Raman standardization landscape

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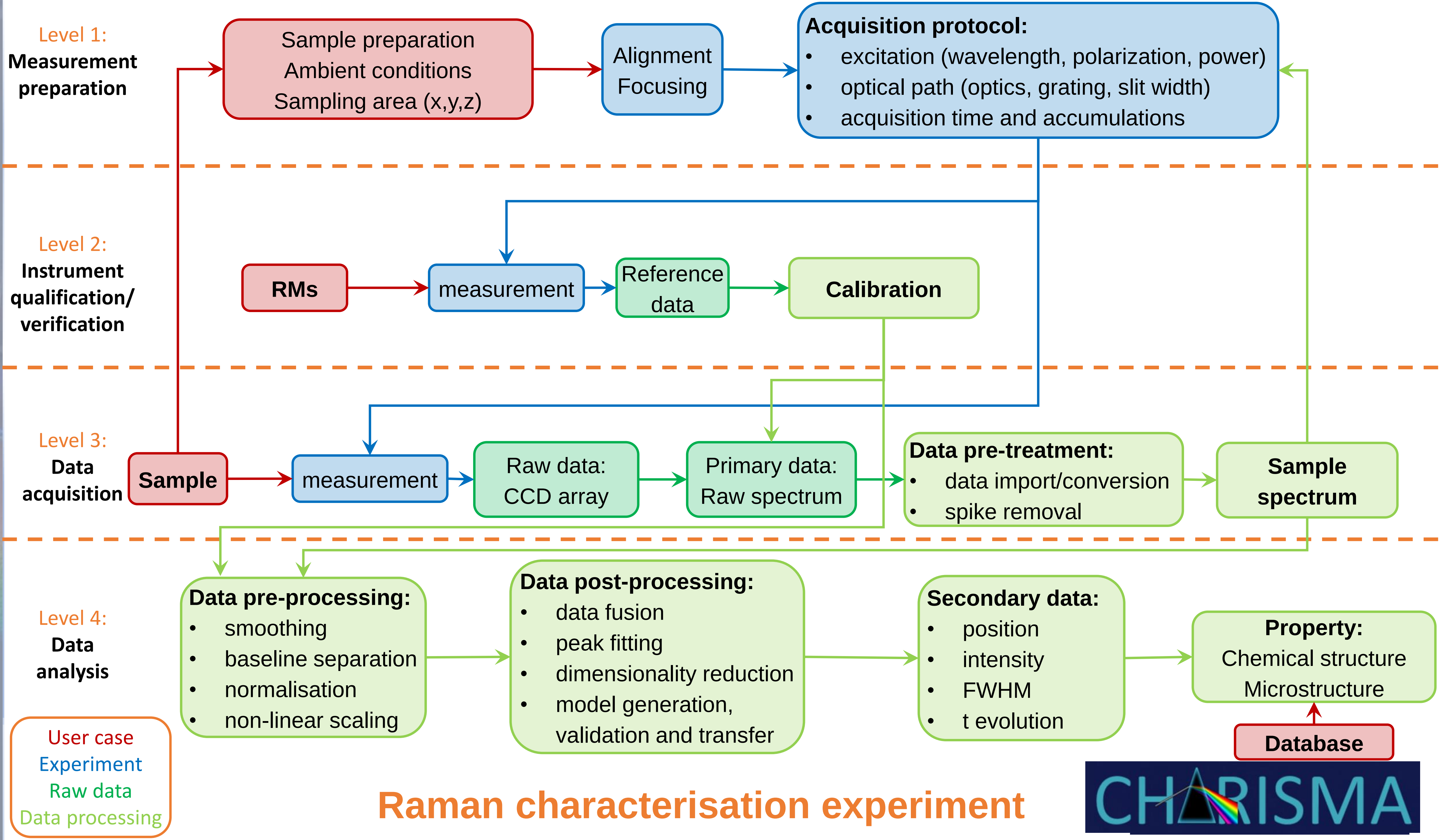

Raman characterisation experiment

Need for standardization in Raman spectroscopy

Direct information from Raman spectra:

- Number of peaks
- Peak position (Raman shift, cm^{-1})
- Peak intensity/area (relative or absolute)
- Peak shape and FWHM (cm^{-1})
- For mapping, spatial position (x, y, z)

Properties:

- Molecules or compounds identification
- Quantities or proportions
- Structural characteristics
- Physico-chemical environment
- Spatial arrangement

Depends on:

- Sample, sample preparation
- Environment
- Operator, acquisition
- Instrument

Procedures
Terminology

Data analysis

- Chemometrics
- Databases

Frecuency:

- Time stability of the device
- Required precision and accuracy

Calibration/qualification

- Raman shift wavenumber calibration (x axis)
- Raman intensity/response calibration (y-axis)
- Spectral (optical) / spatial resolution

Reference materials: Available, stable, inert, well distributed Raman signal, certified

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Impact of standardization in Raman spectroscopy

- Support **academic research** by increasing the comparability of Raman data
- Foster the **industrial implementation of Raman spectroscopy**
  as real-time, in-line and distributed monitoring and control/decision tool,
  improving the business of existing products/processes due to
  improved product quality and trust, waste minimization and time and energy saving.
- Development of **new business** based on Raman-active materials
  that face different societal challenges related to energy, security, or safety.

Difficulties

- **Lack of interoperability**
- **Increasingly softer hardware**
- **Internet of things**

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Standardization Landscape

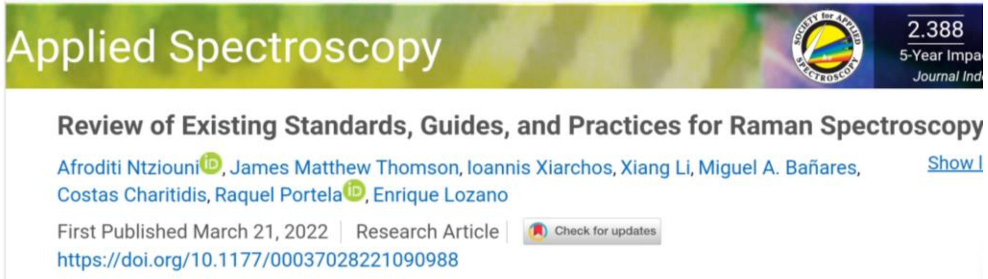
Reference materials and lamps

Certified by metrology institutes

Terminology
Calibrate/Qualify/Verify
Measurement & Data Analysis

Published by standardization bodies

Protocols for specific applications


Applied Spectroscopy
2.388
5-Year Impa
Journal Ind

Review of Existing Standards, Guides, and Practices for Raman Spectroscopy

Afroditi Ntziouni, James Matthew Thomson, Ioannis Xiarchos, Xiang Li, Miguel A. Bañares, Costas Charitidis, Raquel Portela, Enrique Lozano

