-ray powder diffraction patterns for the sum of all crystalline phases, adjusting a wide-variety of crystallographic-, chemical- and modal-abundance parameters until the two are in agreement. The Rietveld method is a full-profile (rather than single peak), diffractogram-fitting technique that generates calculated diffractograms and attempts to match these to experimentally derived ones. It operates by calculating a theoretical diffractogram for all given phases, then proceeds through a series of least-squares iterations wherein a variety of experimental (e.g. background, two-theta displacement)

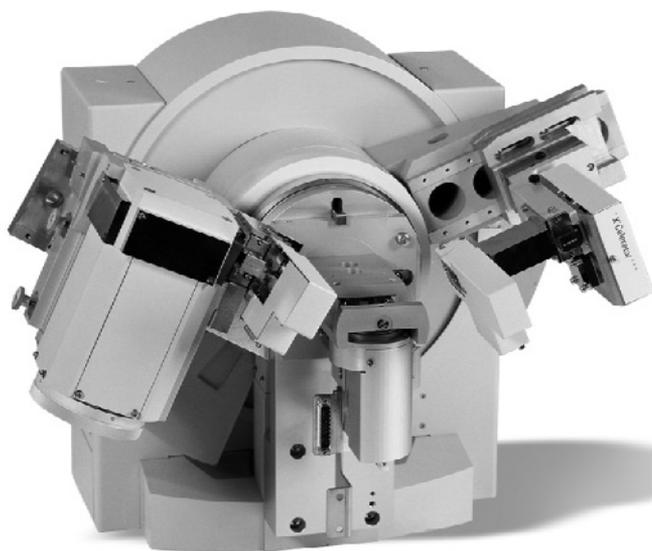


Figure 1. Modern XRD equipment such as this from PANalytical incorporate computer controlled slit optics, a variable speed spinner stage, and a solid state X'Celerator detector to produce high resolution data in a fraction of the time traditionally required—up to 100 times faster

and physical (e.g. unit-cell parameters, site-occupancy factors) parameters are varied until a defined convergence value (goodness of fit; GoF) is obtained.

The result is a calculated X-ray diffraction profile that best fits an experimental profile, in terms of intensity, peak position and peak shape. For samples with amorphous content, a known quantity of an internal standard may be incorporated in the sample to calculate a weight fraction of amorphous content in addition to quantifying the crystalline phases.

The strengths of the Rietveld method (Rietveld 1969) are:

- Suitable for homogeneous or heterogeneous samples
- Works with powdered materials
- Relatively fast
- Cost-effective
- Effective at distinguishing between phases that may differ only subtly from one another
- Capable of producing quantitative modal abundances for the phases being analysed (down to < 1 %)
- Better handling of overlapping peaks compared to traditional methods such as a straight line calibration or the use of relative intensity ratios (RIR).

Some limitations of the Rietveld method include:

- Requires the atomic structure of phases to be known
- If phases are missing, the results are relative weight percentages, not absolute weight percentages
- It is sometimes difficult to extract modal data for samples containing two or more minerals of the same family (e.g. amphiboles)
- The best results are obtained when one has an understanding of mineralogy, crystallography and both the overall philosophy and approach to a successful Rietveld analysis.

Cluster analysis

Modern X-ray diffraction equipment allows the rapid collection of hundreds of scans in a short time. This can be useful in application areas such as process and quality

control in minerals and mining industries. For such a large amount of data, it is impossible to analyse every individual measurement. This implies that a data reduction tool is required. Cluster analysis is a method that uses statistical methods to simplify the analysis of large amounts of data by:

- Automatically sorting all scans of one or more experiments into classes of closely related scans
- Identifying the most representative scan of each class
- Identifying the two most different scans of each class
- Identifying outliers not fitting into any class (non-members).

This drastically reduces the amount of data that has to be processed, because only representative scans, outliers and sometimes the most different scans must be analysed in more detail. Further cluster analysis can be used to discover hidden features/structures in the data.

