**EMPIR Call 2018 – Health, SI Broader Scope, Normative and Research Potential**

Selected Research Topic number: **SRT-n13**
Version: 1.0

# Title: Improving validated methods for identification and quantification of titanium dioxide in nanoparticle mixtures


## Abstract

Titanium dioxide ($TiO_2$) has widespread applications in many technological fields and its properties are strongly related to its crystalline form, of which several polymorphs exist. Valid analytical methods for identification of the crystalline phases are needed. Raman spectroscopy is proposed as a rapid and simple validated technique to distinguish the three different phases of $TiO_2$ in a nanoparticle mixture and to quantify their fraction. Validation would be confirmed by comparison with X-ray diffraction and transmission electron microscopy in high-resolution and in selected area electron diffraction mode, and via international inter-laboratory studies leading to a new work item proposal for international standardisation in CEN and ISO.



## Keywords

$TiO_2$ phases, $TiO_2$ nanoparticles, nanoparticle mixtures, method validation, crystalline phases quantification, anatase, rutile, brookite, Raman metrology, nano-metrology, standardisation, ISO, CEN


## Background to the Metrological Challenges

The global titanium dioxide nanoparticle (NP) industry is a fast growing market and demand is expected to gain strong momentum in the coming years. The main end-user markets are those of paints and pigments, plastics, paper, cosmetics, sunscreens, skin care, catalysts, ceramics, printing inks and glass. In particular, a surge in the use of cosmetics is one of the drivers of the global $TiO_2$ market, together with the growing use of plastics coated by titanium dioxide NPs for the manufacturing of toys and other objects. Around 50 000 tons of $TiO_2$ NPs were produced in 2010, representing around. 1 % of the overall $TiO_2$ market, and the production is projected to increase to around. 200 000 tons in the future.

The awareness of emerging needs and challenges in strategic sectors, like energy production and use, sustainable development, healthcare practices and systems, is attracting and increasing a renewed interest towards the possibility to use $TiO_2$, and in particular nano-$TiO_2$ based systems to attain real, effective and efficient innovation. It has also been largely demonstrated that the properties of the single NPs control the functional properties of nano-enabled systems. This is true for $TiO_2$ NPs-based systems, in a wide range of applications, from healthcare to photo-catalysis and energy. $TiO_2$ occurs in nature as three different polymorphs, which provide different physico-chemical properties. Polymorphs are known as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). These phases exhibit different properties including different photocatalytic performances or light scattering efficiency.

The possibility to perform a critical assessment, typically by comparison with standard systems and procedures, of properties and performances of nanomaterials and/or derived nano-enabled systems is amongst the basic requirements for an effective transfer of knowledge in nano-science into nano-technological know-how, scalable to industrial levels.

The focus of this work should be on the development of an analytical approach based on Raman spectroscopy in combination with chemometric analysis, able to classify and quantify different phases in $TiO_2$ NPs binary mixtures of NP. This activity is strongly aligned with the scopes and aims of ISO/TC 229 (Nanotechnologies) and CEN/TC 352 (Nanotechnologies), which supports standardisation in the field of nanotechnologies including understanding and control of matter and processes at the nanoscale and utilising the properties of nanoscale materials.


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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

## Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on metrology research necessary to support standardisation in the identification and quantification of different polymorphic forms of titanium dioxide in nanoparticle mixtures

The specific objectives are

1. To identify and quantify the crystallographic phases and the crystallite size of $TiO_2$ nanoparticles (NPs) through structural characterization of pure and mixed phases by means of Raman Spectroscopy, X-ray diffractometry (XRD) and Transmission Electron Microscopy.
2. To develop and document a new chemometric analysis approach and validated predictive models able to determine the fraction of different polymorphic forms of $TiO_2$ in nanoparticle mixtures.
3. To standardise Raman Spectroscopy as a method for the identification and fraction quantification of the different polymorphic forms of $TiO_2$ in nanoparticle mixtures.
4. To validate Raman Spectroscopy as a method for distinguishing and quantifying the different polymorphic forms of $TiO_2$ via an international inter-laboratory comparison under the auspices of VAMAS TWA 42
5. To collaborate with the technical committees CEN/TC 352 and ISO/TC 229, and the users of the standards they develop to ensure that the outputs of the project are aligned with their needs, including the provision of a report on “The determination of the different polymorphs of titanium dioxide using Raman spectroscopy” and published recommendations for incorporation of this information into future standards at the earliest opportunity.

The proposed research shall be justified by clear reference to the measurement needs within strategic documents published by the relevant Regulatory body or Standards Developing Organisation or by a letter signed by the convenor of the respective TC/WG. EURAMET encourages proposals that include representatives from industry, regulators and standardisation bodies actively participating in the projects. The proposal must name a “Chief Stakeholder”, not a member of the consortium, but a representative of the user community that will benefit from the proposed work. The “Chief Stakeholder” should write a letter of support explaining how their organisation will make use of the outcomes from the research, be consulted regularly by the consortium during the project to ensure that the planned outcomes are still relevant, and be prepared to report to EURAMET on the benefits they have gained from the project.

Proposers should establish the current state of the art, and explain how their proposed research goes beyond this.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 0.6 M€, and has defined an upper limit of 0.8 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 30 % of the total EU Contribution across all selected projects in this TP.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded partners.

## Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the “end user” community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the $TiO_2$ sector.

You should detail other impacts of your proposed JRP as specified in the document “Guide 4: Writing Joint Research Projects (JRPs)”

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically, the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work

## Time-scale

The project should be of up to 3 years duration.