# Raman Metrology - Towards Traceable and Quantitative Measurements

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Raman spectroscopy/microscopy is a powerful surface analytical technique for rapid, non-destructive characterization of materials. It works under ambient conditions, often without requirement of any sample preparation. Its applications span biomedical, microelectronics, pharmaceutical, security and fundamental investigations of nanomaterials such as the novel 2D and nanocarbon materials. More recently, miniaturized hand-held Raman instruments enable an even broader range of measurement capabilities, such as environmental monitoring, screening of explosives and analysis of illicit drugs, to be brought into field and increasingly these measurements are carried out by non-experts of the scientific or spectroscopic community. Despite nearly a century of development, Raman spectroscopy remains a qualitative analytical technique. A major obstacle in the use of Raman data in regulatory applications is the lack of traceable quantification and the absence of certified reference and documentary standards. This poster summarizes activities under development by the international Raman Metrology Team (iRMT) to develop traceable and quantitative measurements for various Raman measurands. The iRMT is composed of Raman experts from 15 National Measurements Institutes (NMIs) throughout the world that collaborate through monthly meetings on the development of quantitative and traceable Raman measurements as well as standards relevant to Raman spectroscopy. This poster covers the CCQM-SAWG pre-pilot study on the Raman confocal volume measurements and strategy towards traceable and quantitative Raman measurements; Raman shift calibration interlaboratory comparison carried out under VAMAS TWA42; Structural characterization of CVD-grown graphene under VAMAS TWA 41 and Raman spectroscopy for the quantification of phases within $TiO_2$ nanoparticle mixtures.

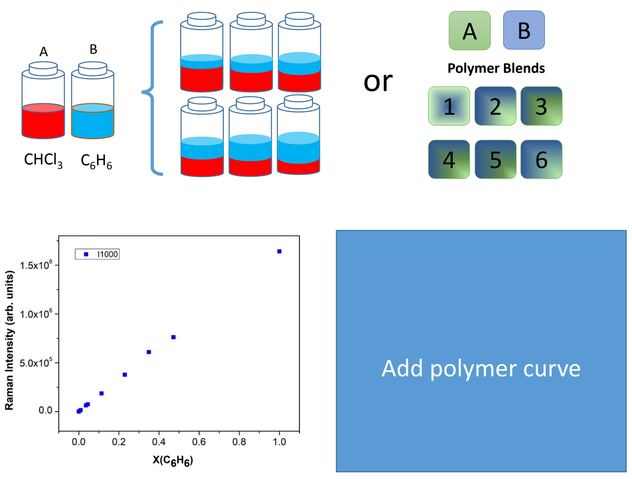
## Traceable Quantitative Measurement with Raman Microscopy Confocal Volume and Traceable Concentration Measurements

**Contact: Li-Lin Tay (NRC-CNRC, Canada)**

Objective is to develop methodology for traceable quantitative measurement with Raman spectroscopy

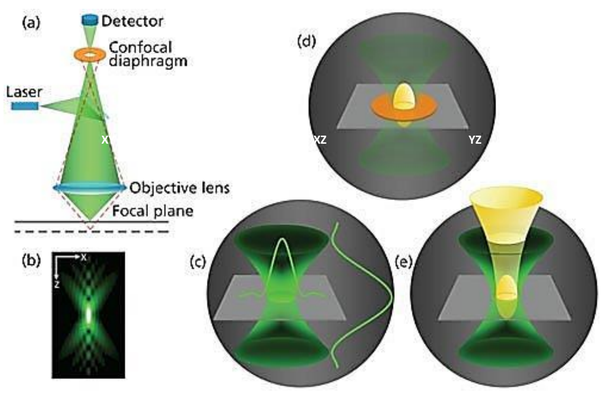
- CCQM-SAWG pre-pilot project was carried out to measure the Raman confocal volume
- Intensity calibration in confocal Raman microscope using samples (solutions / solids) of known traceable concentrations
- Using the calibration curve, concentration of an unknown sample can be measured
- # of molecule = Traceable concentration X Confocal Volume