Comparisons of the full peak and profile of every powder diffraction pattern in a set of n patterns with every other pattern can be presented as a correlation matrix (Figure 2). The correlation matrix is used as input to a hierarchical agglomerative cluster analysis, which puts the patterns into classes defined by their similarity. This method starts with each data-set representing a distinct cluster. At each step of the analysis, two clusters with the highest degree of similarity are merged into a single cluster. The process stops with the final step, when only one cluster containing all data-sets remains. The result of this analysis step is usually displayed as a dendrogram (Figure 3). A well known and in principle unsolved problem is to find the 'right' number of clusters. (Kelley, Gardner, and Sutcliffe, 1996). This means cutting the dendrogram at a given dissimilarity and retaining a meaningful set of clusters, whereas the scans inside a cluster are closely related while the different clusters are different enough to keep them apart. Principal Components Analysis (PCA), Figure 4, can be carried out as an independent method to visualize the quality of the clustering. The correlation matrix is used as input.

Analysis of heavy mineral sands

Heavy mineral sands are a class of ore deposit, which is an important source of zirconium and titanium. These sands are placer deposits formed most often in beach environments by concentration due to the specific gravity of the mineral grains.

Within the 21st century, the lowest cut-off grades of heavy minerals, as a total heavy mineral (THM) concentrate from the bulk sand, in most ore deposits of this type is around 1% heavy minerals, although several are higher grade. Of this total heavy mineral concentrate (THM), the components are typically:

- Zircon, from 1% of THM to upwards of 50% of THM
- Ilmenite, generally of 10% to 60% of THM
- Rutile, from 5% to 25% of THM
- Quartz
- Trash minerals, typically magnetite, garnet and chromite, which usually account for the remaining bulk of the THM content.

Generally, as zircon is the most valuable component and a critical ore component, high-zircon sands are the most valuable. Being ancient stranded dune systems, the tonnage of most deposits is in excess of several tens of millions of tons to several hundred million tons.

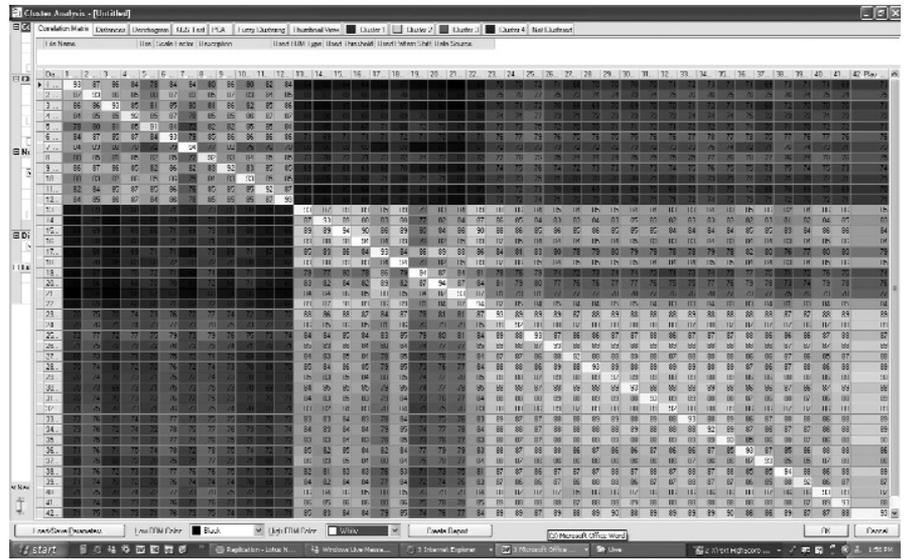


Figure 2. Screenshot of the correlation matrix, generated by comparing data-set with each other. It is used as input to a hierarchical agglomerative cluster analysis, which puts the patterns into classes defined by their similarity (black = low similarity, white = high similarity)

