

Powder characterisation by near infrared spectroscopy

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Introduction

Specific methods to characterise surface physical states are satisfactory for classifying different sample groups, and identifying pretreatments for calibration developments. Relationships, within, and characteristics of a material are preserved, no matter what are chosen as calibration samples, but the correlation between scores of a component and quantitative results of a physical property improves if adequate samples are selected for calibrations, using principal component analysis. An example is introduced that applies the above approach to NIR spectra of TiO_2 powders in different crystal structures.

Multivariate analyses for NIR spectra have qualitative and quantitative programs. Qualitative calibrations are used for identification of different chemical substances and for separation of different qualities of the same substances.¹ The difficulties of qualitative calibrations are that the physical natures of components are a factor in the building of every calibration. If calibrations are built with samples compiled on the basis of other quantitative methods, this should facilitate interpretation and classification the physical components of the samples. Qualitative analysis will identify characteristics on the basis of principal components of the physical attributes of the material, and correlate these to scores based on calibration results. The principal components are orthogonal to each other. Loadings represent the relationships between each of the physical or chemical components and NIR spectra. If a good agreement is found between scores of a sample set and the quantitative results for a component, the component will be associated with the physical properties as determined by the quantitative method. The calibration built from the data can identify physical and chemical parameters of the samples by encompassing them into the calibration, which can then be used to characterise the substances. These ideas are summarised in Figure 1.

Materials and methods

Eight titanium dioxide (TiO_2) powders with three different crystal structures were selected on the basis of ingredient brochures. The different crystal structures were Amorphous, Anatase and Rutile. Anatase is a low temperature modification of Rutile. The eight TiO_2 samples were

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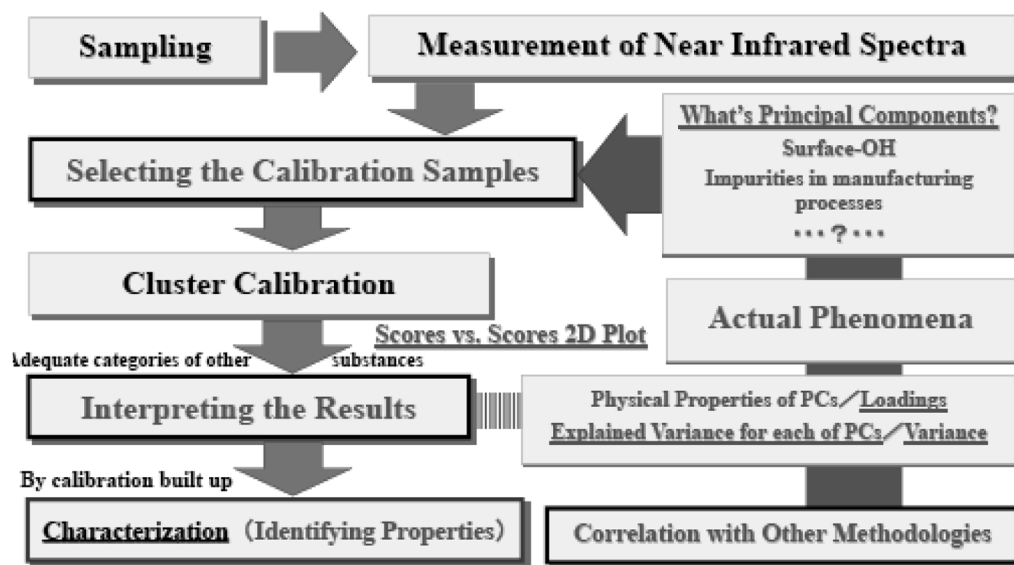


Figure 1. Characterisation combined with multivariate calibration and other quantitative methods.

numbered: (1) Amorphous, (2–4) Anatase, (5–7) Rutile and (8) (Nano-) Rutile. The calibration samples were selected on the basis of the information on brochures, and verified by Infrared spectra (IR), using a Field Emission - Scanning Electron Microscope (FE-SEM), a Temperature Gravimeter Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD).

Six vials of each TiO_2 powder were prepared for measurements. The vials had 15 mm outer diameter and 45 mm height, with flat base and PE cap. The vials were filled with TiO_2 powder to over 1 cm depth from the bottom. NIR spectra were observed using a NIRFlex N-500 (BÜCHI Labortechnik AG, Flawil, Switzerland), with an add-on six vials cell holder. Diffuse reflectance spectra were acquired from 12,500 to 4000 cm^{-1} with 4 cm^{-1} intervals (2126 points). Data analyses were performed using the software installed in the instrument (NIRCal software v.5.2.3000 Std. Ed.). Two spectral pretreatments were applied: [1] normalisation and first derivative, and [2] primarily first derivative, followed by normalisation. The region for calibration was set between 10,000 and $4,000\text{ cm}^{-1}$ (1501 points) to exclude noise. In order to evaluate the performance of a calibration, spectra were divided into two sets: 2/3 spectra as calibration and other 1/3 as validation. The V- and C-Sets were same for all calibrations. The calibration method was Cluster analysis.

