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Interlaboratory comparison on relative quantification of titanium dioxide (TiO_2) polymorphs in binary mixtures by Raman spectroscopy

Titanium dioxide (TiO_2) is a prominent semiconductor in industry and research that can be employed for a variety of applications. It is the most widely utilized white pigment in dyes and paints in the world, while also being of interest for its photocatalytic activity, as a component in pharmaceutical production, and as a food additive (E171). Its polymorphs of most industrial interest are anatase and rutile. These forms exhibit distinct physical and chemical properties (e.g. density, color, ultraviolet absorption, band gap) and differ in market price: from this, the industrial necessity of analytical methods for distinguishing and quantifying them arises.
ASTM D3720−90(2019) establishes the use of X-ray diffraction (XRD) as the current standard technique to quantify relative concentrations of these two TiO_2 phases; however, the method focuses on samples approaching 100 % purity of one of the two forms [1]. Moreover, this is a rather lengthy procedure, whose measurements can be affected by variability in the preparation of specimens and by specific contaminants.
Raman spectroscopy is a convenient technique for the characterization of TiO_2 and its polymorphs, because of the high cross section and distinct signals of its forms, and the minimal sample preparation required. The main limitation to the diffusion of Raman as a normatively accepted quantification technique is the lack of standardization, in terms of reference materials as well as analytical procedures and data processing; this has been exacerbated in the last few years by the widespread adoption of multivariate analysis methods in the field, often providing little information about employed procedures and parameters and with no reproducibility effort [3]. For these reasons, the Versailles Project on Advanced Materials and Standards (VAMAS) formed the Technical Working Area 42 (TWA 42) – "Raman spectroscopy and microscopy" [2].
In this prenormative study, the development and results of the interlaboratory comparison (ILC) conducted in the framework of VAMAS TWA 42 as Project 2 – "Raman spectroscopy for TiO_2 nanoparticles mixtures", will be presented. The ILC, comprising 10 participants from 9 countries and 11 experimental setups, investigated the feasibility and metrological uncertainty of Raman microspectroscopy for relative quantification of anatase-rutile binary mixtures sourced from commercial powders (E171) throughout the whole spectrum of ratios, and established standard operating procedures for preparation of stable samples apt for international transportation, low-variance spectral acquisition by surface mapping, and multivariate data analysis by partial least squares (PLS). All models succeeded to estimate the ratios with accuracies and precisions of less than 3 % in the 5 % – 95 % range, while models constructed on most datasets suggested the possibility of surpassing this performance by a great margin. These results demonstrate the potential of Raman spectroscopy for becoming an official method for relative quantification of great industrial impact worldwide.

References

[1] ASTM International, ASTM D3720−90(2019), "Standard Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-Ray Diffraction".
[2] http://www.vamas.org/twa42/index.html
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