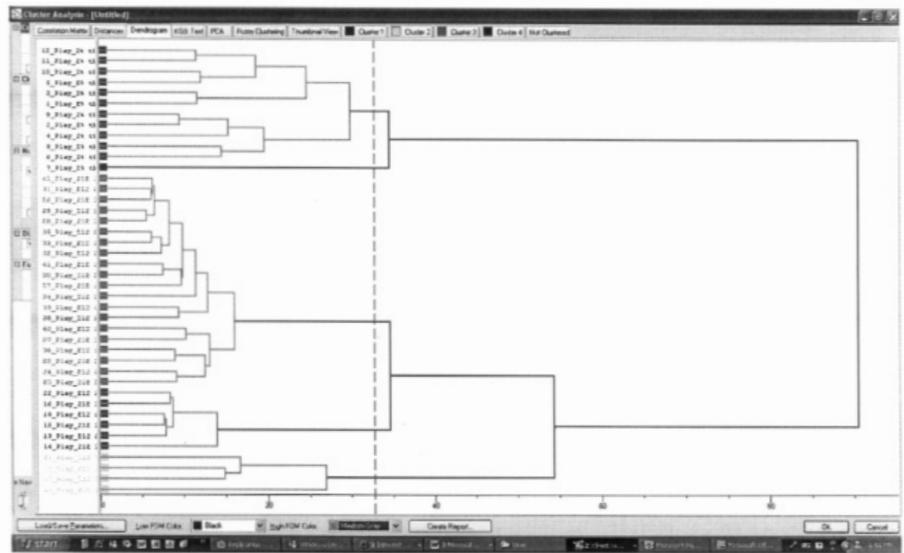


Figure 3 The dendrogram (screenshot) is a graphical display of the result of an agglomerative hierarchical cluster analysis (actual cut-off indicated by a stippled line). Each pattern starts at the left side as a separate cluster, and these clusters amalgamate in a stepwise fashion, linked by vertical tie bars. The horizontal position of the tie bar represents a dissimilarity measure

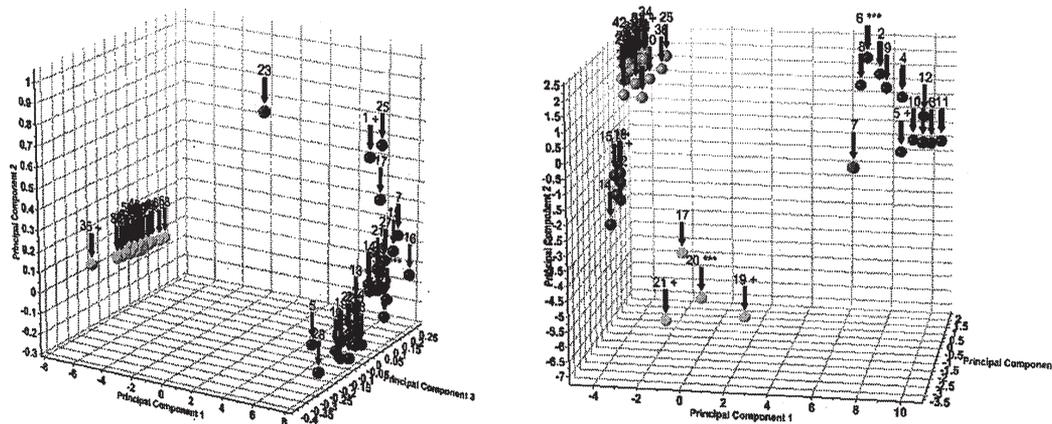


Figure 4 The PCA score plots for the two different experiments (left the reproducibility measurements, right the samples from the different process steps)

Sample preparation

The grain size of heavy mineral samples from typical heavy mineral dune sand is too large to be analysed directly since the suggested particle size for powder XRD measurements should be less than 10 μm (Brindley 1945). The samples were ground for 20 seconds in a disk mill with a tungsten carbide (WC) grinding vessel before pressing it for 30 seconds with 10 tons into steel ring sample holders, which can be used with (semi-) automatic sample preparation equipment with a piston diameter of 35 mm (Figure 5, right). 10% wax was added to the samples as a binder.