### Traceable Concentration and Raman Calibration Curve

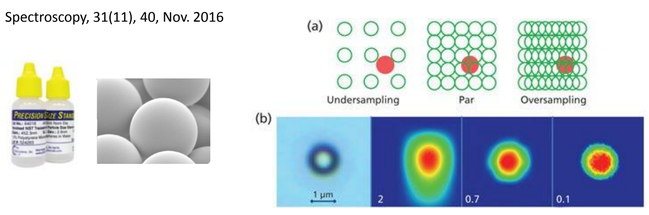



- Raman intensity calibration can be established from traceable mixture samples prepared by gravimetric weighing methods
- Samples of various mole fraction can be prepared either from mixture of non-interacting solutions or miscible polymer blends
- Concentration of an unknown sample can be determined through calibration curve and subsequently the number of molecules can be determined

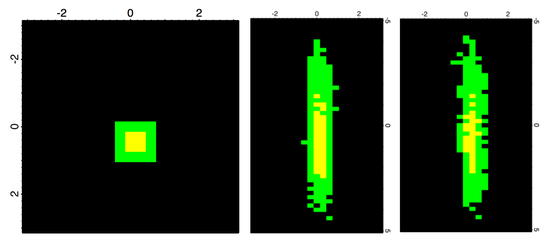
### Strategy for Confocal Volume Measurements




Spectroscopy, 31(11), 40, Nov. 2016




Use NIST SRM polystyrene bead as a point source to sample the confocal volume of confocal Raman microscope



NRC data of the 1003 cm-1 intensity profile as mapped by 1 µm NIST polystyrene bead

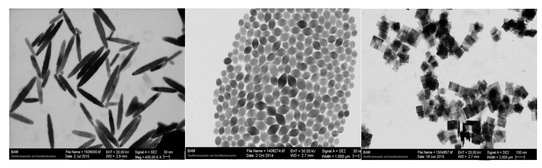
## Raman Spectroscopy for Validation and Quantification of Titanium Dioxide Nanoparticle Mixtures

**VAMAS TWA 42: Raman Spectroscopy and Microscopy**

**Contact: Andrea M. Rossi and Chiara Portesi (INRIM, Italy)**

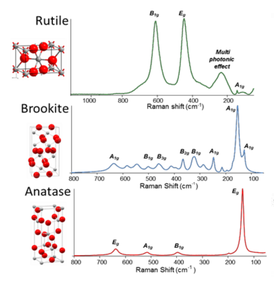
Objective is to develop validated procedures based on Raman spectroscopy, for the identification and quantification of the three $TiO_2$ polymorphs in titanium dioxide nanoparticles (NPs) binary mixtures.

In nature, three $TiO_2$ polymorphs exist (anatase, rutile and brookite) with individual physical and chemical features, that lead to distinct functional properties.

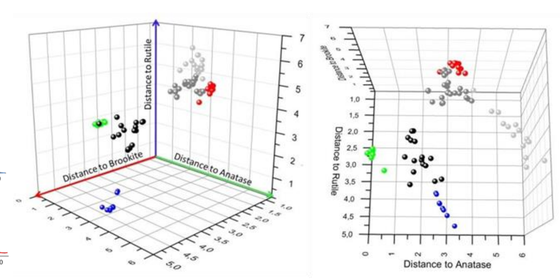


HR-SEM images of rutile, anatase and brookite $TiO_2$ nanoparticles

Due to their different crystalline structure and subsequent different spatial distribution of the atoms, anatase, brookite and rutile provide different Raman fingerprint spectra.




Raman spectra of the three different polymorphs




Discriminant analysis classification of pure (colored dots) an binary (grey scale dots) $TiO_2$ mixtures

So far, no standard exists for the identification and quantification of the three polymorphs in binary mixtures, and the development of a validated procedure based on Raman spectroscopy will guarantee both manufacturers ad end users about the quality and the performances of the final products.

