

CEN

CWA 18133

WORKSHOP

September 2024

AGREEMENT

ICS 17.180.30

English version

Raman instruments calibration and verification protocols

This European Standard was corrected and reissued by the CEN-CENELEC Management Centre on 11 September 2024.

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Ref. No.:CWA 18133:2024 E

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Foreword

This CEN Workshop Agreement (CWA 18133:2024) has been developed in accordance with the CEN-CENELEC Guide 29 “CEN/CENELEC Workshop Agreements – A rapid prototyping to standardization” and with the relevant provisions of CEN/CENELEC Internal Regulations - Part 2. It was approved by a Workshop of representatives of interested parties on 2024-07-11, the constitution of which was supported by CEN following the public call for participation made on 2023-12-20. However, this CEN Workshop Agreement does not necessarily include all relevant stakeholders.

The final text of this CEN Workshop Agreement was provided to CEN for publication on 2024-07-17.

Results incorporated in this CWA received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 952921.

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Introduction

Although Raman spectroscopic data intrinsically depends on how the Raman signal is obtained - instrument and acquisition configuration, sample and sampling environment- and (pre)treated/processed to generate and analyse the Raman spectra, there is consensus neither within academia nor among standardization bodies or manufacturers on the best way to calibrate Raman instruments and harmonize Raman data. The need for the user to calibrate, verify and maintain the Raman instrument is a daily challenge and a source of deviations. An example of the existing divergence in the procedures is the relative intensity correction, fundamental to compare spectra acquired with different instruments or excitation wavelengths. A limited number of manufactures offer intensity correction procedures, using external or internal references, which can be luminescent glasses certified by metrology institutes (wavelength specific) or a calibrated irradiance source (valid for multiple excitation wavelengths), as indicated in ASTM E2911. The calibration frequency and protocol depend on the type of Raman instrument, target application/user, or availability of references. Differences created by the optical path, reference material, operator, or algorithms in the resulting calibration are unclear. Operations relative to the y-axis calibration can be affected by several factors, such as the use of polarisers, sampling geometry, focal point volume, depth of analysis, dispersion, detector-related factors (integration time, saturation, gain, etc.), fluorescence or luminescence effects, electronic noise, environmental light contamination, cosmic radiation, etc. Operations relative to the x-axis calibration are more frequent and better understood and covered in a good number of available standard protocols and methods (sometimes diverse). These operations include:

- Spectrometer wavelength/wavenumber calibration to correlate pixels with an equivalent wavelength/wavenumber (in absolute nm or cm^{-1}).
- Raman shift calculation (in relative cm^{-1}), defined by the laser line.
- Spectral dispersion over the observation window, which drives the valid spectral range -and consequently pixel resolution.
- Spectral resolution.
- Pixel adjustments, related to, e.g. the elimination of hot pixels and data point interpolation.

The existing standard reference materials and guides for calibration and validation in Raman spectroscopy have proven to be valuable for many years, but they are incomplete. For example, how spectral resolution might affect calibration is not indicated, Raman shift values provided in ASTM E1840 were obtained with single-mode laser lines only, mainly with FT-Raman systems -a technique currently in decline-, and no corrections were introduced for polarizability or resonance effects, or the now extensively used multimode lasers. Moreover, they lack interconnection, which is critical for easy and extended applicability and to avoid divergencies, and there is no clear indication to run a complete system calibration or to harmonize data in the standardization landscape.

This has created a need for a more comprehensive protocol which not only calibrates the x and y axes, but verifies the resolution variation across the entire spectral range. This document introduces one such protocol, which aims to facilitate inter-instrument comparison of data.

1 Scope

This CEN Workshop Agreement (CWA) provides a data harmonization protocol for Raman instruments that allows:

- Calibration adjustment of data and instruments already calibrated by the manufacturer;
- Calibration of instruments without any previous calibration;
- Verification of the calibration for instruments that were calibrated with this protocol in the past.

The protocol consists of the following calibration and verification stages: x-axis positions, x-axis resolution and y-axis relative intensity correction. In addition to the use of the full protocol to harmonize an instrument, independent sections of the protocol can be used to verify/calibrate certain qualities (x-axis calibration, resolution, or y-axis calibration) of the instrument.

The protocol is applicable to any kind of Raman instrument within the boundaries described in chapter 5. Primary use of this protocol is for fixed grating dispersive spectrometer systems. In scanning spectrometer systems, the exact settings of the scanning are to be considered as part of the optical path.

The protocol may have application beyond the boundaries stated, such as systems using 514.5 nm or 633 nm excitation sources, but it has been developed using only 532 nm and 785 nm instruments, and as such its effectiveness with other excitation wavelengths is unconfirmed.

NOTE Term 'calibration' can have legal meaning in a metrology environment, this is not the focus of this CEN Workshop Agreement.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ASTM E1840, *Standard Guide for Spectrometer Calibration and Validation of the Raman shift axis*

ASTM E2911, *Standard Guide for Relative Intensity Correction of Raman Spectrometers*

3 Terminology

Where used, this document follows the definitions outlined in ISO 18115 series.

For the purpose of this document, the following terms, definitions, symbols and abbreviations apply.

NOTE The definitions below may be linked to different terms by other manufacturers and bodies. The terms below have been chosen to reduce confusion when being used together.

3.1 Terms and definitions

3.1.1

counts corrected

units for the y-axis of the Raman spectrum after an intensity correction algorithm has been used

3.1.2

laser zero position

the wavelength of the laser excitation, which becomes 0 Raman shift (cm^{-1}) on the Raman shift x-axi

3.1.3**optical path**

the list of components (e.g. collection lens, slit, grating) that the Raman scatter passes through, from the sample, to reach the detector

3.1.4**pixel resolution**

FWHM of neon emission on either the pixel, wavelength, wavenumber, or Raman shift x-axis

3.1.5**pixel resolution curve**

a function fit of the FWHM vs the position of the neon peaks in the spectral range, in either the pixel, wavelength, wavenumber, or Raman shift x-axis

3.1.6**primary Raman data**

Raman data as obtained from the software, and thus has already some level of mathematical treatment to create a full Raman spectrum (e.g. pixel binding, stitching data segments, spectrometer offset correction or applying corrections that contaminate the spectrum such as hot pixels). This data will be already displayed in cm^{-1} or Δcm^{-1}

3.1.7**Raman focus**

the act of adjusting the focus on the sample to maximise the intensity of the Raman signal

3.1.8**raw Raman data**

a set of (unprocessed) data that is given directly as output from the detector. (Based on an excerpt from CWA 17815:2021)