The measurements were done on a PANalytical X'Pert PRO MPD (Multi-Purpose Diffractometer) using the X'Celerator detector and a cobalt tube with incident iron filter. This type of radiation is especially suited to iron bearing materials, as it produces high resolution data unhampered by the sample fluorescence, which is an issue for copper radiation (Klug and Alexander 1974). A measurement time of 4 minutes 50 seconds was chosen to get sufficient intensities for the peaks. In order to get a better peak to background ratio, the beta filter (Fe) was placed into the incident beam path (Figure 6).

Phase identification

Figure 7 shows the results for phase identification of a concentrate of a typical heavy mineral dune sand sample. Ten phases were identified. The sample contains, besides ilmenite, rutile, and zircon also significant amounts of haematite. Additional smaller amounts of anatase, quartz, actinolite, epidote, diopside and almandine were identified.

The peak around 25 $^{\circ}2\theta$ is caused by the wax used for the preparation and is not taken into account for identification and quantification.

The identification was done with the software X'Pert HighScorePlus. The search-match algorithm used the reference database PDF4+ of the International Center for Diffraction Data (ICDD) to identify the phases.

The ICDD database contains a relative intensity ratio (RIR) value for a number of entries, which allows the calculation of semi-quantitative results. Due to the preferred orientation of some phases, this method is not recommended for samples containing, for example, amphiboles and pyroxenes. This leads to a strong overestimation of these phases, resulting in the incorrect calculation of all other phases since the RIR method calculates all identified phases to 100%. More reliable results were found using the full pattern refinement H. Rietveld (1969). A comparison between the results of the two methods is shown in Table I.

Quantification

The quantification of the phase content can be made using two different methods besides the semi-quantitative RIR method:

- Straight line calibration using standard mixtures
- Standardless Rietveld method using the whole powder pattern, 10 to 70 $^{\circ}2\theta$.