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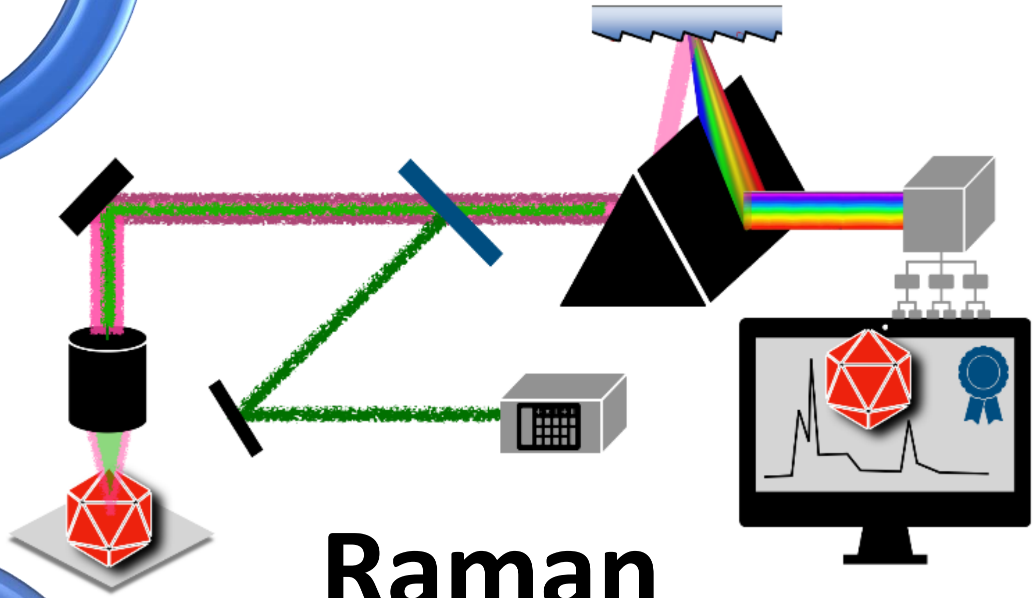
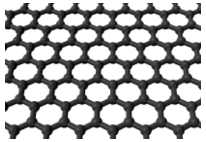
https://doi.org/10.1177/00037028221090988



Raman

Pharmarcopoeia Graphene LNG Microplastics


Standardisation bodies and committees that published and are currently discussing Raman related documents

ISO

TC 229 Nanotechnologies
TC 201 Surface chemical analysis
TC 61 Plastics
TC 147 Water Quality

IEC

E113 Nanotechnology for electrotechnical products and systems

ASTM INTERNATIONAL
Standards Worldwide

E 56 Nanotechnology
E 13 Molecular Spectroscopy and Separation Science
E 55 Manufacture of pharmaceutical products
E 54 Homeland Security

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Metrology institutes offering Raman CRMs

NIST SRMs 2241-6 (y-axis)
NIST atomic spectra database
https://www.nist.gov/pml/atomic-spectra-database

NMIJ RM8158-a (x-axis)
NMIJ CRM 5606-a (x-axis)

NIM GBW 13651-4, 13664 (x-axis)
NIM GBW 13650 (y-axis)

Other MIs involved in Raman standardization activities

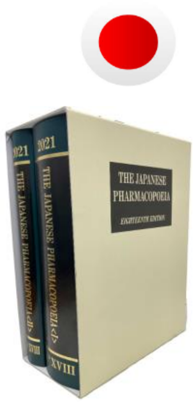
Main pharmacopoeias

Official publication defining specifications, standards and standard test methods that ensure the quality of medicines.

General description of Raman spectroscopy, apparatus, calibration/verification and measurements

EP-11, January 2023
2.2.48

USP44-NF39, 2021
858 and 1858



JP-18, June 2021
2.26.

ChP, 2020
4th part, 2.8

Interlaboratory studies (ILS) and consultations surveys involving Raman aiming at standards development

Versailles Project on Advanced Materials and Standards

40th aniversary in 2022!!

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

  1. Calibration of the Raman shift
  2. Raman spectroscopy for TiO_2 nanoparticles mixtures
  3. Measurement of lateral and axial resolution of Raman microscope
  4. Measurement of laterial resolution of Raman microscopy with nanowire artefacts
  5. Consultation survey

  Factors affecting reproducibility in Raman Spectroscopy
  https://www.surveymonkey.com/r/LQKCPGD

VAMAS

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

  1. Structural characterisation of CVD-grown graphene: Coverage on substrate, number of layers, level of disorder
  11. Determination of disorder and number of layers of graphene flakes by Raman Spectroscopy

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Terminology

Raman terminology

Terminology standards:

- **Directly related to Raman:**
  - **Molecular spectroscopy** ASTM E131-10
  - **Charge-Coupled Device (CCD) detectors** ASTM E2642-09
  - **Optical interface analysis** ISO/DIS 18115-3
- **Transversal** (e.g. ASTM E456 quality and statistics, ISO Guide 30:2015 reference materials)

Raman-relevant terms in other kind of standards:

- **Raman related** (e.g. ISO 23978:2020 natural gas)
- **Other techniques** (e.g. ASTM E2719 fluorescence)

- Repeated and/or different definitions
- Missing terms
- Open access

On line open access terminological databases:

- **IUPAC Gold book:** https://goldbook.iupac.org
- **ISO open database:** https://www.iso.org/obp
- **IEC Electropedia:** https://www.electropedia.org

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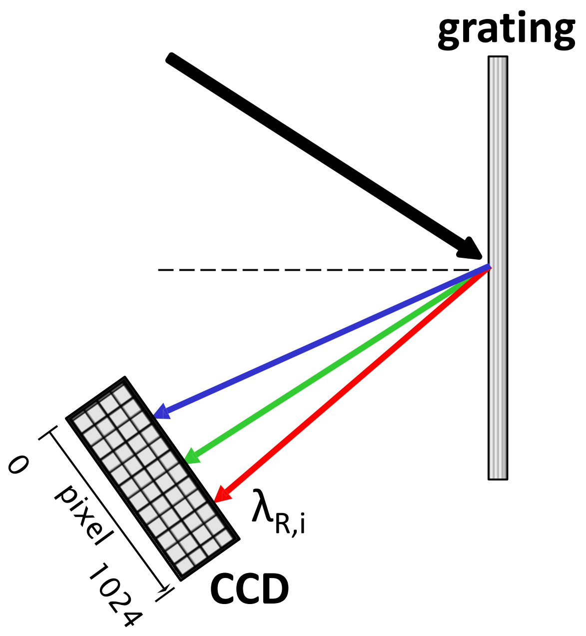
Raman terminology

ASTM E131-10 (2015) (Standard Terminology Relating to **Molecular Spectroscopy**)
ASTM E2642-09 (2015) (Standard Terminology for Scientific **Charge-Coupled Device Detectors**)
ASTM D8333 (Standard Practice for Preparation of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers Using Raman Spectroscopy, IR Spectroscopy, or Pyrolysis-GC/MS)
ASTM D6122 (Standard Practice for Validation of the Performance of Multivariate Online, At-Line, Field and Laboratory Infrared Spectrophotometer, and Raman Spectrometer Based Analyzer Systems)
ASTM E2719 (Standard Guide for Fluorescence—Instrument Calibration and Qualification)
ASTM E1655 (Standard Practices for Infrared Multivariate Quantitative Analysis)
ASTM E456 (Standard Terminology Relating to **Quality and Statistics**)
ASTM E2056 (Standard Practice for Qualifying Spectrometers and Spectrophotometers for Use in Multivariate Analyses, Calibrated Using Surrogate Mixtures)
ASTM D7940 (Standard Practice for Analysis of Liquefied Natural Gas (LNG) by Fiber-Coupled Raman Spectroscopy)
ISO/TS 80004-13:2017 (Nanotechnologies — Vocabulary — Part 13: Graphene and related two-dimensional (2D) materials)
ISO/TS 80004-6:2021 (Nanotechnologies — Vocabulary — Part 6: Nano-object characterization)
ISO 18115-1:2013 (Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy)
ISO 18115-2:2013 (Surface chemical analysis — Vocabulary — Part 2: Terms used in scanning-probe microscopy)
ISO/DIS 18115-3 (Surface chemical analysis — Vocabulary — Part 3: Terms used in **optical interface analysis**)
ISO 23978:2020 (Natural Gas - Upstream area - Determination of composition by Laser Raman spectroscopy)
ISO Guide 30:2015 (**Reference materials** — Selected terms and definitions)