3.1.9**spectral distribution**

the width of wavelengths/wavenumbers the pixel collects. Taken as the halfway point between $\text{Pix}(n-1)$ and $\text{Pix}(n)$ - the halfway point between $\text{Pix}(n+1)$ and $\text{Pix}(n)$, for $\text{Pix}(n)$

3.1.10**spectral resolution**

the minimum distance between two peaks to be separated unambiguously, based on the FWHM of calcite on the Raman shift x-axis

3.1.11**spectral resolution curve**

an adjustment of the pixel resolution curve based upon the spectral resolution(s)

3.2 Symbols and abbreviated terms

c.c.	Counts corrected
ASTM	American Society for Testing and Materials
CRM	Certified reference material
FWHM	Full width at half maximum
NIST	National Institute of Standards and Technology

SpeD:SRes	Ratio of spectral distribution to spectral resolution
SRM	Standard reference material, a registered trademark (™) belonging to NIST
SNR:	Signal-to-noise ratio

4 Overview and significance

This calibration and verification protocol focuses on three parameters of the Raman instrument:

- x-axis positions;
- x-axis resolution;
- y-axis relative intensity correction.

x-axis positioning is required to transform the raw Raman data from the detector pixels into a spectrum, with signal intensity as a function of wavelength or Raman shift, in an accurate, reproducible manner, allowing for noting peak shifts or for successful identification -primary Raman data-. x-axis resolution assessment is required for adjusting and comparing data between instruments of varying resolution. y-axis relative intensity correction is required to evaluate relative intensities, especially for comparing visible laser instruments to NIR laser instruments, as their detectors have wildly different quantum efficiency profiles, though they differ even in systems of the same laser wavelength.

The objectives that motivate the development of the harmonization protocol are:

1. Create more accurate x-axis calibrations.

Current x-axis calibrations are defined by the manufacturer. This can lead to variability in the precision, and therefore peaks from two spectrometers might not align within accepted tolerance if the instrument variance exceeds the expected variation in the peak position.

2. Facilitate correction of each instrument based on their resolution across the whole range.

Resolution of instruments is often taken as a flat figure, normally evaluated at one point in the spectrum. However, it is known that the resolution of an instrument does in fact vary across the detector. If this resolution behaviour across the entire detector can be defined, then a function that adjusts the spectrum can be used to better compare two instruments with different resolution curves.

3. Correct the intensity for quantum efficiency-based intensity discrepancies.

The instrument response depends on many factors such as the sample properties (geometry, size, density, cross-section, matrix), sampling parameters (time, accumulations, temperature), excitation wavelength and power density, spectrometer, grating, detector, optics, focus, refractive indexes, polarization of irradiated or scattered light, or type of filters. A known issue when comparing Raman spectra originating from systems with a different excitation wavelength, is that the detector responds differently to different wavelengths of light. This is in part due to the transmission curves of the optics, favouring some wavelengths over others. Primarily the difference in intensities seen at different wavelengths is due to the quantum efficiency of the sensor.

5 Requirements of the calibration and verification protocol

The next considerations shall be met in order to ensure the harmonization protocol provides the desired results. Any instrument beyond the scope of these boundaries can attempt the full protocol to qualify the behaviour of the instrument, but the resulting calibration has not been confirmed to be within the accepted tolerance of calibration and verification.

5.1 Boundaries

Due to the breadth of Raman instrumentation, the calibration and verification protocol has the boundaries of use included in Table 1.

Table 1 — Boundaries of use

Boundary	Explanation
Excitation wavelength	The protocol has been developed primarily with 532 nm and 785 nm Raman systems.
Laser stability	Some lasers drift (i.e. change wavelength) when operating at different laser power. The protocol should use the same laser power for all spectra collected (i.e. 100 %). Transfer to different laser power may require a linear shift of the x-axis calibration if drift occurs.
Not designed for full calibration of scanning systems	The protocol can be used to calibrate one mode of a scanning system. However, due to the movement of certain components within the optical path, separate experimental days will require independent calibration.
No polarisation	The effects of polarisation on the Raman peaks have not been considered in this protocol.
No resonance	The effect of resonance on the Raman peaks has not been considered in this protocol.
No discrimination between confocal vs non-confocal	The effect of confocality on the Raman peaks has not been considered in this protocol.
Pixel resolution < 0.8 nm	Defined resolution useable with the protocol, based on the FWHM of the Ne lines. (Note: Pixel resolution above that threshold can use the protocols, but the results have not been evaluated)
Backscattered spontaneous Raman	Only 180° backscattered Raman has been used to develop this protocol, and as such, techniques like transmission, SERS, etc. cannot be confirmed to use this method.
Stokes only, no THz/GHz Raman	Only Stokes Raman scattering is considered for this protocol, excluding GHz/THz Raman scattering. Anti-Stokes is not considered.
Valid only for one optical path	The calibration spectra shall be collected with the same optical path and laser. Changes to either require their own calibration. x-axis calibration can be shared by similar optical paths, but requires specific verification. y-axis calibration shall be done for each optical path.
Post-acquisition calibration of data	The protocol is designed for post-acquisition calibration of data. It can be used: *to calibrate new instruments by manufacturers. *to create a virtual calibration, with existing instruments. It does not add a new calibration to the instrument.

Boundary	Explanation
Full protocol is required for calibration of an instrument	The individual steps and sections shall ALL be followed to consider the system calibrated. The protocol is broken down into branches for ease of understanding. Individual branches are useful for verification of parameters.

5.2 Reference materials

The required qualities of the materials used in the protocol are defined in Table 2. Sample-specific guidance on how to measure is included in Table 4 (Section 5.3.2) and Annex A.

Table 2 — Samples and their required quality

Material	Quality
Neon	Shall not contain non-neon lines which interfere with the analysis of the neon lines. The relative intensity of the peaks should be a close match for literature values ^{5,6} , e.g. 585 nm peak should be the strongest peak. Variation in exact intensity is expected as spectrum will not be intensity calibrated.
Silicon	Only one silicon sample is required The surface can be smooth or rough . The dopant of the silicon can be undoped (N) or doped with boron (B) or phosphorus (P). The orientation of the silicon crystal can have (100) or (111) crystal orientation if undoped or (100) crystal orientation for any of the mentioned dopants.
Calcite	The spectrum shall not have strong fluorescence. The fluorescent maximum should not be higher than 20 % of the 1085 cm ⁻¹ peaks raw maximum. Calcite should be cut, as this reduces the likelihood of fluorescence being observed, compared to forced cleaving.
Polystyrene	The surface shall be polished. Shall be a solid extruded, clear, with minimal additives. The thickness of the sample should be 5 mm or larger, with a sampling area of minimum 2 mm diameter or larger. Molecular weight of the polystyrene is recommended to be approximately 185000 g/mol. Significantly lower values (e.g. 35000 g/mol) cause thermal instability, and significantly higher values (e.g. 400000 g/mol) have deviations from the anticipated peak positions.
NIST SRMs	Specific dependent on wavelength of excitation (only 532 nm and 785 nm covered). ^{7,8}
ELODIZ LED	Specific dependent on wavelength of excitation (only 532 nm and 785 nm covered).
White light source	Traceable source will preferably function over the entire spectral range

5.3 Data quality

5.3.1 Data quality

The reference spectra need to be checked for quality according to the information included in Table 3.