Calibration based method

In this method, quantitative phase analysis is done by

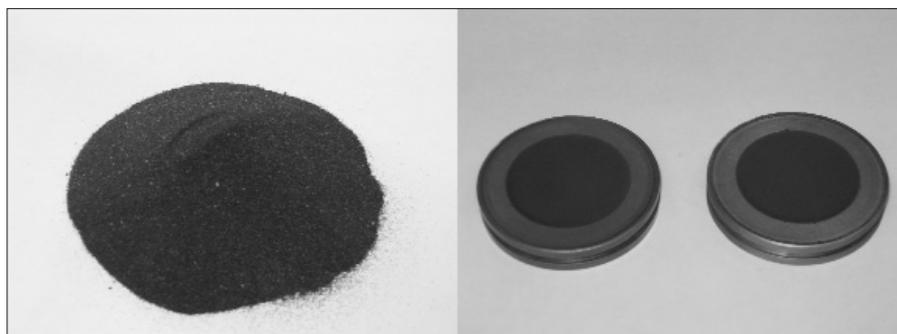


Figure 5. Raw (left) and prepared (right) heavy mineral samples

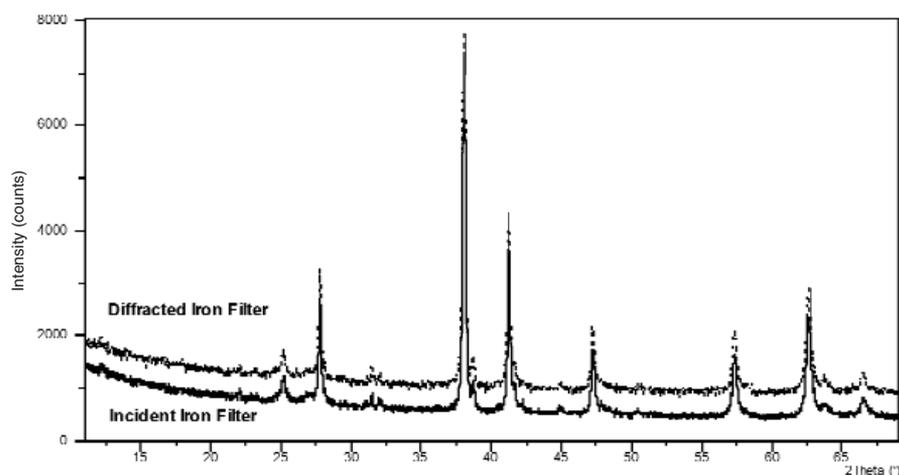


Figure 6. Comparison using the beta filter in the incident or diffracted beam

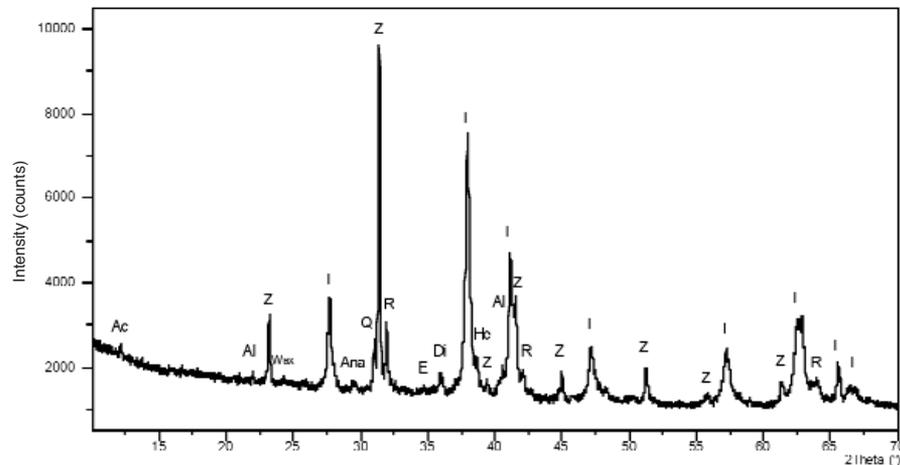


Figure 7. Measurement and phase identification for a typical heavy mineral concentrate sample (Z = zircon, I = ilmenite, R = rutile, Q = quartz, Ac = actinolite, Al = almandine, Ana = anatase, Di = diopside, He = Haematite, E = epidote)

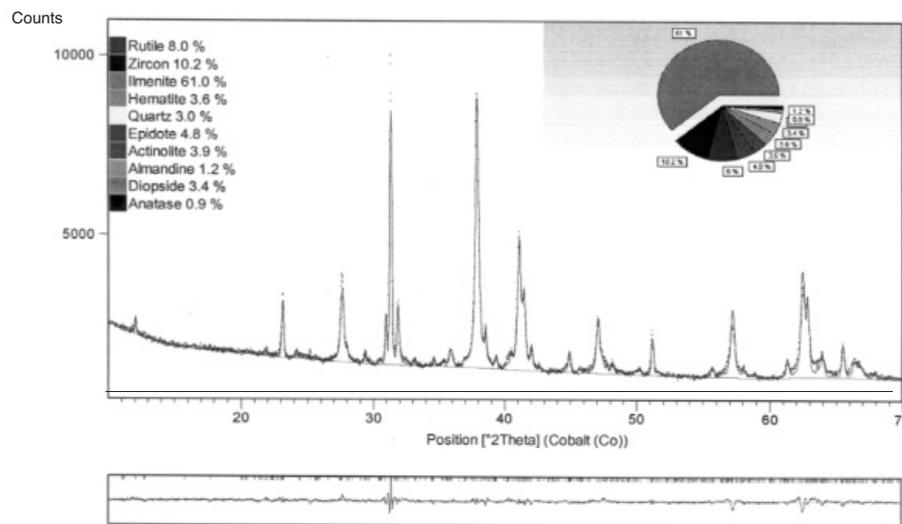


Figure 8. Rietveld refinement for a heavy mineral concentrate sample, above = measurement and calculation, below = difference plot; $R_{Profile} = 3.6$

measuring one or more diffraction peaks of a phase and converting the net intensity into the weight fraction or concentration. This is possible because the intensity of a diffraction peak is proportional to the concentration of the corresponding chemical compound or phase. It has to be ensured that the sample preparation method is reproducible as the sample density affects results.

In order to use the same calibration over a long period of time a monitor correction must be used. The calibration based method is based on measurements on standard samples for the specific materials. Depending on the material, different calibration methods are applicable. In many cases the straight line model produces reliable results.

