Semi-Quantitative Analysis by XRD

Background

X-ray diffraction is often used to semi-quantitatively determine the weight fraction of constituents. By comparing the integrated intensities of the diffraction peaks from each of the known phases, their fraction can be identified. In addition, complex mixtures containing more than two phases also can be quantified. Even if one phase is amorphous, diffraction can still yield the relative amount of each phase. In some situations though, it is necessary to prepare calibration standards to obtain the highest accuracy.

Example 1

Figure 1 shows the X-ray diffraction patterns of Y_2O_3, ZnO, and a 50/50 mixture of the two. For clarity, the vertical scale of the pattern from the mixture (at the top) has been enlarged. Quantitative analysis can be performed by determining the integrated intensity of the strongest line from each of the constituents and comparing each to the integrated intensity in the pure phase. In this example, the Y_2O_3 has an integrated intensity of 9380 in the mixture and 14,280 in the pure phase, while ZnO has intensities of 6825 and 17,736 in the mixture and pure samples, respectively.

Applications

Corrosion products	Quantitative multiphase analysis
Forensic analysis	Amorphous/crystalline contents
Intermetallics	Quality control
Contaminants	Phase transformations
Mineral assays	Catalysts
Pharmaceuticals	Fiber analysis

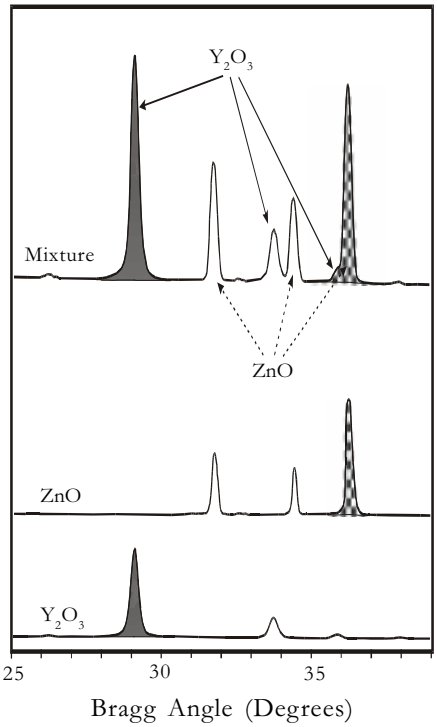

Figure 1 Diffraction patterns of ZnO, Y_2O_3 and a 50/50 mixture.

Klug's equation gives the weight fraction f_1 of phase 1:

$$f_1 = \frac{(I_1^{mix}/I_1^{pure})A_2}{A_1-(I_1^{mix}/I_1^{pure})(A_1-A_2)}$$

where I_1^{mix} and I_1^{pure} are the phase 1 intensities in the mixture and pure material, respectively, and A_1 and A_2 are the mass absorption coefficients. Thus, for Y_2O_3 in this sample:

$$f_1 = \frac{(0.657)50.75}{102.42-(0.657)(102.42-50.75)}$$

$$= 48.7\%$$

which is close to the actual value of 50%. When the values for ZnO are substituted in, the fraction of ZnO is found to be 52.3%. Examination of the diffraction pattern, however, reveals that the ZnO peak overlaps a small yttria peak. Correction for this contribution leads to a final calculated ZnO value of 51.7%.

Example 2

The method described in Example 1 is useful only when the mixture contains two crystalline phases. In the general case, a more robust method must be used. One such example is the matrix flushing method or the normalized *RIR* (Reference Intensity Ratio) method first reported by Chung (*J. Appl. Cryst.*, 8(1975)17-19). This technique performs a least squares fitting of the full experimental pattern to the identified phases in the mixture.

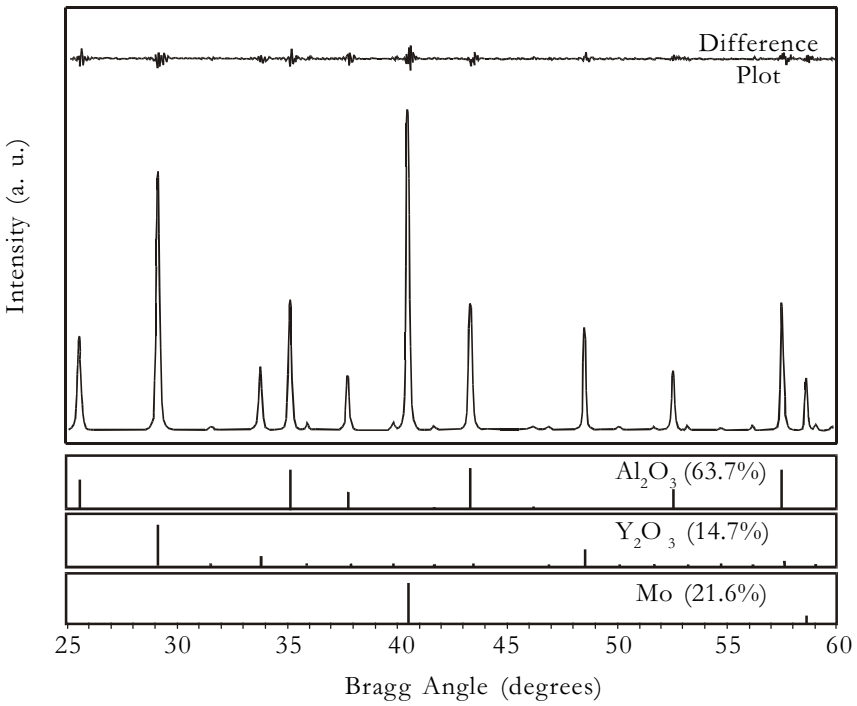

Figure 2 Diffraction pattern of mixture of three phases. Shown at the top is the difference plot between the experimental and the fitted mixtures.

In the example shown in Figure 2, an X-ray diffraction pattern from a mixture is shown after noise removal through FFT filtering, background subtraction, and $K\alpha_2$ stripping. Once the phases in the mixture are identified by the usual search/match procedures, the weight fraction of each phase can be determined. In this example, the calculated fractions (63.7% Al_2O_3/ 14.7% Y_2O_3/ 21.6% Mo) were found to be very close to the actual values (63.3% Al_2O_3/ 14.9% Y_2O_3/ 21.9% Mo). A convenient way to visualize the accuracy of the weight fraction calculation is with the difference plot (top of Figure 2), which shows the errors in matching both the position and intensity of each peak.

Before the full pattern method can be applied, the phases within the mixture must be identified. Also, the RIR value, which gives the intensity ratio between the target material and a known standard such as corundum , must be known. When both of these conditions are met, the full pattern analysis has been proven to be a powerful and accurate method of quantitative analysis.

Our Pledge

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