Calibration/qualification/verification

Raman shift wavenumber calibration (x-axis)

Affected by temperature and mechanical drifts



Parameters to be determined:

a) Wavenumber calibration:

Correspondence **pixel position (i) - Raman scattering wavelength ($\lambda_{R,i}$)**

b) Raman shift calculation (laser zeroing): Exact excitation wavelength (λ_0)

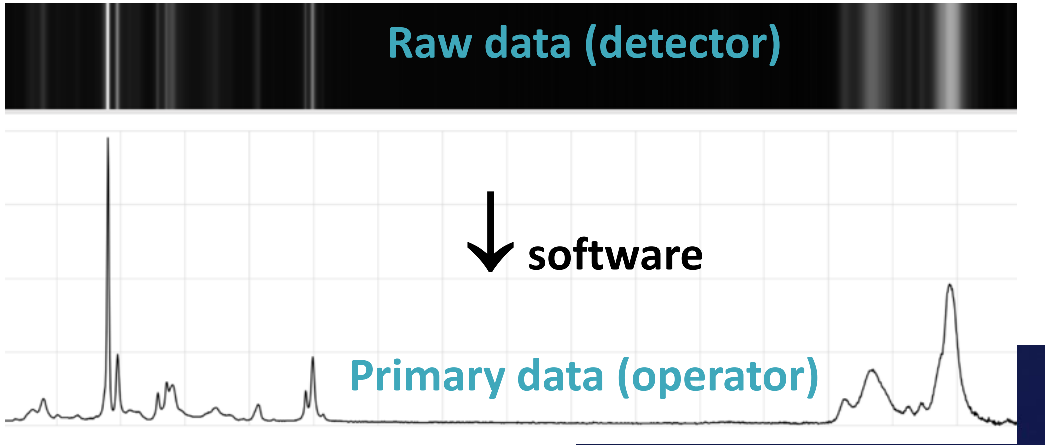
- Gas lasers: stable and known. Accuracy ~1 pm (0.04 cm^{-1} at 500 nm)
- Solid and semi-conductor lasers: must be evaluated

$$\textbf{Raman shift} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{R,i}}$$

Procedure (at least daily for a given laser and grating)

1. Select the required **accuracy**
2. Select the Raman shift **range**
3. Select relevant reference **sample(s)**
4. Select the laser **wavelength and grating**
5. **Acquire** the reference spectrum
6. Generate/modify the **correlation curve**

https://www.elodiz.com/calibration-and-validation-of-raman-instruments/

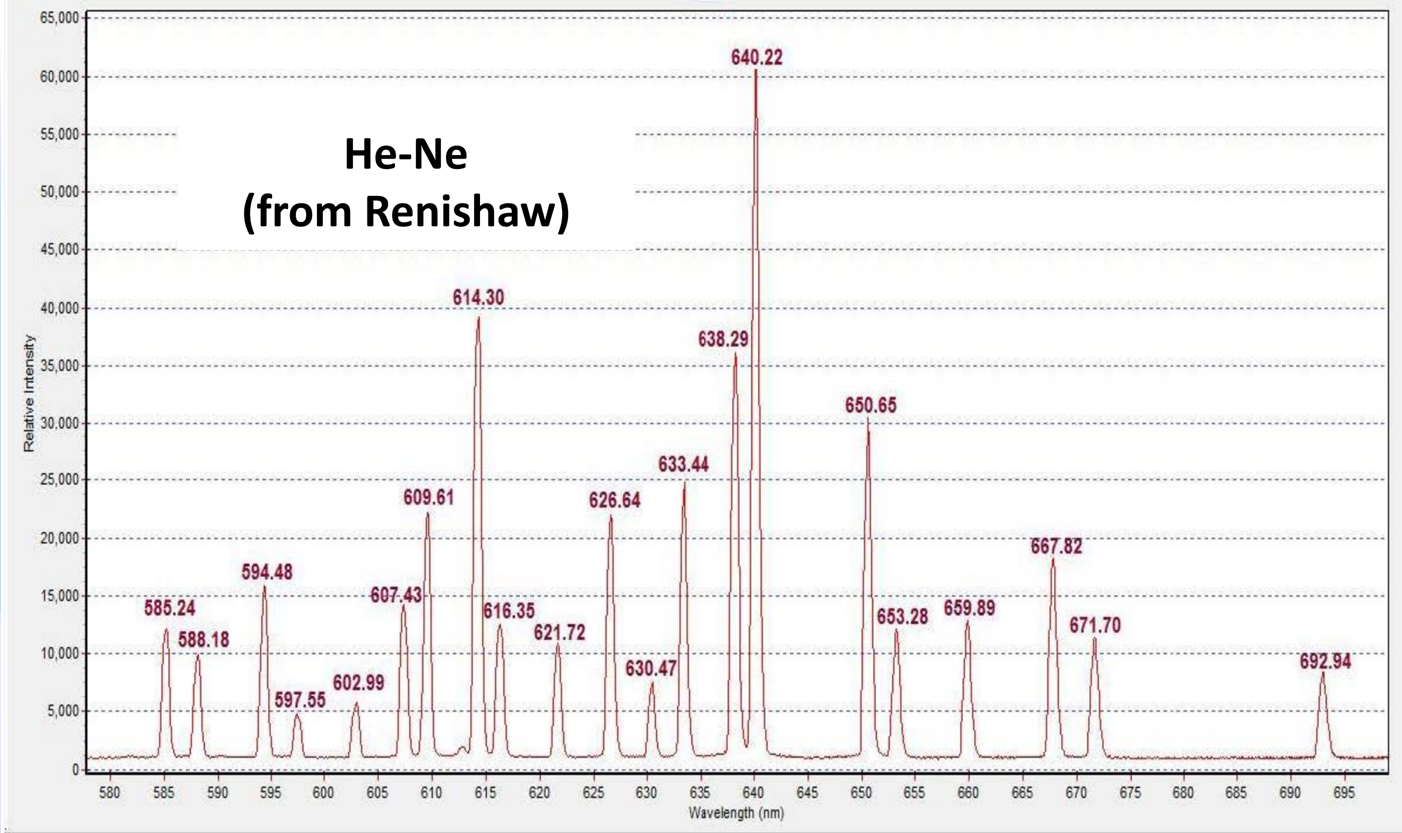


Raman shift wavenumber calibration (x-axis)

- **RMs for high accuracy (< 1 cm^{-1})**

ASTM E1840-96 (2014): Low-pressure arc lamp emission lines
ATSM E2529-06 (2014): Ar, Kr and Xe provided, not Ne or Hg
➔ NIST spectra database
manufacturer