Rietveld analysis

A Rietveld refinement was performed on a heavy mineral concentrate sample. Figure 8 shows the match between the measurements and a calculated pattern using least-squares fit. The difference plot indicates the difference between measured and calculated powder pattern.

A standard Rietveld refinement requires crystal structure data, such as atomic positions for all crystalline phases. The ICSD database was used to evaluate all structural input for the refinement of the heavy mineral concentrate sample.

In addition to structural information, the scale factors calculated for a mixture of phases are proportional to the weight fractions, making standardless quantitative analysis possible. Besides the quantity, Rietveld calculates the preferred orientation, the precise lattice parameters for the material, possible solid solutions, crystallite sizes or amorphous parts of the sample. The $R_{Profile}$ indicates the mathematical quality of the fit. It is calculated with the following equation:

Table I
Comparison of Rietveld and RIR quantification

| No. | Phase | Rietveld % | RIR % |
|-----|------------|------------|-------|
| 1 | Rutile | 8 | 8 |
| 2 | Zircon | 10 | 16 |
| 3 | Ilmenite | 61 | 42 |
| 4 | Haematite | 4 | 6 |
| 5 | Quartz | 3 | 5 |
| 6 | Epidote | 5 | 7 |
| 7 | Actinolite | 4 | 6 |
| 8 | Almandine | 1 | 4 |
| 9 | Diopside | 3 | 5 |
| 10 | Anatase | 1 | 1 |

$$R_p = \frac{\sum |Y_{io} - Y_{ic}|}{\sum Y_{io}}$$

where Y_{io} and Y_{ic} are the observed and calculated diffraction intensity at the i th point in the pattern respectively.

The quantitative results of the refinement and the RIR analysis are given in Table I. The RIR values differ from the Rietveld calculated weight fractions, because they do not take into account any preferred orientation.

The enlarged region of the diffraction pattern in Figure 9 shows how well the Rietveld calculated pattern explains the intensities seen in the measured pattern.

To evaluate the reproducibility of the sample preparation the milled sample was prepared and measured 27 times (using all available sample materials). The precision of the analysis method was tested by repeating a measurement of one sample 37 times (about 3 h measurement time). The results are illustrated in Table II. Figure 10 shows the width of distribution (standard deviation or sigma). Two-thirds of the results in the plots are within \pm sigma, 95% are within \pm two sigma and all results are within three sigma.

Clustering

Two different calculations were performed with the cluster analysis tool. In a first test the 64 scans from the reproducibility measurements were analysed. The PCA score plot at Figure 4 separated two different clusters and one outlier clearly. The scans of the clusters correspond, as expected, with 27 scans made for reproducibility of the preparation and the 37 scans performed on one sample. The outlier belongs to the first cluster. The different clusters show different distributions in the PCA plot. While the measurements for the precision test are concentrated in a small area, the scans for the different preparations are widely spread in the PCA plot, representing a higher standard deviation. A possible future application within a production control environment is to distinguish between stable and unstable processes, or between different raw material qualities. Cluster analysis can be performed before further investigations on the measurements such as phase identification and quantification. The most representative and scans that differ most can be used as starting point for more detailed investigations. The second test was done on several scans from samples coming from different steps