### Work Programme

- Develop a calibration procedure with traceability, combining experimental data and chemometrics
- Evaluate measurement uncertainty.
- Development of standardized procedures

## Raman Spectroscopy for the Structural Characterization of CVD-Grown Graphene

**VAMAS TWA 41: Graphene and Related 2D Materials**

**Contact: Andrew Pollard & Piers Turner (NPL, UK)**

Graphene is a 2D material with exceptional properties with potential for many industrial applications. Raman spectroscopy and microscopy is particularly powerful technique for studying carbon nanostructures. The goal of this international interlaboratory study is to determine the uncertainties in measurement of the surface coverage of graphene, number of layers and level of disorder using Raman spectroscopy.

VAMAS

**Graphene and Related 2D Materials**
Technical Work Area 41

Project 1
**Structural characterisation of CVD-grown graphene: Coverage on substrate, number of layers, level of disorder**

**Objectives**

- Validate methodology for characterisation of CVD-grown graphene supported by a substrate, using Raman spectroscopy;
- Determine the uncertainties associated with the measurement and data analysis;
- Input into ISO TC229 JWG2, for ISO/PWI 21356 'Structural Characterisation of Graphene'.

**Background**

Graphene is predicted to impact many different application areas such as solar cells, biosensors, displays, composites, flexible electronics and energy storage due to its exceptional properties. One of graphene's many achievements is that it is the first truly two-dimensional material, being only 1 atom thick. The isolated research into a whole new family of other 2D materials has indicated that the new materials show exciting and complementary properties to graphene, revealing potential for many other industry applications.

**Standardization Needs**

As industry uptake on this material increases, international standardization is critical to enable commercialization. Reliable, accurate, and reproducible measurements are important due to the multiple production routes and producers of the material in order to maintain quality in manufacture.

Several standards are under development within ISO TC229 'Nanotechnologies', jointly with IEC, including ISO/PWI 21356 'Structural characterisation of graphene', which will focus on determining the physical properties of graphene flakes and CVD -grown graphene. This will require interlaboratory comparisons to help develop best practice and understand the associated uncertainties.

**Work Programme**

CVD-grown graphene transferred onto $SiO_2$ will be used for Raman spectroscopy measurements. The CVD -grown graphene will be sourced by an industrial collaborator. Samples will be prepared by the project leadership and provided to each participant following a normalisation spectra measurement by Raman spectroscopy.

**Call for Participation**

**Deliverables and Dissemination**

This interlaboratory study will be disseminated in a peer-reviewed scientific journal, and used to develop ISO/PWI 21356 (Nanotechnologies -- Structural characterisation of graphene)

**International Participation**

Current participation includes volunteers from Australia, Brazil, China, France, Spain, UK and USA. More volunteers are welcome.

**Funding**

Participants fund their own involvement in the project.

**Project Status**

Approved by the VAMAS Steering Committee for start-up.

The project is due to start in May 2017

**For more information on participation, please contact:**

**TWA Co-Chairs**

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www.vamas.org

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## Calibration of Raman Spectral Shift

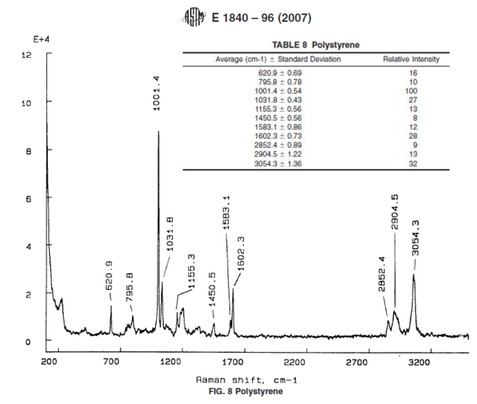
**VAMAS TWA 42: Raman Spectroscopy and Microscopy**

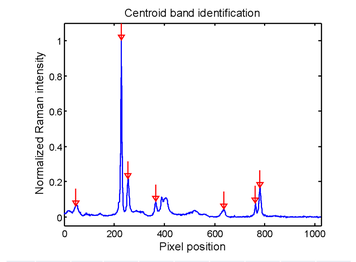
**Contact: Erlon H. M. Ferreira (INMETRO)**