Table 3 — Data quality considerations

Issue	Explanation
Saturation	The peaks being analysed and the areas in close proximity shall not be saturated.
SNR	Signal to noise ratio of peaks to be analysed shall be at least > 8, and ideally > 100. SNR is calculated using $(S-B)/N$, where S is the peak maximum, B is the peak base level, and N is the standard deviation of the noise from a flat region of the spectrum without any peaks.
Spikes	Spikes shall be removed from the spectra using a spike removal algorithm, as they can distort peak fitting and other processing steps.
Pedestalling	The spectrum should not have pedestalling, which is where the entire spectrum is above a y-axis value. The y-axis offset should be set to zero in the spectra.
Environmental contamination	Background subtraction shall be applied to each spectrum to remove effects from the environment, such as light emissions, etc. The background shall be collected using the same acquisition parameters (i.e. exposure time, number of averages/accumulations) with the sample and probe in the same positions as during the spectrum acquisition, with the laser off. No shutters or covers should be used that prevent the environmental light from reaching the detector during background acquisition.
Raw-data files	The data acquired should not have any pre-processing (smoothing, baseline correction, etc.) except those necessary to generate a readable spectrum file (such as binding or stitching).

5.3.2 Sample specific guidance

The particular guidance to be considered for the samples is defined in Table 4.

Table 4 — Sample specific considerations

Reference material	Specific consideration
Neon	<p>Make sure the emission port for the neon is in the focal plane.</p> <p>It may be required to use additional optics for delivery of the emission to the optical path, or reduction of intensity to avoid saturation. These accessories shall not interfere with the resulting spectrum.</p> <p>Adjust the acquisition time to ensure the peaks are not saturated.</p> <p>In uncooled detectors, a second spectrum may be required to see some weaker peaks. This will require a longer exposure time than the first, and will result in some of the originally visible peaks becoming saturated. The widest range of peaks should be usable.</p>
Silicon	<p>Due to polarization phenomena, rotate the sample in the plane orthogonal to the laser to maximize signal.</p> <p>Different silicon types have different tolerances – see Appendix 1</p> <p>Rougher surface is a stronger scatter when exposed to 785 nm laser excitement.</p> <p>Maximize signal using Raman focus.</p> <p>WARNING: NIR lasers may easily heat the sample, creating a broad peak near 2500 cm^{-1}. This broad emission may need to be saturated (using increased acquisition time) to allow for better visibility of the silicon peak at 520.45 cm^{-1}. Limit sample exposure to laser radiation before taking a spectrum.</p>
Calcite	<p>Maximize signal using Raman focus</p> <p>Due to polarization phenomena, rotate sample in the plane orthogonal to the laser to further maximize signal.</p>
Polystyrene	<p>Maximize signal using Raman focus.</p> <p>WARNING: Caution with highly focused collection optics, since high power density can cause deformation and damage the sample. Limit the laser power to prevent damage.</p>
NIST SRMs	Use as indicated by the NIST and ASTM E2911.
ELODIZ LED	<p>Warm up LED for 60 s to achieve stability.</p> <p>Maximize the intensity at the centre of the irradiation, focus on the surface of the glass.</p>
White light source	Use as indicated by the manufacturer

5.3.3 Metadata

Some information is required to accompany the spectra and the resulting calibration.

Mandatory metadata include:

- Make and model of the instrument
- Serial number of the instrument
- Instrument type
- Optical path details

- o Laser wavelength
- o Focusing optics
 - Numerical aperture
- o Grating
- o Slit size
- o Pinhole, if present
- Acquisition parameters
 - o Exposure time
 - o Number of averages/accumulations
 - o Laser power in mW at sample position

Optional metadata include:

- Number of data points
- Cut off filter wavelength/Raman shift
- Temperature in the lab
- Laser spot size
- Any stitching or binding processing used to create the full spectrum

6 x-axis calibration and verification protocol

6.1 Prerequisites and purposes

Prerequisites for the x-axis calibration protocol are:

- A. Neon spectrum¹
- B. Silicon spectrum²
- C. Calcite spectrum³
- D. Polystyrene spectrum⁴
- E. Laser wavelength integer

Detailed information on these prerequisites can be found in Annex A. Sample-specific guidance on how to measure the samples is included in Table 4 and sample requirements in Table 2.

¹ NIST tabulated neon values – found in ANNEX A, Table 5.

² Tabulated silicon values – found in ANNEX A, Table 6.

³ Tabulated calcite values – found in ANNEX A, Table 7.

⁴ ASTM tabulated polystyrene values – found in ANNEX A, Table 8.

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A. Neon spectrum

The neon peak positions are used to create a wavelength x-axis. These need to be correlated with NIST absolute peak position values. The neon peak widths are used to find the pixel resolution.

B. Silicon spectrum

The silicon spectrum is used to calculate the Raman shift x-axis based on the silicon peak position in the wavelength x-axis.

C. Calcite spectrum

The calcite spectrum is used to verify the calibration steps and to make a final adjustment to the Raman shift x-axis (with the polystyrene peaks), as well as to assess the Raman spectral resolution.

D. Polystyrene spectrum

The polystyrene spectrum is used to verify the calibration steps and make a final adjustment to the Raman shift x-axis (with the calcite peaks).

E. Laser wavelength integer

The laser wavelength integer is required to turn the Raman shift x-axis that already exists on an instrument to an approximate wavelength x-axis.

Algorithm/techniques required to be used are:

- a) Peak base approximation / baseline
- b) Peak finding / peak candidate generation
- c) Peak fitting using
 - o Gaussian peak shape
 - o Pearson IV peak shape
 - o Voigt peak shape
- d) Polyharmonic spline
- a) Peak base approximation / baseline

Peak base approximation is required to give the peak fitting method a grounding point for the peak to be fit upon.

