Quantification of TiO_2 nanoparticles in samples of crystalline TiO_2.

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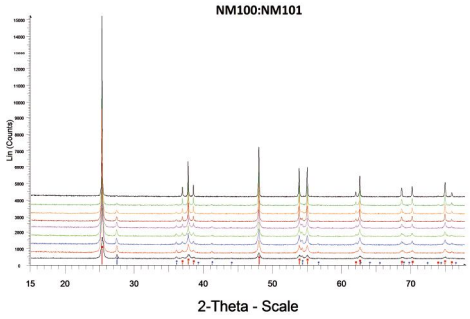
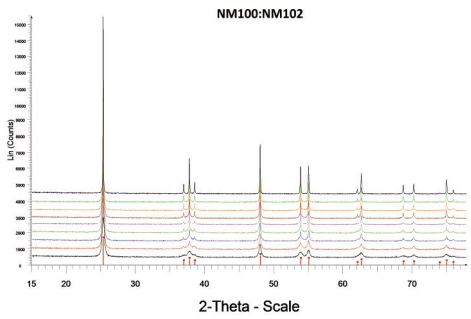
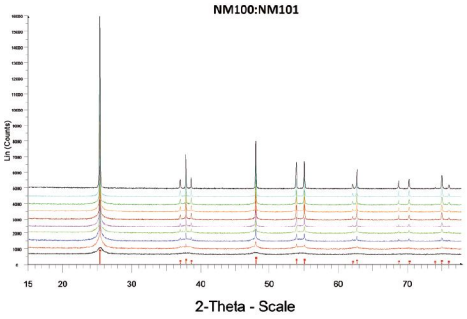
There is an increasing use of Powder X-ray Diffraction to determine the size of the crystals through profile analysis. The uncertainty depends e.g. on data quality and on the degree of monodispersity, but size determination from XPD is a useful tool for obtaining information from a large quantity of crystals in a sample. However, the challenges arises when the sample is single phased and consists of crystals with two or more different sizes.

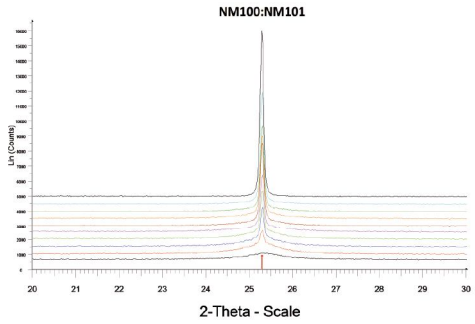
This poster presents the preliminary results from an on-going investigation on the quantification of small anatase crystals (~10 nm - ~ 25 nm) in a mixture with large anatase crystals (~200 nm). Four different programs have been used on the data; TOPAS 4.1 from Bruker, GSAS, PowderCell and Fityk. In TOPAS, GSAS and PowderCell the structure was used to do Rietveld refinement of profile/fwhm and weight ratio of the two size fractions. In Fityk the individual reflections were refined, the ratio between the areas of the reflections were calculated and the average reported.

All programs have been used by refinement of the profiles on the pure phases and then calculation of the ratio of the mixtures – all do very well. In most cases the results are the expected ratios ± a few w%.









The figures show some of the data from the study on quantification of small anatase crystals mixed with large anatase crystals. In all the figures the black curves show the data from the pure samples. The sample on the top is NM100, with the crystal size of approximately 200 nm (reported by the producer), whereas the curves on the bottom represent the small anatase crystals, NM101 (reported as <10 nm), NM102 (reported as "ultra fine" (approximately the same crystal size as NM105)) and NM105 (reported as 21 nm).

A closer look at the first reflection in the NM100:NM101 mixture reveals the graduate change in the shape of the reflection depending on the mixing ratio.

The colour coding in the figures is as follows: black = pure samples (top:NM100, bottom NM101 / NM102 / NM105), red = 1:9; blue = 1:4; green = 1:3; pink = 1:2; dark red = 1:1, orange = 2:1 and dark green = 3:1.
The red and blue marking on the x-axis mark the expected position of Anatase (and Rutile in NM105).