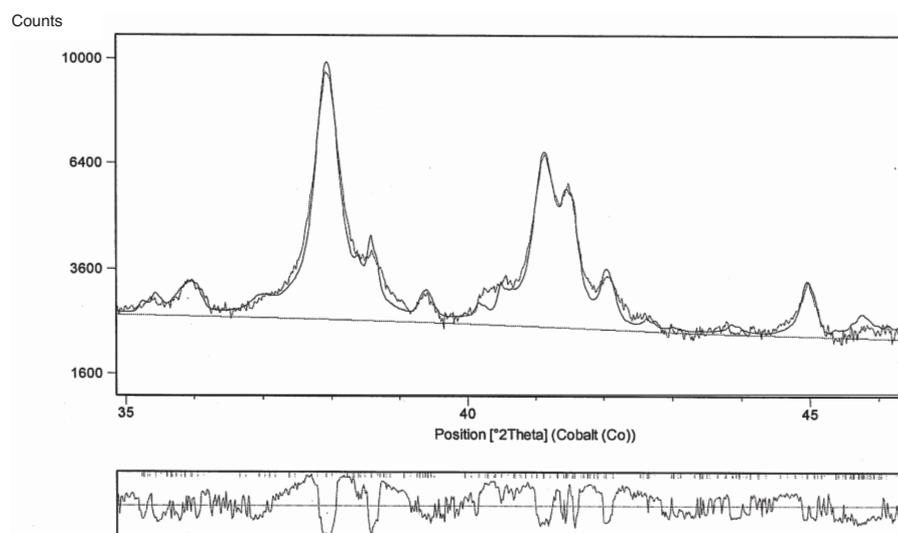


Figure 9. A portion of the Rietveld simulation overlaid with the measured data

Table II

Quantitative results showing the precision of the Rietveld method, based on 37 measurements for 1 prepared sample and showing the reproducibility of the preparation method, based on 27 prepared samples

| | Rutile | Zircon | Ilmenite | Haematite | Quartz | Epidote | Actinolite | Almandine | Diopside | Anatase |
|--|------------|-------------|-------------|------------|------------|------------|------------|------------|------------|-------------|
| Reproducibility of the sample preparation (27 preparations for 1 sample) | | | | | | | | | | |
| Mean | 8.0 | 10.3 | 58.9 | 3.9 | 2.9 | 4.9 | 5.4 | 1.3 | 3.8 | 0.8 |
| Median | 7.9 | 10.3 | 59.3 | 3.9 | 2.9 | 4.8 | 5.4 | 1.3 | 3.7 | 0.8 |
| Stand. Dev. | 0.2 | 0.5 | 1.9 | 0.2 | 0.5 | 0.6 | 0.9 | 0.1 | 0.3 | 0.1 |
| Variability | 0.2 | 0.4 | 1.7 | 0.2 | 0.4 | 0.5 | 0.8 | 0.1 | 0.3 | 0.1 |
| Minimum | 7.6 | 9.0 | 55.7 | 3.5 | 2.1 | 3.8 | 3.8 | 1.1 | 3.4 | 0.7 |
| Maximum | 8.5 | 11.1 | 62.0 | 4.3 | 4.1 | 6.0 | 6.7 | 1.4 | 4.5 | 0.9 |
| Precision of the method (1 preparation measured 37 times) | | | | | | | | | | |
| Mean | 7.9 | 10.7 | 57.2 | 4.0 | 2.4 | 5.2 | 6.6 | 1.3 | 4.0 | 0.8 |
| Median | 7.9 | 10.7 | 57.1 | 4.0 | 2.4 | 5.1 | 6.6 | 1.3 | 4.0 | 0.8 |
| Stand. Dev. | 0.1 | 0.2 | 0.7 | 0.1 | 0.4 | 0.4 | 0.4 | 0.1 | 0.2 | 0.1 |
| Variability | 0.1 | 0.1 | 0.5 | 0.1 | 0.3 | 0.3 | 0.3 | 0.1 | 0.2 | 0.04 |
| Minimum | 7.8 | 10.9 | 58.6 | 4.2 | 3.6 | 5.9 | 7.2 | 1.4 | 4.5 | 0.9 |