- b) Peak finding / peak candidate generation

Peak candidates are the rough parameters of the peak used as a first approximation of the peak. The included factors are position (of the highest pixel), height (amplitude of highest pixel) and FWHM (geometrically calculated).

- c) Peak fitting

Peak shapes used are Gaussian, Voigt and Pearson IV. The peak shapes are used to find the precise position and the FWHM of the peak observed. Shape selected is based upon the associated error of the fit and the accuracy and precision of the results.

- d) Polyharmonic spline

Polyharmonic spline is a function used to interpolate and extrapolate the rest of the x-axis from the ideal/absolute values and the observed values.

6.2 Position and resolution calibration and verification protocol

The calibration and verification protocol for x-axis positioning and resolution is described in Figure 1, Figure 2 and Figure 3, where:

- Green shaded box = instruction
- Yellow shaded box = acquired before protocol
- Orange shaded box = acquired during protocol
- Blue shaded box = needs testing / confirmation

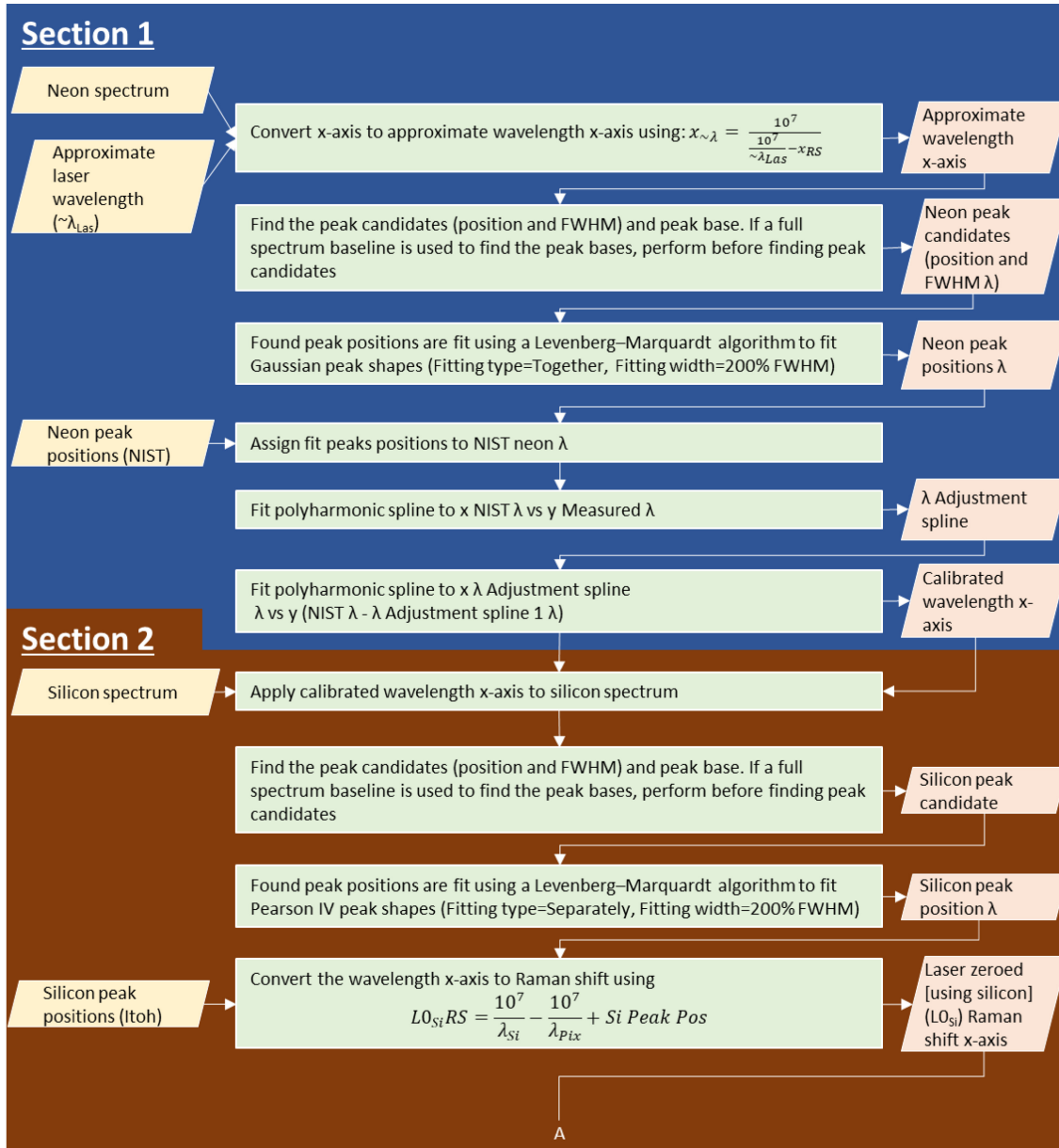


Figure 1 — Section 1 and 2 of the x-axis position and resolution calibration and verification protocol