- Alignment
- Dense spectra
- λ_0 must be determined



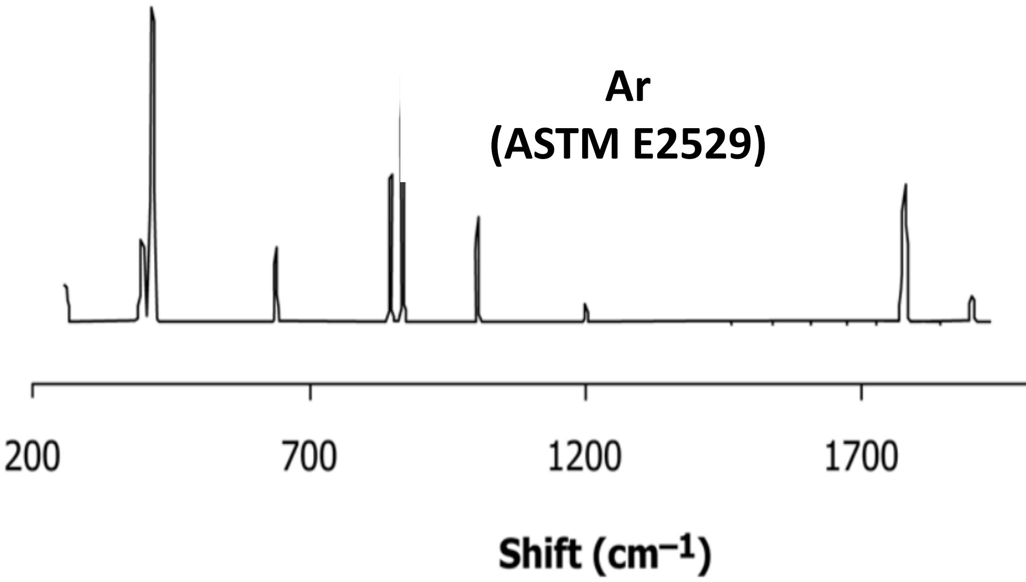


FIG. 2 Emission Spectra of Argon Plotted in Shift Units from 12 738.85 cm^{-1} (785 nm)

Raman shift wavenumber calibration (x-axis)

RMs for lower accuracy (> 1 cm^{-1})

- **Silicon:** NMIJ CRM 5606-a Single-crystal {100} for positron defect measurements

Itoh, J. Raman Spectrosc. (2020): **520.45 cm^{-1}** ± 0.28 cm^{-1}

- Manufacturers and users option, but no CRM
- Doping, residual stress, orientation
- Just one Raman band

NIM GBW

13651	13652	13653	13654	
Sulfur	Naphthalene	Cyclohexane	Paracetamol	
83.2 ± 2.2	513.7 ± 2.3	384.1 ± 2.3	214.1 ± 2.4	968.5 ± 2.3
153.2 ± 2.2	763 ± 2.2	426.5 ± 2.4	328.8 ± 2.3	1104.6 ± 2.7
219.2 ± 2.1	1019.8 ± 2.2	801.9 ± 2.4	391.8 ± 2.2	1168.2 ± 2.3
473.2 ± 2.1	1146.3 ± 2.3	1028.1 ± 2.2	465.3 ± 2.2	1236.5 ± 2.3
	1381.3 ± 2.2	1157.6 ± 2.4	504.3 ± 2.4	1371.2 ± 2.4
	1463.5 ± 2.3	1266.4 ± 2.3	651.8 ± 2.4	1515.2 ± 2.3
	1576.3 ± 2.2	1444.2 ± 2.2	710.9 ± 2.2	1561.4 ± 2.3
	3055.1 ± 2.3	2664.2 ± 2.2	797.1 ± 2.4	1648.5 ± 2.6
		2852.4 ± 2.2	834 ± 2.3	2930.4 ± 2.2
		2923.4 ± 2.2	857.5 ± 2.2	3064.6 ± 2.2
		2937.5 ± 2.2		

Raman shift range **85-3327 cm^{-1}**

- **ASTM E1840-96 (2014): solid and liquid organic RMs**

1. Naphthalene
2. 1,4 bis(2-methylstyryl)benzene
3. Sulfur
4. Cyclohexane — EP
5. Paracetamol, 4-acetamidophenol, Tylenol (IUPAC's N-(4-hydroxyphenyl)ethanamide)
6. Benzonitrile
7. Toluene/acetonitrile
8. PS

EP

NIST SRM 706a broad molecular mass distribution pellets
NIST SRM 1921b IR transmission wavelength/wavenumber
No Raman shift information/certification

Next slide for Raman CRM from NIM and NMIJ

- Mostly FT-Raman
- Uncertainty not provided
- No reference to CRM

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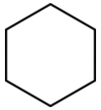
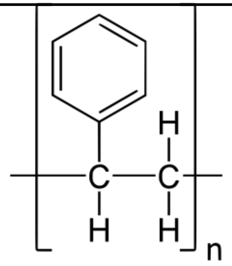
Raman shift wavenumber calibration (x-axis)

Differences!!!! (ASTM, NMIJ, NIM)

values from ASTM higher tolerances (Pharmacopoeia)

Raman shift (cm^{-1})	ASTM		NMIJ	NIM		Pharmacopoeia		
	E1840	E1683	RM8158-a	GBW13664	GBW13653	United States	European	Japanese
 Cyclohexane	384.1 ± 0.78	384.1			384.1 ± 2.3			
	426.3 ± 0.41				426.5 ± 2.4			
	801.3 ± 0.96	801.3			801.9 ± 2.4		801.3 ±2.5	
	1028.3 ± 0.45				1028.1 ± 2.2		1028.3 ±2.0	
	1157.6 ± 0.94				1157.6 ± 2.4			
	1266.4 ± 0.58				1266.4 ± 2.3		1266.4 ±2.0	-
	1444.4 ± 0.30	1444.4			1444.2 ± 2.2		1444.4 ±2.5	
	2664.4 ± 0.42				2664.2 ± 2.2			
	2852.9 ±0.32	2852.9			2852.4 ± 2.2		2852.9 ±3.0	
	2923.8 ± 0.36				2923.4 ± 2.2			
					2937.5 ± 2.2			
 Polystyrene	620.9 ± 0.69		620.7±1.2	621.2±2.1		620.9 ±3	620.9 ±2.5	620.9 ±1.5
	795.8 ± 0.78		795.1±1.2	795.5±2.2				
	1001.4 ±0.54		1001.2±1.2	1001.0±2.1		1001.4 ±3	1001.4 ±2.0	1001.4 ±1.5
	1031.8 ± 0.43		1031.5±1.2	1031.2±2.1		1031.8 ±3	1031.8 ±2.0	1031.8 ±1.5
	1155.3 ± 0.56		1154.9±1.2	1154.6±2.3				
	1450.5 ± 0.56	-	1448.4±1.2	1449.0±2.1		Qualitative	Handheld	
	1583.1 ± 0.86		1582.7±1.2	1583.2±2.2				
	1602.3 ± 0.73		1602.1±1.2	1602.4±2.1		1602.3 ±1.5	1602.3 ±3.0	1602.3 ±1.5
	2852.4 ± 0.89		2851.0±1.1	2851.3±2.3				
	2904.5 ± 1.22		2906.2±1.2	2907.5±2.5				
	3054.3 ± 1.36		3055.1±1.1	3055.7±2.4		3054.3 ±3.0	3054.3	3054.3 ±3.0