Results and discussion

“Bridge O-H (free)” was assigned to the peak at the highest wavenumber in the 1st overtone region of OH stretching. “Bridge O-H” refers to a hydroxyl function composed of oxygen combining to titanium on both sides. The hydroxyl group chemically bonded to Ti is called terminal O-H.²

Pretreatment of spectra before calibration

1. (Ncl & db1). Ncl is referred to as “normalisation by Closure”.¹ The formula is written as $[NC=N \cdot T / \sum T_i]$ (Martens, Naes 1989). Db1 is the 1st derivative of the 1st BCAP. In these pretreatments, small absorptions are not distinguished very clearly. The wavelength areas where absorption is strongest are the 1st loadings of the 1st component of PCA. Most of the variance in spectral data is explained by the 1st principal component. In this study several absorbers associated with the hydroxyl group changes were observed.
2. (Db1 & SNV). The SNV transformation (standard normal variate) centres each spectrum and then divides it by the standard deviation of the spectral data of the population, which reduces the mean to zero and the variance to one. By pretreatment of spectral data with the first derivative the influence of baseline differences is reduced. This pretreatment makes it easier to differentiate among spectra, because baseline differences are essentially removed. Loadings also strongly depend on sample selection for the calibration, and the explained variance for each component is also influenced by sample selection.

Sample selection to build a calibration model

Samples of (1), (4) and (7)

The crystalline state affects the prediction of the characteristics of the material. This suggests that samples for building calibration models should have essentially the same crystalline form for the most effective identification of quality parameters of the same substance.

Samples of (4), (7) and (8)

These samples have in effect the same crystalline system (tetragonal), but different crystal structures of Anatase (4) and Rutile (7). Sample (8) was classified into Rutile of nano-particles according to the brochure, but the IR spectrum was different from that of other Rutiles of (5), (6) and (7). The IR spectrum and XPS data suggested that N was present, possibly in the form of NO_3^- . The calibration results with two pretreatments provided specific profiles of the substances. Using the (ncl & db1) treatment the first principal component identified the differences among most of free OHs (72.1%). The second component (26.5%) was assessed at being associated with other OHs having some interactions versus free OHs. Using the (db1 & SNV) treatment the 1st component identified free OHs versus other OHs, having some interactions (maybe hydrogen bonding and/or some weak interactions) (Figure 2 and Figure 3).

Free OH changes seemed to be associated with C=O, probably in the form of Ti-O-C(O)-, which had the same loadings for absorptions near 4600 cm^{-1} . The explained variance of PC1 was 56.3%. The 2nd principal component (39.3%) seemed to show the relations between OHs (positive loadings) and C=O bands (negative loadings). Possibly the physical properties of the 2nd component would be verified by Temperature Programmed Mass Spectroscopy (TPMS), to observe evaporating gases and other changes. Correlations between Scores of PC1 and $[\text{O}]/[\text{Ti}]$ obtained for samples by XPS were getting close to 1 as follows; for samples of (1), (4) and (7) with pretreatment (ncl & db1) r was 0.9501 (PC2 in this case), samples of (4), (7) and (8) with pretreatment (ncl & db1) r was 0.9585, and the same sample selection with pretreatment (db1 & SNV) r was 0.997 (Figure 4).

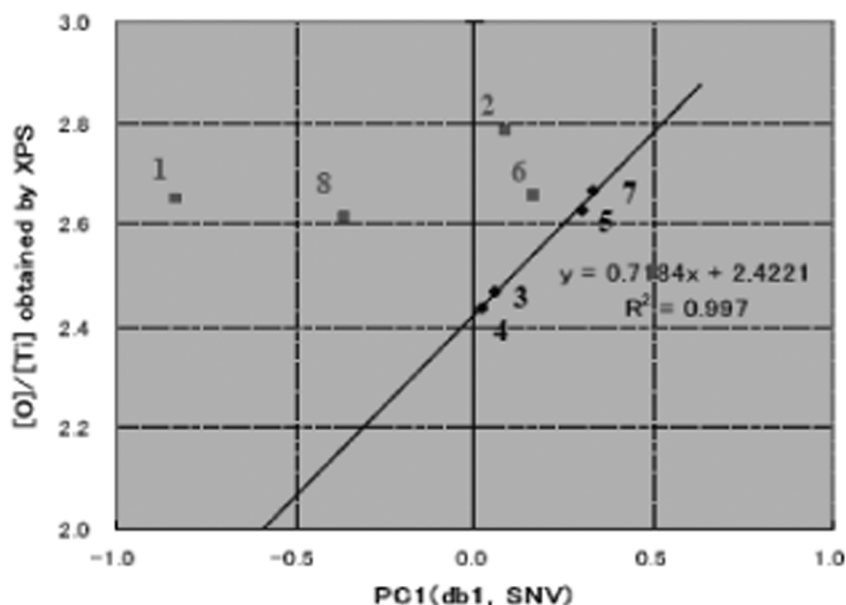


Figure 4. PC1 Scores versus [O]/[Ti] obtained by XPS for calibration of samples (4), (7) & (8) with pretreatments of db1 & SNV. If transformation from reflectance to absorbance is added before db1, the correlation coefficient increases to 0.9978.

Samples of (4), (2), (5) and (6)

Referring to the relationship of the loadings to the spectra, the selection of samples above seemed to provide clear differences in identifying small changes, based presumably on some impurities. Identification and discussion of these would be helpful for bands assignment of NIR spectra of these materials, and could provide information of process defects.

Acknowledgements

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References

1. *NIRCal Software Quick Guide*, version A. BÜCHI Labortechnik AG, Flawil, Switzerland.
2. M. Kiyono, *Titanium Dioxide -Physical properties and Application*. Gihodo, Tokyo, Japan (1991).