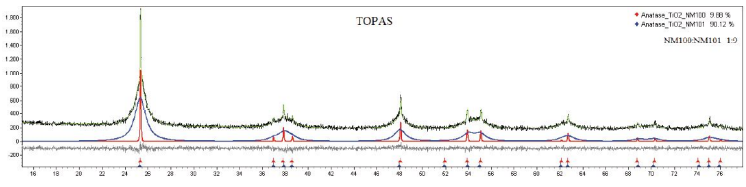
Samples: All mixtures were measured 3 times. The samples were analysed at room temperature (25°C) with a Bruker D8 Advanced diffractometer in transmission mode with Bragg-Brentano geometry. The instrument has a sealed Cu X-ray tube run at 40 kV and 40 mA, wavelength 1.5406 Å ($Cu_{K\alpha1}$) from a primary beam Ge monochromator, linear PSD detector (Lynx-eye) with opening angle 3.3°, fixed divergence slit 0.2°. The step size was 0.015 °2θ and the samples were measured from 5 to 75 in °2θ.

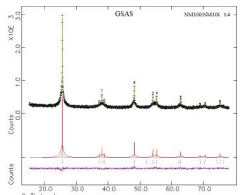
In most cases refinement of the profiles afterwards hardly changes the values. The changes that appear are on the mixtures 1:9 and 3:1.

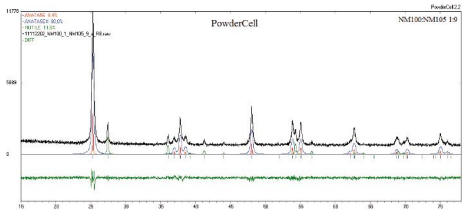
Refinement without knowing the profiles of the pure samples.

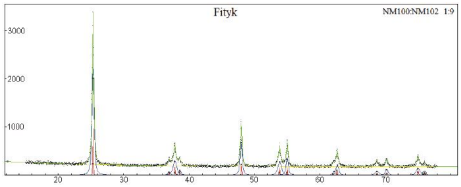
- Refinement on the mixture of NM100:NM101 went well, though there were difficulties, especially with the ratio 2:1. The shape of the profiles are quite different and all programs recognise two different sizes, and can be used for determination of the ratio.
- Refinement on NM100:NM102 and NM100:NM105 proved more challenging. (It has not yet performed with the GSAS program.) The profiles are more alike and thus more difficult to separate. From the NM:105 sample, also containing rutile, it is seen, that the amount of rutile is close to the expected, whereas the ratio between the two anatase sizes may be far from the expected. Most difficulties with the ratios 3:1, 2:1 and 1:9.

NM100: NM101		TOPAS	TOPAS *	GSAS	GSAS *	Pcw	Pcw *	Fityk	Fityk *
3:1	0,25	0,31	0,31	0,26	0,25	0,23	0,19	0,3	0,25
2:1	0,33	0,44	0,44	0,40	0,39	0,40	0,37	0,43	0,38
1:1	0,50	0,52	0,53	0,49	0,47	0,46	0,46	0,51	0,49
1:2	0,67	0,68	0,69	0,67	0,66	0,61	0,61	0,68	0,64
1:3	0,75	0,75	0,75	0,73	0,72	0,69	0,69	0,75	0,73
1:4	0,80	0,80	0,81	0,80	0,79	0,75	0,75	0,80	0,79
1:9	0,90	0,91	0,91	0,91	0,9	0,88	0,86	0,91	0,90









Bruker AXS, TOPAS Version 4.1; Copyright 1999, 2008 Bruker AXS.
Larson, A.C. and Von Dreele, R.B., 2004. General Structure Analysis System (GSAS). Los Alamos National Laboratory Report (2004) LAUR 86-748.
PowderCell for Windows, Version 2.4 by W. Kraus and G. Nolze, Federal Institute for Materials Research and Testing, Germany.
Fityk; M. Wojdyr, (2010) J. Appl. Cryst. 43, 1126.

The samples used in this investigation were provided by the JRC (Joint Research Centre, EU) in connection with the Nanogenotox project.