Raman intensity/response calibration (y-axis)

Response/intensity depends on:

(absolute and relative)

- Laser wavelength and intensity →
- Spectrometer
- Grating (grooves/mm)
- Detector
- Optics, focus, refractive indexes
- Polarization of irradiated or scattered light
- Filters (edge filter)
- Sampling (time, accumulations, temperature)
- Sample (geometry, size, density, cross-section, matrix)

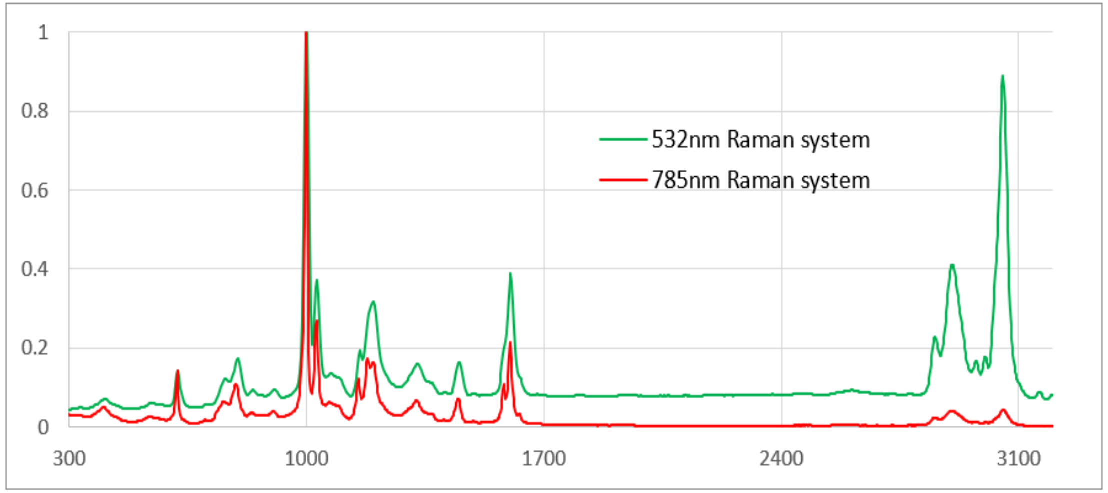


Figure 2. Comparison of the two Raman instruments analysing the same sample - each using a different excitation laser wavelength, 532nm & 785nm.

Procedure (after system modification)

1. Select relevant reference **sample(s)**
2. Select the **configuration** (optics, grating, etc.)
3. **Acquire** the reference spectrum
4. Generate the **instrument response function (IRF)**

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Raman intensity/response calibration (y-axis)

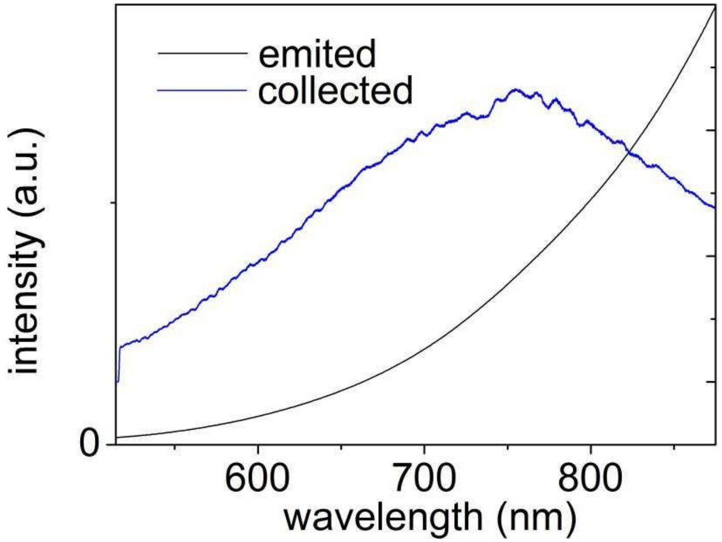
RMs for relative intensity calibration: **ASTM E2911-13**

- luminescent glasses: **NIST SRMs 2241-6**

wavelength-specific (missing samples), limited Raman shift range, rough (focus?), T dependent, stock problems, price

- Broadband white light lamp, e.g. tungsten (W)

Unpractical (positioning, heating), recalibration needed



- **Semi-quantitative measurements:**

  Internal standard + calibration curve

- **Correlate absolute intensity with sample amount in the sampling V:**
  - Packing and particle-size differences
  - Homogeneity and opacity differences
  - Fluorescence variations
  - Absorption by the matrix or the sample itself
  - Polarization effects
  - Sample heating: phase change, burning, polymorph conversion

HCA Kaiser

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Raman intensity/response calibration (y-axis)

CRM	Composition	Laser
NIST SRM 2241 (out of stock, 2022?)	0.02 mol % Cr_2O_3 Na borosilicate glass	784-786 nm
NIST SRM 2242a	0.15 wt % MnO_2 Borate glass (69.85% B_2O_3,5% SiO_2,5% ZnO,5% Li_2O)	532.2 nm
NIST SRM 2243 (discontinued 2014)	0.15 wt % MnO_2 Borate glass (Same as 2242)	514.5 nm 488 nm
NIST SRM 2244	0.7 wt % Cr_2O_3 Borosilicate glass	1064 nm
NIST SRM 2245	Bi-doped oxide (0.11 mol %) Phosphate glass	633 nm
NIST SRM 2246 (out of stock)	Cr-doped oxide (0.30 mol %) Borosilicate glass	830 nm
NIM GBW13650 (not to Europe)	Zn borosilicate glass	514.5 nm

