APPLICATION NOTE

Quantitative determination of rutile versus anatase in heavy minerals by both calibration and Rietveld refinement

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Introduction

Rutile and anatase are polymorphs of TiO_2, which are both naturally occurring. They are widely used as whitening pigments in paints, polymers and cosmetics. The abundant rutile is, besides ilmenite, the second important source for titanium smelting and is used in semiconductor industry to produce dye-based solar cells (Grätzel cells). On the other hand, anatase shows a high photocatalytic activity which limits the usability as a pigment in polymers, but also opens certain applications as a catalyst. Therefore, it is important to precisely determine the composition of TiO_2 containing mixtures as the properties of both rutile and anatase are varying strongly.

Instrument

The Thermo Scientific™ ARL™ EQUINOX 100 X-ray diffractometer (cf. Figure 1) employs a custom-designed Cu (50 W) or Co (15 W) micro-focus tube with mirror optics. Such a low wattage system does not require external water chiller or other peripheral infrastructure, allowing the instrument to be easily transported from the laboratory to the field or between laboratories.

Figure 1: ARL EQUINOX 100 X-ray diffractometer.

The Thermo Scientific™ ARL™ EQUINOX 1000 diffractometer uses a 3 kW generator powering a long fine focus X-ray tube connected to flat HOPG (002) or Ge (111) monochromators for applications requiring high throughput or high resolution and parallel beam.

The ARL EQUINOX 100 and ARL EQUINOX 1000 diffractometers provide very fast data collection times compared to other conventional diffractometers thanks to its unique curved position sensitive detector (CPS) that measures all diffraction peaks simultaneously and in real time. Therefore, both reflection and transmission measurements are easily obtainable.

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Experimental

For X-ray diffraction (XRD) measurements, powdered mixtures of rutile and anatase with known compositions were measured in reflection geometry (20 minutes with ARL EQUINOX 100; 10 minutes with ARL EQUINOX 1000) using Cu Kα radiation (ARL EQUINOX 100: mirror optics; ARL EQUINOX 1000: HOPG (002) monochromator). Qualitative and quantitative analyses were carried out using MDI JADE 2010 with the ICDD PDF4+ database or MAUD (Rietveld refinement) and Crystal Impact MATCH! (qualitative phase analysis). Calibration curves were determined by evaluating maximum intensity of the strongest reflections of rutile and anatase. To obtain a calibration curve the ratio between both was calculated and plotted against the composition. Additionally, Rietveld refinements were carried out.

Results

The calibration curves for ARL EQUINOX 100 (orange) and ARL EQUINOX 1000 (blue) diffractometers intensities are similar but deviate for very low concentrations of anatase (cf. Figure 2). Therefore, data quality of an ARL EQUINOX 1000 is sufficient to quantify concentrations of 0.8% anatase (cf. Figure 3). Additionally, Rietveld refinements yield compositions very close (refined: 79.9 wt%; reference 80 wt% rutile) to reference values.

Figure 2: Calibration curve for rutile content.

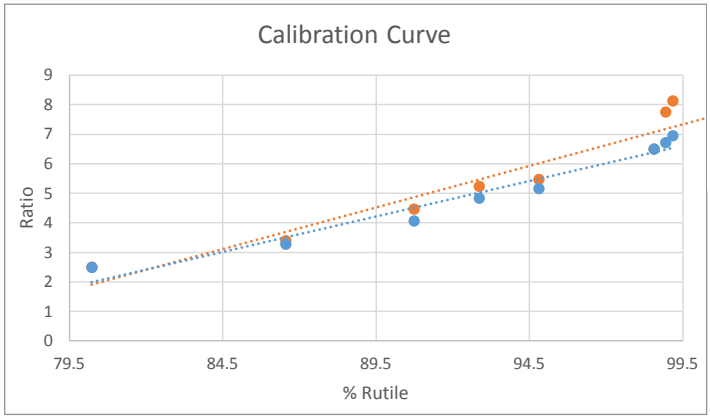
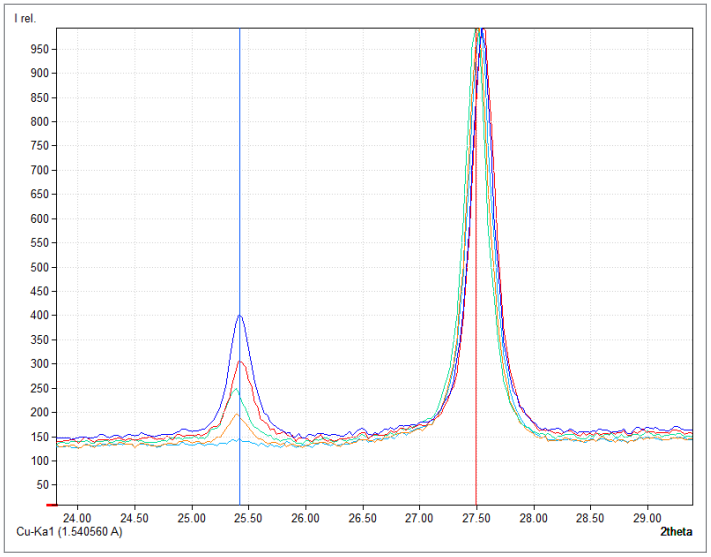


Figure 3: Strongest reflections of rutile (right, red) and anatase (left, blue) for different concentrations measured by ARL EQUINOX 1000 diffractometer.



Conclusion

The ARL EQUINOX 100 benchtop XRD instrument in combination with the MDI JADE 2010 software suite and ICDD pdf4+ database or MAUD and Crystal Impact MATCH! software is a suitable solution to conveniently determine the composition of rutile and anatase mixtures with both calibration curves and Rietveld refinements for concentration of anatase >1.5%. The ARL EQUINOX 1000 benchtop XRD instrument can determine concentrations of anatase >0.8%. As such analyses are often carried out in production lines by inexperienced users an easy-to-use method is required. Such a method is supplied by determining a calibration curve, which reduces possible errors and therefore increases quality.

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