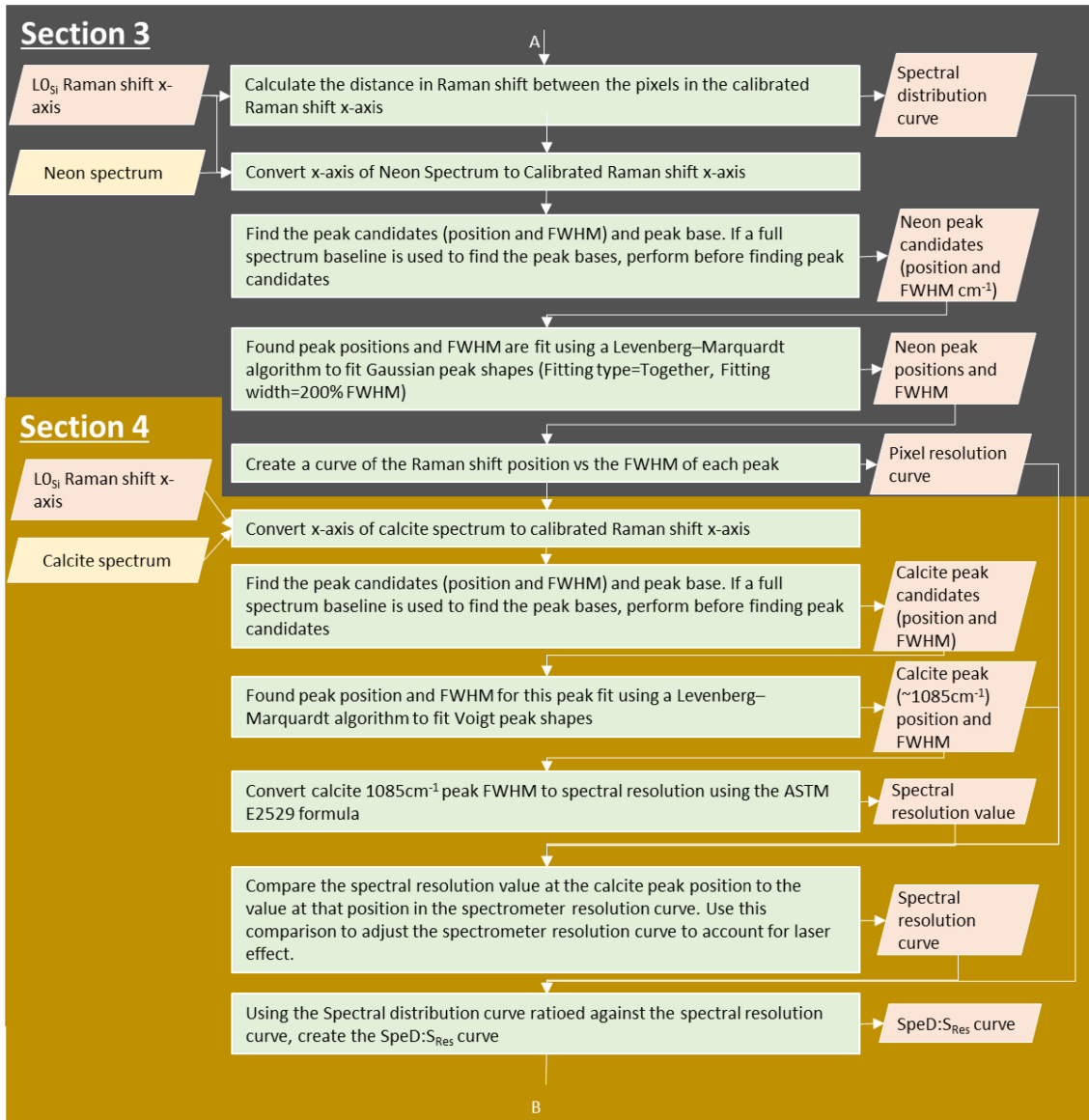


Figure 2 — Section 3 and 4 of the x-axis position and resolution calibration and verification protocol

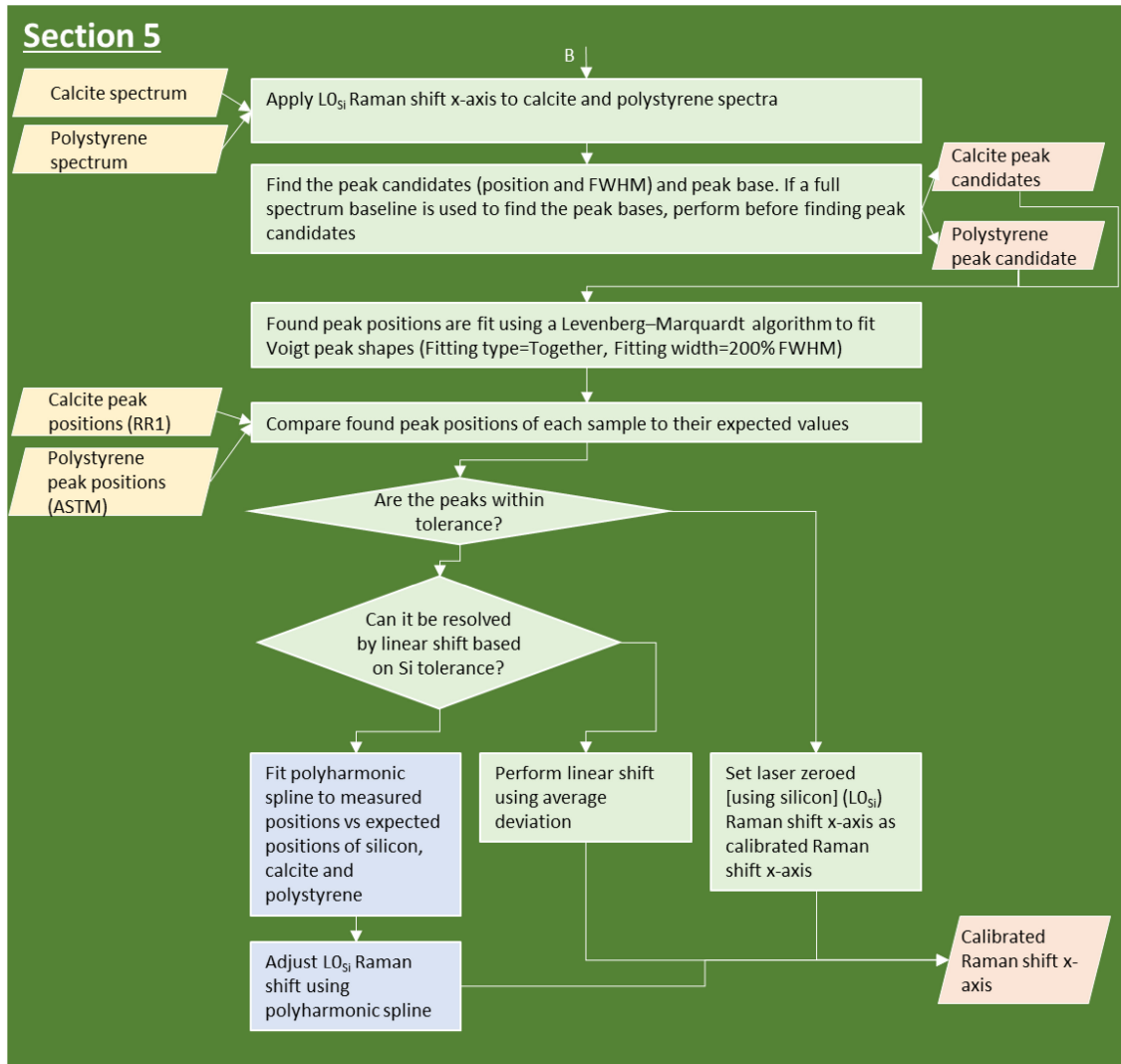


Figure 3 — Section 5 of the x-axis position and resolution calibration and verification protocol

6.2.1 Section 1- Wavelength x-axis

Use a neon spectrum and an approximate wavelength x-axis to match the neon peaks to their NIST assignments, and then calibrate the x-axis to a wavelength x-axis (Figure 1).