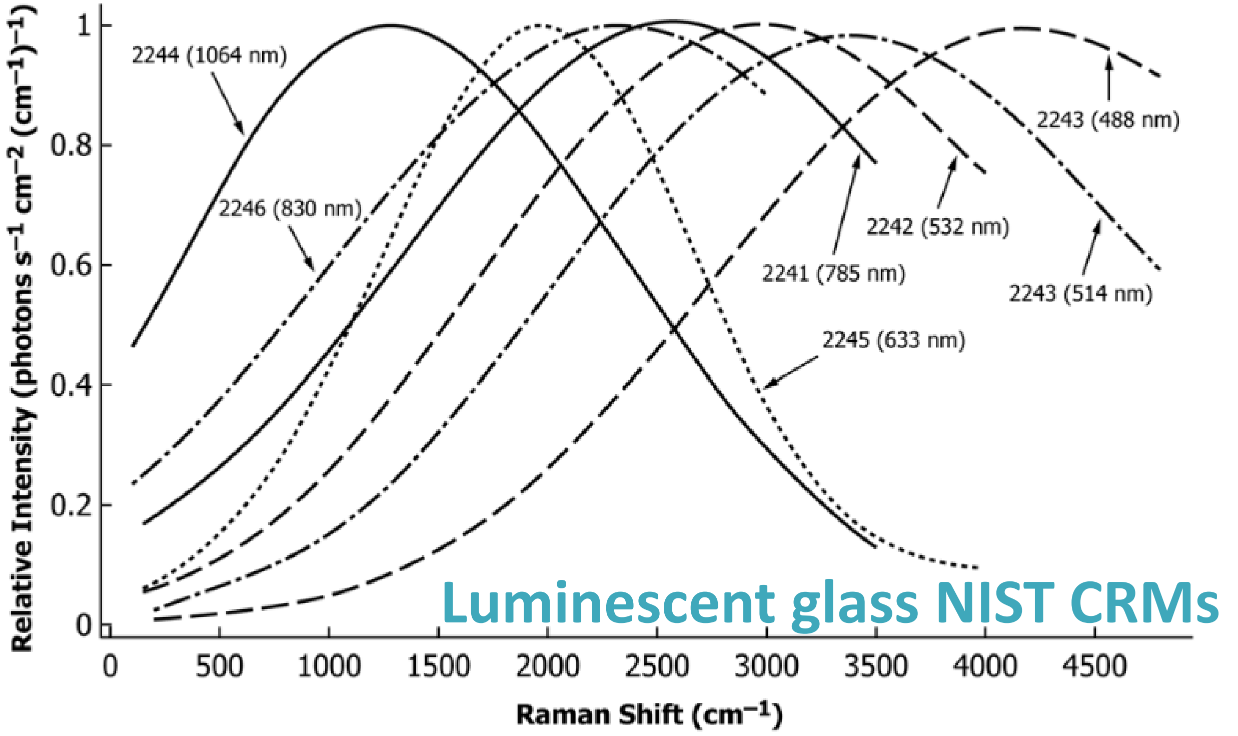

FIG. 2 Certified Models of the Corrected Luminescence Spectra of SRMs 2241 through 2246 as a Function of Raman Shift from the Specified Laser Excitation Wavelength

Commercial Raman units

Handheld & Portable Raman units

- Factory calibrated

Micro-Raman units

- (Auto) alignment: laser beam, CCD area, slit center and opening
- Quick calibration: (internal) Si peak position and counts
- Advanced calibration: x- and y-axes
  - (Internal) Ne lamp
  - (Internal) W filament (white light)
  - External RM: Organic compounds

- few information and access to the algorithms
- Internal lamps not for the full optical path

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Spectral resolution

Adjacent bands resolution

Resolution factor ↓ Spectral range ↓

$$\delta\lambda = \frac{RF \cdot \Delta\lambda \cdot W_s}{n \cdot W_p}$$

- Model transfer
- Detect laser broadening, misalignment

δλ decreases (resolution improves) with:

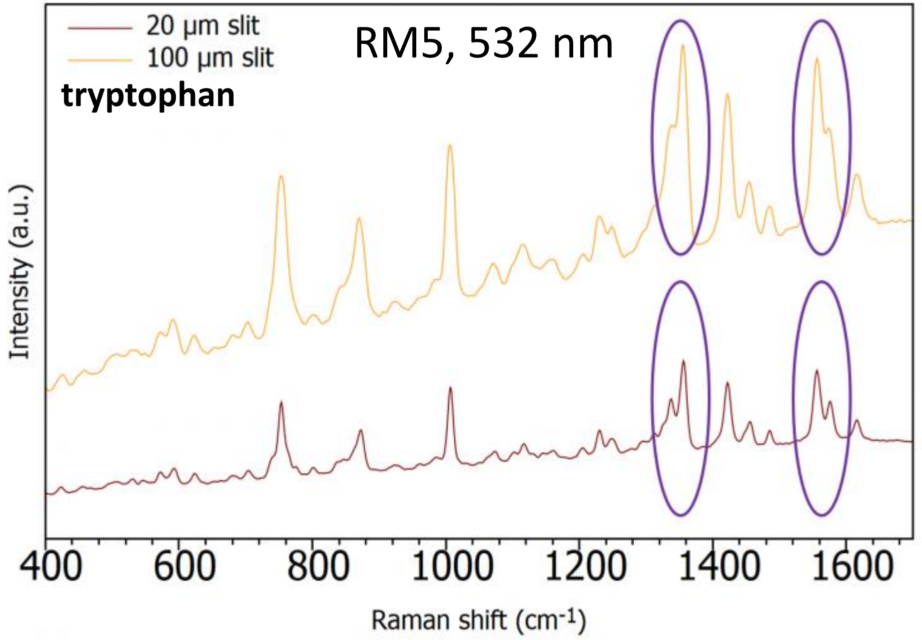
- ↑ Laser wavelength
- ↑ Grating
- ↑ Focal length
- ↑ CCD pixel number (n) and width (W_p)
- ↓ Slit width (W_s)
- ↓ Natural bandwidth of the peak

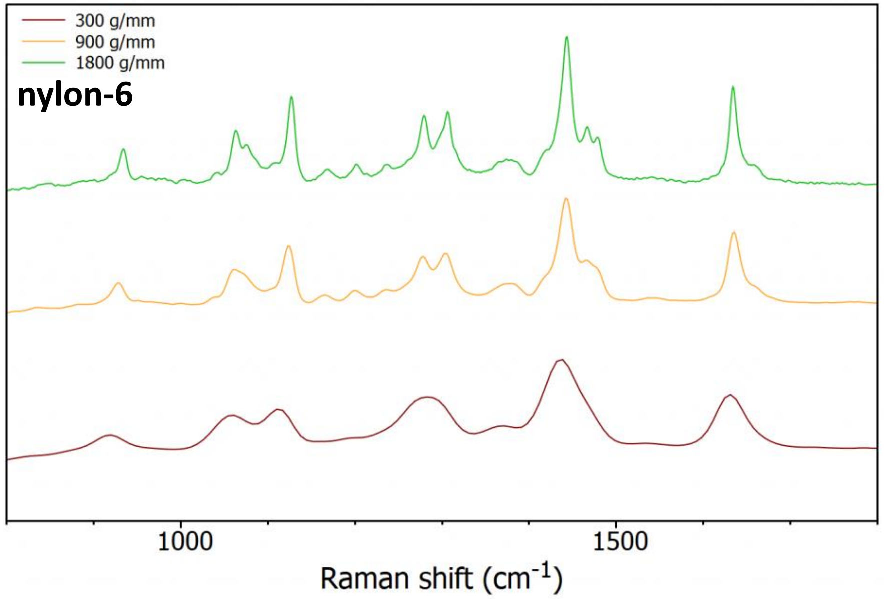
May vary in the low, middle, and long Raman shift regions

Procedure (after system modification)

1. Select relevant reference **sample**
2. Select the **configuration**
3. **Acquire** the reference spectrum
4. Fit the peak and calculate FWHM

https://www.edinst.com/blog/spectral-resolution-in-raman-spectroscopy/





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Spectral resolution

ATSM E2529-06 (2014) Testing the resolution of a Raman spectrometer

- **low-pressure arc lamp emission lines** as for x-axis calibration (Lorentzian function)
  Ar, Kr and Xe provided