Objective is to develop a methodology for wavenumber (Raman Shift) calibration with traceability to SI and dissemination through reference materials. Currently the only published Raman wavenumber standard, ASTM-E1840, does not provide traceability nor uncertainty analysis for wavenumber calibration

### Raman Shift Calibration Protocol

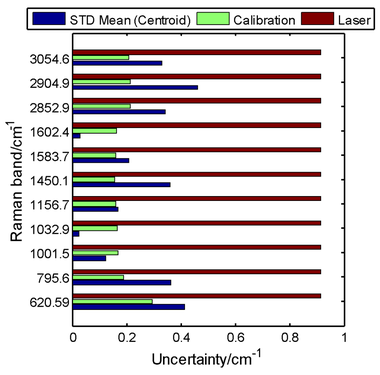
- **Measure a calibration lamp (neon)**
  - **Spectral range: - 500 $cm^{-1}$ to 3500 $cm^{-1}$**
  - **Test the reproducibility and repeatability**
    - **Align the lamp, collect 5 spectra, take out the lamp**
    - **Repeat 2 more times**
- **Measure the laser : 5 spectra**
- **Measure the reference material (PS sample)**
  - **Keep the same spectrometer configuration**
  - **Test the reproducibility and repeatability**
    - **Align sample, collect 5 spectra, take out sample**
    - **Repeat 2 more times**
- **Repeat procedure for a different microscope objective**



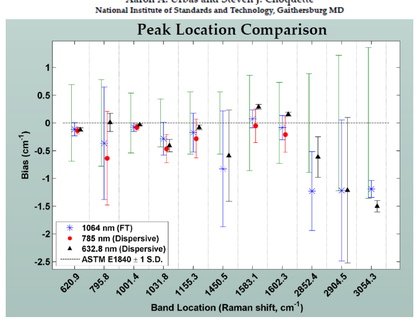




| | | Band | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|
| REPRODUTIBILITY | 1 | pxl | 48.58 | 228.24 | 254.56 | 365.69 | 639.02 | 764.01 | 782.10 |
| | | u | 0.72 | 0.06 | 0.07 | 0.18 | 0.59 | 0.55 | 0.06 |
| | 2 | pxl | 47.47 | 228.26 | 254.62 | 365.06 | 637.26 | 763.60 | 781.96 |
| | | u | 0.99 | 0.05 | 0.06 | 0.06 | 0.77 | 0.43 | 0.13 |
| | 3 | pxl | 50.53 | 228.34 | 254.68 | 365.11 | 638.0 | 764.72 | 781.97 |
| | | u | 0.26 | 0.03 | 0.07 | 0.68 | 1.5 | 0.44 | 0.15 |
| Grand-mean | | pxl | 48.86 | 228.28 | 254.62 | 365.29 | 638.09 | 764.11 | 782.01 |
| | | U | 0.51 | 0.03 | 0.04 | 0.23 | 0.58 | 0.28 | 0.06 |

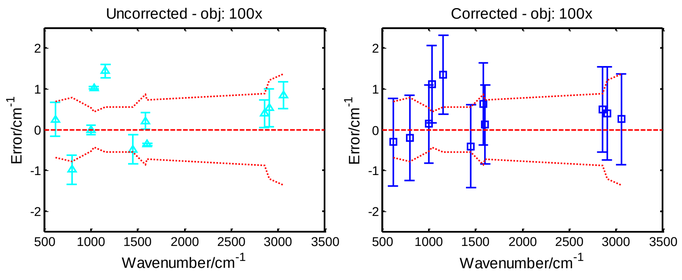
### Uncertainty budget




### Revisiting the ASTM E1840 Raman Shift Standards




### Comparing with ASTM E1840




**Error = Measured values – ASTM reference values**

| Residual sum of squares (all peaks) | | |
|---|---|---|
| **Uncorrected** | 5.72 | $cm^{-2}$ |
| **Corrected** | 4.28 | $cm^{-2}$ |

Error bars:
Uncorrected: std error of the mean
Corrected : combined uncertainty

## Members of the International Raman Metrology Team

NIST, DFM, NMIJ, CENAM, NRC-CNRC, NIM, KRISS, NPL-India, INRiM, PTB, NPL