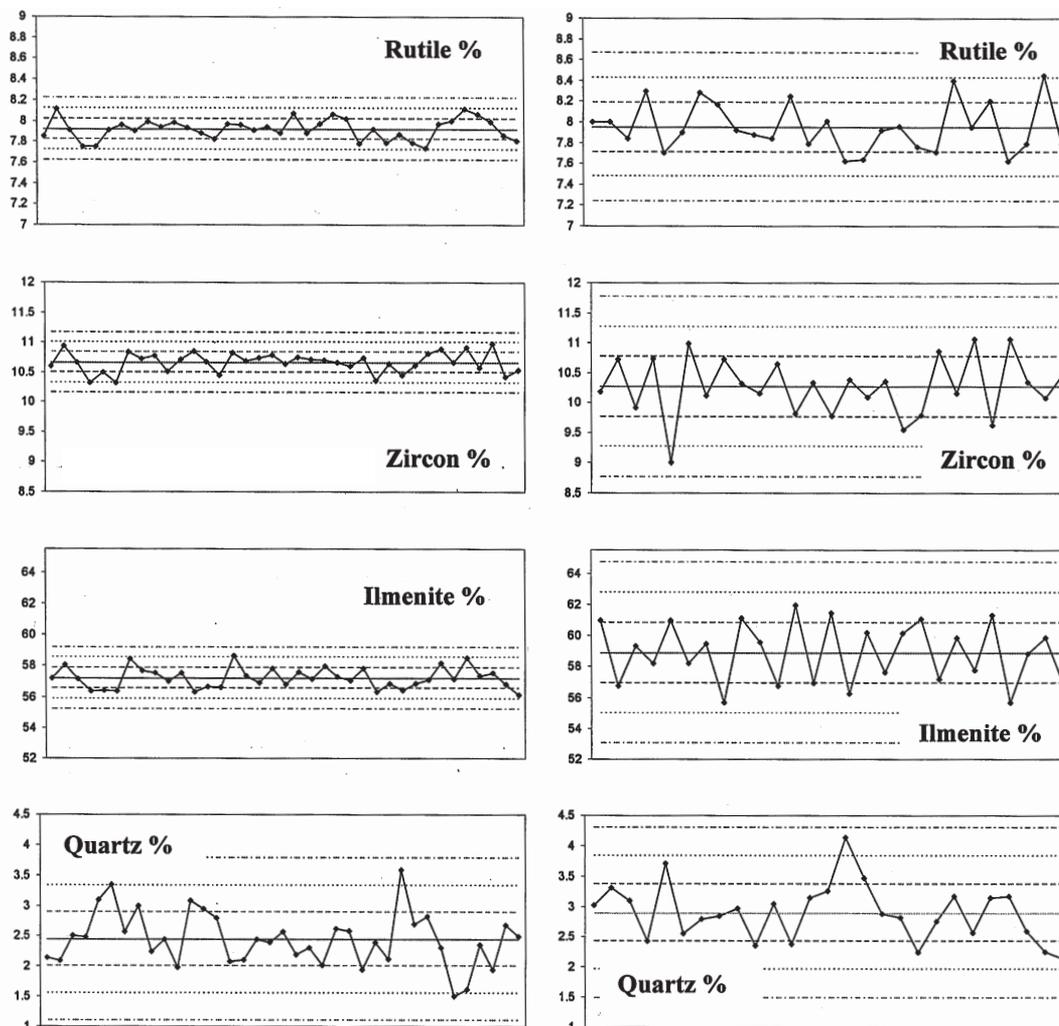


Figure 10. Standard deviations for the main phases of the sample. Left: precision of the method, 37 measurements for one prepared sample. Right: reproducibility of the preparation, 27 prepared samples (levels of confidence: solid = mean, dashes = 1 sigma, dotted = 2 sigma, dashes-dotted = 3 sigma)

during the processing of the samples (screening). Four different groups and one outlier were calculated. The clusters correspond with a higher and a lower concentrated sample and different particle sizes of the sample material.

Conclusions

Modern X-ray diffraction can provide valuable information for mining and process control in the heavy minerals industry through standardless quantification and fast, statistical evaluation of large data-sets through cluster analysis. Today's optics, detectors, and software can provide rapid and accurate analyses, suitable for process control environments as well as research. Within an automated sample preparation environment it is possible to analyse up to 6 samples per hour (sample preparation, XRD measurement and quantitative analysis).

Further investigations on more samples covering the spread of all process steps, raw materials and end products are the objective of future determination in order to improve production control, analysis time and limits of the method.

The detection limits on XRD Rietveld analysis is ~0.5 wt%. To overcome these high detection limits, XRD can be combined with XRF analysis, using the two techniques in tandem to provide mineral information as well as trace

element or contaminant information in routine operations. XRD and XRF analysis are fast and reliable techniques that can both be performed on pressed powder pellets.

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