- **Calcite** ($CaCO_3$) (Voigt function)

reference FT-Raman
↓

$$\delta\lambda = \frac{FWHM_{1085} - 0.684}{1.029}$$

- No CRM
- 20% accuracy
- for 785 nm

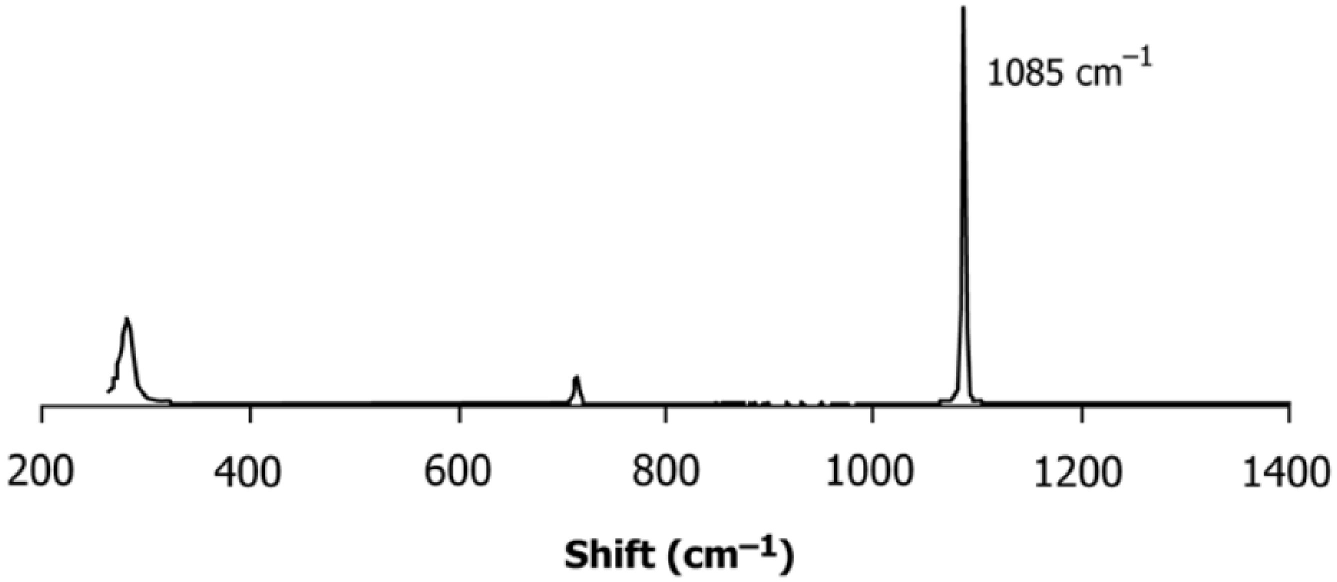

FIG. 1 Calcite Raman Spectrum

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Qualification, performance validation and more

a) **ASTM E1683-02 (2014)**
- carbon tetrachloride (toxic), indene, cyclohexane, L-cystine: no CRM
- pen lamp

b) **ASTM E1866-97 (2021)** Guide for multichannel, FT-Raman, pulsed laser, safety concerns, etc.

Univariate tests:
- energy level
- photometric noise
- short-term baseline stability
- optical contamination
- purge contamination
- wavelength stability
- resolution stability
- photometric linearity

Multivariate tests:
pass/fail spectrophotometer performance tests

- **ASTM E1654-94 (2013)** Ionizing radiation-induced spectral changes in optical fibers and cables for use in remote Raman fiberoptic spectroscopy

- **IEC/TC 86 “Fibre optics". SC 86C "Fibre optic systems and active devices”**
  - processes (IEC TS 61290-6)
  - performance testing (IEC TS 61290-10:5, IEC TR 62324)
  - safe use (IEC TS 61292-4)

Related to telecommunication systems

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Spatial resolution of Raman microscope

minimum size that can be individually analyzed

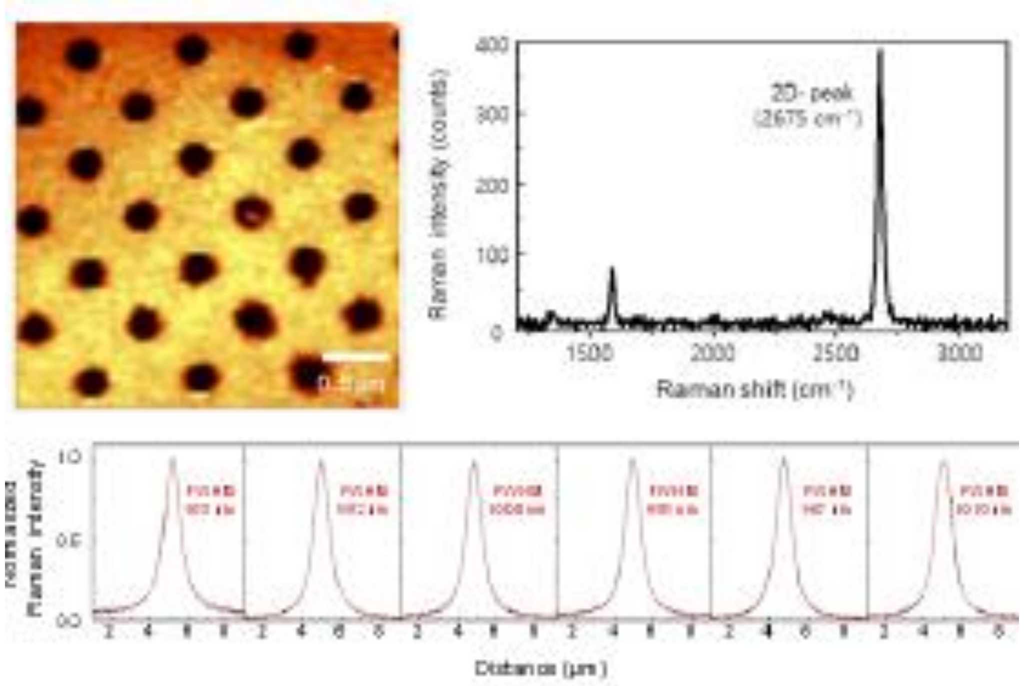
Spatial resolution increases (δxyz decreases) with:

- ↓ Laser wavelength
- ↑ N.A. of objective
- ↑ refractive index of the medium (oil vs. air)

- ISO 18516:2019
  beam based imaging methods
  Straight edge, narrow line and grating methods

- ISO 18337:2015 (2022)
  Confocal fluorescence microscopy
  Point spread function (PSF)
  (by imaging an object of negligible size)

Applicable to Raman? → VAMAS TWA 42



Axial line profile of 2D Raman band of suspended graphene layer

Spatial resolution of Raman microscope

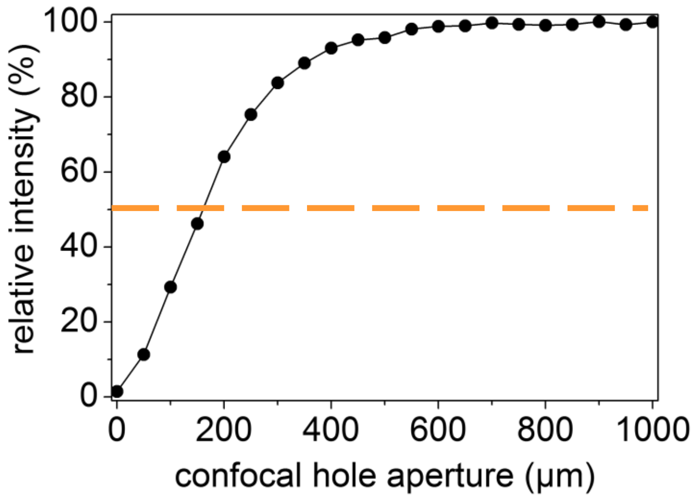
a) Lateral resolution: light diffraction limit