6.2.2 Section 2- Laser zeroed Raman-shift x-axis

Apply the wavelength x-axis to the silicon spectrum. The silicon peak is then used to find the laser zero position and convert the wavelength x-axis to the Raman-shift x-axis (Figure 1).

6.2.3 Section 3- Spectral distribution and Pixel resolution curves

Use the laser zeroed Raman-shift x-axis to find the spectral distribution across the detector. The laser zeroed Raman-shift x-axis is then applied to the neon spectrum to create a spectrometer resolution curve from the FWHM of the neon peaks (Figure 2).

6.2.4 Section 4- Spectral resolution and SpeD:SRes curve

Applies the laser zeroed Raman-shift x-axis to the calcite spectrum to find the Raman spectral resolution, which in turn is used to adjust the pixel resolution curve to make a Raman spectral resolution curve and SpeD:SRes curve (Figure 2).

6.2.5 Section 5– Calibrated Raman-shift x-axis

Apply the laser zeroed Raman-shift x-axis to the calcite and polystyrene spectra using the peak position information to make a final adjustment to the laser zeroed Raman-shift x-axis to create the calibrated Raman-shift x- axis (Figure 3).

7 y-axis (relative intensity) correction protocol

Relative intensity correction shall be performed after the calibration of x-axis, as the conversion formula requires the use of the x-axis values.

y-axis correction involves the measurement of a certified reference material that can be:

- NIST SRM fluorescent glass sample
- Traceable LED light source (e.g. ELODIZ Raman intensity correction LEDs)
- Traceable white light source (e.g. Tungsten lamp)

The expected curve will accompany the sample, usually in the form of a formula, and shall be compared to the measured curve. The ratio between the two is used to apply a multiplier to each pixel's intensity value.

y-axis after calibration should be in c.c. units to indicate that a correction algorithm has been applied to the data.

8 Calibration files

Calibration files contain the necessary information needed to apply the calibration to an instrument (by a manufacturer) or to data (post-acquisition, by an end user).

For x-axis calibration, the file contains:

- Metadata as listed in section 5.3.3
- Date of the calibration
- Calibration curve, consisting of points of uncalibrated shift values as independent variable and calibrated shift values as dependent variable
- The silicon peak position in wavelength/wavenumber
- The calibrated laser wavelength in nm (optional)

The intended purpose of the calibration curve points is to generate a spline function with these points, and then to retrieve the calibrated Raman shift values. Thus, the calibration curve may or may not have as many points as the original spectra. However, the spline generated by the curve points shall match the original calibration data with sufficient accuracy. The first and the last point should correspond with the minimum and maximum shift value of the spectral range, respectively.

For y-axis calibration, the file contains:

- Reference to x-axis calibration used
- Metadata as listed in section 5.3.3
- Date of the calibration

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- Calibration curve, consisting of points of calibrated shift values as independent variable and intensity factors as dependent variable.

The intended purpose of the calibration curve points is to generate a spline function with these points, and then to retrieve the intensity factors as function values of this spline. Thus, the calibration curve may or may not have as many points as the original spectra. However, the spline generated by the curve points shall match the original calibration data with sufficient accuracy. The first and the last point should correspond with the minimum and maximum shift value of the spectral range, respectively.

Annex A (normative)

Requirements for x-axis calibration and verification protocol

The following spectra shall be acquired for x-axis calibration, before the beginning of the calibration protocol, in the same analysis session. Neon and polystyrene may require collection of a second over-exposed spectrum to enhance low intensity peaks within the spectrum.

- Neon spectrum
 - o Neon over exposed spectrum
- Silicon spectrum
- Calcite spectrum
- Polystyrene spectrum
 - o Polystyrene over exposed spectrum

Laser wavelength integer is the wavelength of the laser in the Raman instrument, as indicated by the supplier. It is infrequent that the manufacturer provides an accurate laser wavelength value but the unit will be sold with a laser wavelength such as 532 nm, or 785 nm, which is what is referred to as the laser wavelength integer.

Table 5 — Neon peak positions (NIST)⁹

Peak #	Peak position in wavelength / nm	Uncertainty / nm	Peak #	Peak position in wavelength / nm	Uncertainty / nm
1	533.07775	0.00004	38	705.91079	0.00004
2	540.05616	0.00004	39	717.39380	0.00004
3	556.27662	0.00004	40	724.51665	0.00004
4	565.66588	0.00004	41	748.88712	0.00004
5	571.92248	0.00004	42	753.57739	0.00004
6	574.82985	0.00004	43	754.40439	0.00004
7	576.44188	0.00004	44	794.31805	0.00004
8	580.44496	0.00004	45	808.24576	0.00004
9	582.01558	0.00004	46	811.85495	0.00004
10	585.24878	0.00005	47	813.64061	0.00004
11	587.28275	0.00004	48	830.03248	0.00004
12	588.18950	0.00005	49	836.57464	0.00004
13	590.24623	0.00004	50	837.76070	0.00010

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Peak #	Peak position in wavelength / nm	Uncertainty / nm
14	594.48340	0.00005
15	596.54710	0.00004
16	598.79074	0.00004
17	602.99968	0.00005
18	607.43376	0.00005
19	609.61630	0.00005
20	612.84498	0.00004
21	614.30627	0.00005
22	616.35937	0.00005
23	618.21460	0.00004
24	621.72812	0.00005
25	626.64952	0.00005
26	630.47893	0.00005
27	633.44276	0.00005
28	638.29914	0.00005
29	640.22480	0.00010
30	650.65277	0.00005
31	653.28824	0.00005
32	659.89528	0.00005
33	667.82766	0.00005
34	671.70430	0.00005
35	692.94672	0.00004
36	702.40500	0.00004
37	703.24128	0.00004

Peak #	Peak position in wavelength / nm	Uncertainty / nm
51	846.33569	0.00004
52	849.53591	0.00004
53	854.46952	0.00004
54	857.13535	0.00004
55	859.12583	0.00004
56	863.46472	0.00004
57	870.41122	0.00010
58	877.16575	0.00010
59	878.37539	0.00004
60	885.38669	0.00004
61	891.95007	0.00010
62	898.85564	0.00010
63	914.86720	0.00010
64	920.17588	0.00010
65	927.55191	0.00010
66	930.08532	0.00010
67	932.65072	0.00010
68	937.33079	0.00010
69	942.53797	0.00010
70	945.92110	0.00010
71	948.66825	0.00010
72	953.41640	0.00010
73	954.74052	0.00010
74	966.54200	0.00005