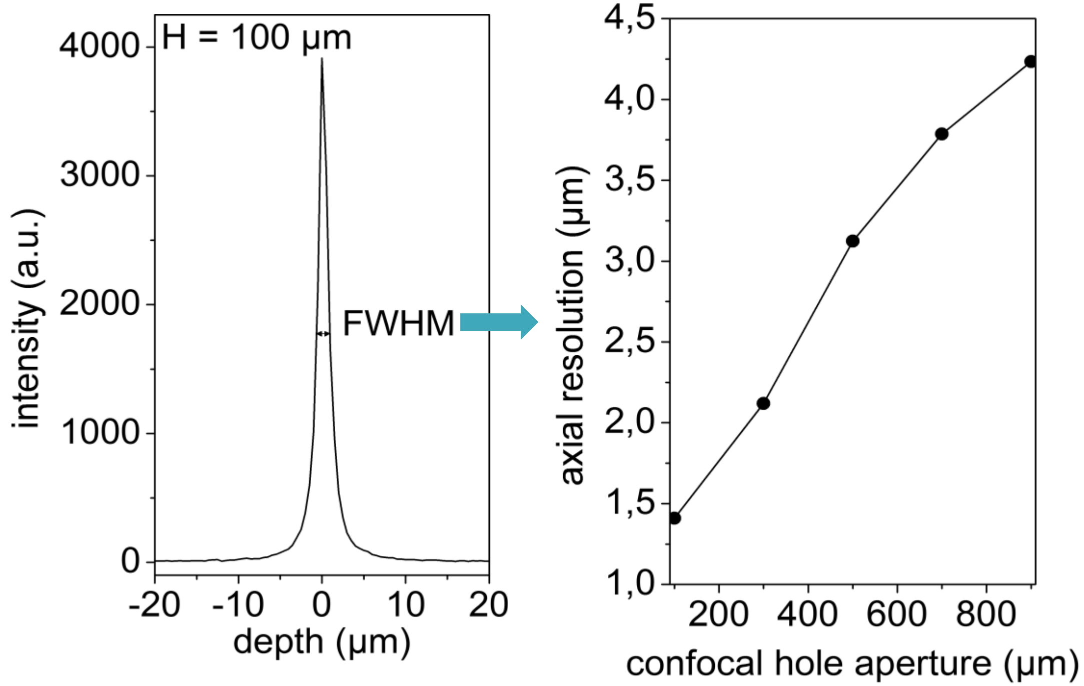
b) Confocality/axial/depth resolution: optical alignment indicator

- Confocal pin hole
- CCD area

Procedure:

1. **Si** spectrum as a function of **depth** and **hole apperture** (H).
2. **Intensity** vs. H
3. **FWHM of depth profiling intensity peak** (axial resolution) vs. H
4. **Compare** intensity and axial resolution curves with previous ones





Dubessy et al. Instrumentation in Raman spectroscopy part 2 : how to calibrate your spectrometer

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Measurement and data analysis

Measurement and data analysis

Specific applications of Raman spectroscopy:

- **Water ASTM D8333 – 20**

  Sample preparation for microplastics identification and quantification
  - wet peroxide oxidation
  - enzimatic digestion
  - sample transferred in a microscope glass slide
  - QA/QC: reference 150–250 µm spheres

- **Liquefied Natural Gas (LNG) ASTM D7940 and ISO 23978**
  - volume fractions of individual molecular species by fiber-coupled Raman

- **Nanoobject ISO/TR 18196:2016**
  - Technique matrix
  - advantages, limitations and relevant standards on Raman spectroscopy

Measurement and data analysis

Specific applications: Graphene

- **ISO/TS 21356 -1** (and -2) “Nanotechnologies — Structural characterization of graphene”
    - characterisation sequence
    - example Raman spectra

- **IEC TS 62607 series** “Nanomanufacturing-Key control characteristics”. **Part 6:** graphene-based materials

Standard	Description
IEC TS 62607-6-6	Part 6-6: **Strain** uniformity: spatially-resolved Raman spectroscopy • for single-layer graphene • Uses the width of the 2D Raman peak
IEC TS 62607-6-11	Part 6-11: **Defect** density: Raman spectroscopy • films grown by CVD and exfoliated flakes
PNW TS 113-570 ED1	Part 6-12: Number of **layers**: Raman spectroscopy, optical reflection
IEC TS 62607-6-14	Part 6-14: **Defect** level: Raman spectroscopy • Films, I_D/I_G • Powders, $I_{D+D'}/I_{2D}$ (pressed onto metallic, glass or silicon wafer)
PWI 113-131	Part 6-28: Number of **layers**: Raman spectroscopy
PNW TS 113-580 ED1	Part 6-29: **Defectiveness**: Raman spectroscopy

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Measurement and data analysis

Chemometrics

Mathematical, statistical and other methods using formal logic to:

a) design or select optical measurement procedures and experiments
b) Provide maximum information by analyzing chemical data

Growing number of standards!

Multivariate data analysis (MVDA)

- Raman as **process analytical technology** (PAT):
spectra predicted or classified by as a quality control

- **Qualification and validation** of Raman instrument

Mostly limited to:

- partial least squares (specifically PLS-1)
- principal component regression (PCR)
- multi linear regression (MLR)

MVDA-specific standards related to Raman:

- **Surrogate calibration and testing: ASTM E2056-04 (2016)**
- **Empirical calibration: ASTM E2617-17**
- **Liquid petroleum products and fuels: ASTM D6122-20a**
- **Pharmaceuticals: ASTM E2891-20**

Other relevant standards

- ASTM E1655-17 IR spectrometer calibration
- ASTM E1866-97 (2021) spectrophotometer perf
- ASTM E178-21 outliers (univariate)
- Etc.

Pharmacopeiae

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Take-home message:

standardisation landscape in Raman spectroscopy is incomplete, complex, and evolving

Manufacturers:

- Access to calibration methods
- Access to raw data

Standardisation bodies/documents:

- New/updated/extended standards: broader scope and state-of-the-art industrial and academic advances
- Easy to use documents
- Consensus/coherence
- Open access

Metrology institutes/CRMs:

- Complete the list for the actual needs and uses (e.g. NIST SRM for laser of lower wavelength, Si, Ne)
- More detailed information
- Improve availability: stock, price, multilingual

Academia and users:

- Understand and remove setup-induced spectral variations
- Engagement in standardization development

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Take-home message:

Broadening the scope of standardization documents:

- **Different Raman techniques**
- **Polarization**
- **Handheld devices**
- **Fitting**
- **Data storage: ontologies and FAIR databases**
- **Sampling/sample preparation** (filtering, digestion, etc.)
- **Sample characteristics** (substrate, matrix, particle/crystal size, packing)
- **Sample environment** (T, humidity) and **positioning** (orientation, focus)
- Laser **power density** (heating/degradation)

IEC TR 61292-4:2014 Maximum permissible optical power for the damage-free and safe use of optical amplifiers, including Raman amplifiers

NIST SRM 2241
"No significant changes in the shape of the luminescence spectrum occur over the range of laser power densities commonly used in Raman instruments"

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Applied Spectroscopy

2.388
5-Year Impa
Journal Ind

Review of Existing Standards, Guides, and Practices for Raman Spectroscopy

Afroditi Ntziouni, James Matthew Thomson, Ioannis Xiarchos, Xiang Li, Miguel A. Bañares, Costas Charitidis, Raquel Portela, Enrique Lozano

Show I

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Thank you!

Questions?

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