Table 6 — Silicon peak positions

Dopant	Orientation	Peak position in Raman Shift / cm^{-1}	Standard deviation / cm^{-1}	Source
None	100	520.45	0.28 [†]	Itoh et al. ¹⁰
None	100	520.66*	0.53	RR1 Silicon study
None	111	520.47*	0.46	RR1 Silicon study
Boron	100	520.40*	0.34	RR1 Silicon study
Phosphorus	100	520.27*	0.41	RR1 Silicon study
Phosphorus	100	520.45*	0.47	RR1 Silicon study
All	All	520.45*	0.46	RR1 Silicon study
* average of all spectra collected in Round Robin 1 (RR1) Si study performed by CHARISMA H2020 project (GA 952921, see Annex B), normalised to 520.45 cm^{-1} (Raman shift) value provided by Itoh et al. ¹⁰				
† expanded uncertainty (coverage factor $k = 2$)				

Table 7 — Calcite peaks positions

Peak position in Raman Shift* / cm^{-1}	Standard deviation / cm^{-1}	Source
155.21	1.37	RR1 Calcite study
281.26	1.08	RR1 Calcite study
711.95	0.71	RR1 Calcite study
1085.91	0.56	RR1 Calcite study
1435.22	0.67	RR1 Calcite study
1748.91	0.7	RR1 Calcite study
* Spectra collected in Round Robin 1 (RR1) study performed by CHARISMA H2020 project (GA 95921, see Annex B), were calibrated using neon and silicon.		

Table 8 — Polystyrene peak positions from ASTM E1840

Peak position in Raman Shift / cm^{-1}	Standard deviation / cm^{-1}	Relative intensity	Source
620.9	0.69	16	ASTM E1840
795.8	0.78	10	ASTM E1840
1001.4	0.54	100	ASTM E1840
1031.8	0.43	27	ASTM E1840
1155.3	0.56	13	ASTM E1840
1450.5	0.56	8	ASTM E1840
1583.1	0.86	12	ASTM E1840
1602.3	0.73	28	ASTM E1840
2852.4	0.89	9	ASTM E1840
2904.5	1.22	13	ASTM E1840
3054.3	1.36	32	ASTM E1840

Annex B (informative)

Harmonization protocol development process

This protocol is the culmination of several tasks and studies performed by the H2020 CHARISMA (Grant Agreement No. 95921)

Round robin 1.1

This round robin utilized the materials defined earlier in the CHARISMA project. Each sample was analysed using every optical path of each instrument available within the consortium. This collection of data are the cornerstone of the protocol development as these are the training development. The data collected here would primarily be used to harmonize the x-axis for both position and resolution purposes.

The instruments within the consortium include various configurations (i.e. hand-held, portable, and scanning instruments) as well as different laser wavelengths, though the only wavelengths that appear in more than 1 instrument were 532 nm and 785 nm.

Silicon study

This study utilized several silicon materials. It was noticed by a consortium member that the Raman peak for silicon could noticeably change by moving the sample, as well as by day to day, which adds on to the well-known effect of sample rotation in an axis perpendicular to the beam. Thus, a study was devised to analyse the silicon samples in different positions and orientations over several days, to assess this variability. With laser power, humidity and temperature recorded to check for any dependence in the ranges analysed.

Polystyrene study

This study utilized the polystyrene defined earlier in the CHARISMA project, as well as other recommended standard polystyrene source and polystyrene samples with divergent characteristics (e.g. high molecular weight). These were studied to see the effect of the different polystyrene characteristics on the Raman spectrum.

Peak fitting and protocol development task force

To facilitate the development of the algorithms and fine tuning of the data processing used for the protocol, a task force was assembled of members from WP3, 4 and 5. This task force has experimented with different methods of peak fitting and x-axis calibration.

Round robin 1.2 (Relative intensity correction)

The second part of the internal consortium round robin utilized the material defined earlier in the CHARISMA project and is still under development. These data are used to harmonize the relative intensity response of the instrument.

Note on existing standards

ASTM E2911 was created in tandem with the NIST SRMs, and outlines the method of relative intensity correction in more detail. In late 2022, this standard was temporarily removed without explanation. As such, CHARISMA have developed a relative intensity correction protocol, which is performed with ELODIZ LED light sources

Annex C (informative)

Software (Altaxo, Oranchada)

Two software have been developed as part of the H2020 project CHARISMA that can be used for calibration purposes. These are described in this annex.

C.1 Oranchada

Orange, an open source data mining and machine learning tool, primarily focuses on workflow design for data analysis and modelling.^{11,12} Orange provides a visual interface for designing and executing data analysis workflows. The primary purpose of workflow design is to create a structured sequence of data processing and analysis steps. Orange provides a user-friendly visual interface where users can create and modify workflows using drag-and-drop components called widgets. These widgets represent data processing and analysis tasks. Users can design workflows by connecting widgets in a modular fashion. Each widget performs a specific function, such as data loading, data pre-processing, visualization, and modelling. The visual canvas allows for flexibility in structuring the workflow. Workflows can include data transformation steps, where users apply various operations to manipulate and pre-process data. This might involve filtering, scaling, imputation, and feature selection. Users can include widgets for data visualization, allowing them to gain insights from the data and assess the results of their analyses. Orange provides widgets for machine learning and predictive modelling, enabling users to build and evaluate models for classification, regression, clustering, and more. Data flows through the workflow from one widget to another, and users can observe how data changes at each step, making it a powerful tool for interactive data analysis. Like dedicated workflow systems, Orange supports iterative design and experimentation. Users can modify their workflows, re-run analyses, and refine their models based on the results. Orange offer some scripting and programming capabilities, which allow for customization and the integration of Python code within the workflow and / or developing custom widgets or set of widgets, known as add-ons.

Oranchada add-on guide is available at Zenodo.¹³

Figure 4 shows the Orange main screen with Oranchada Pro widgets on the left: Add Baseline, Add Noise, Subtract, Find Peaks, Fit Peaks, Generate Spectra, HDR Merger, HHT Sharpening, Load File, Load Test Spectra, Merger, Moving minimum, Normalize, RS to WL, Recover Spikes, Resample NUDFT, Select, Set x-axis, WL to RS, x-axis fine calibration and Load File Names.¹⁴

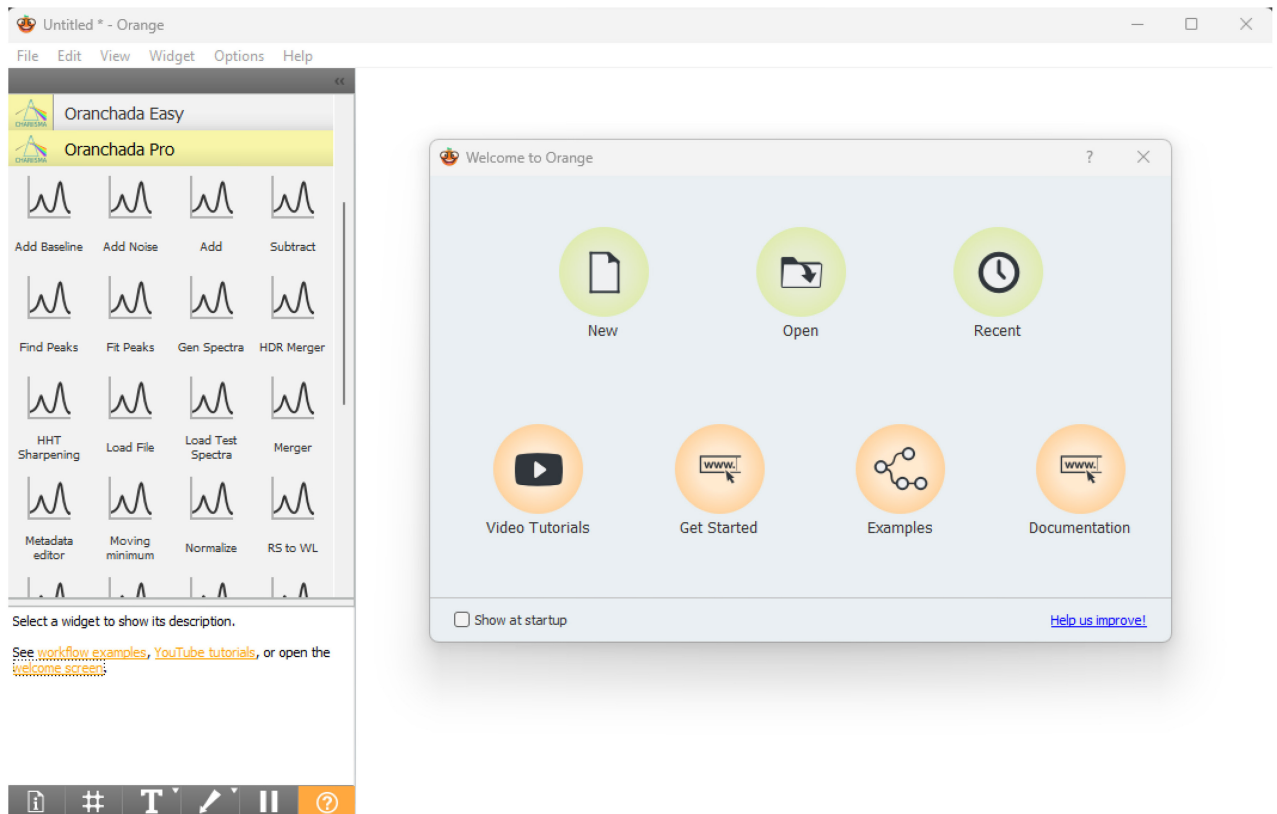


Figure 4 — Main screen of Orange data mining with Oranchada add-on. “Welcome to Orange” shows some important basic functions create a new project, open an existing one, or choose from the ones we recently worked on. There are also links to helpful information on how to work with Orange

Oranchada widgets for spectra processing have a common structure, described at Figure 5.

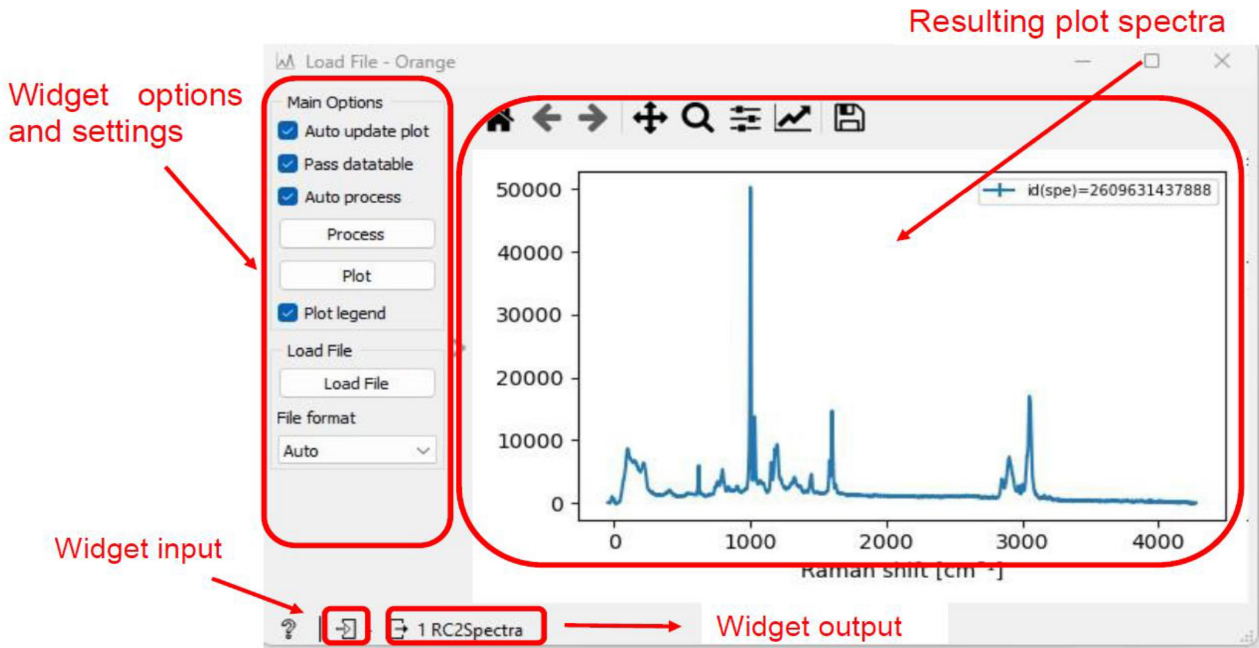


Figure 5 — Basic structure for Oranchada Spectra processing widgets

Widgets have input and output channels. For example, the “HHT Sharpening” widget Input channels are “RC2Spectra” and respectively Outputs channels are “RC2Spectra” and “Data” (Figure 6 left). When connecting a widget to another widget with multiple channels, as in the example workflow (Subtract widget at Figure 6 right), a popup window asking users for information which channels to connect will appear.

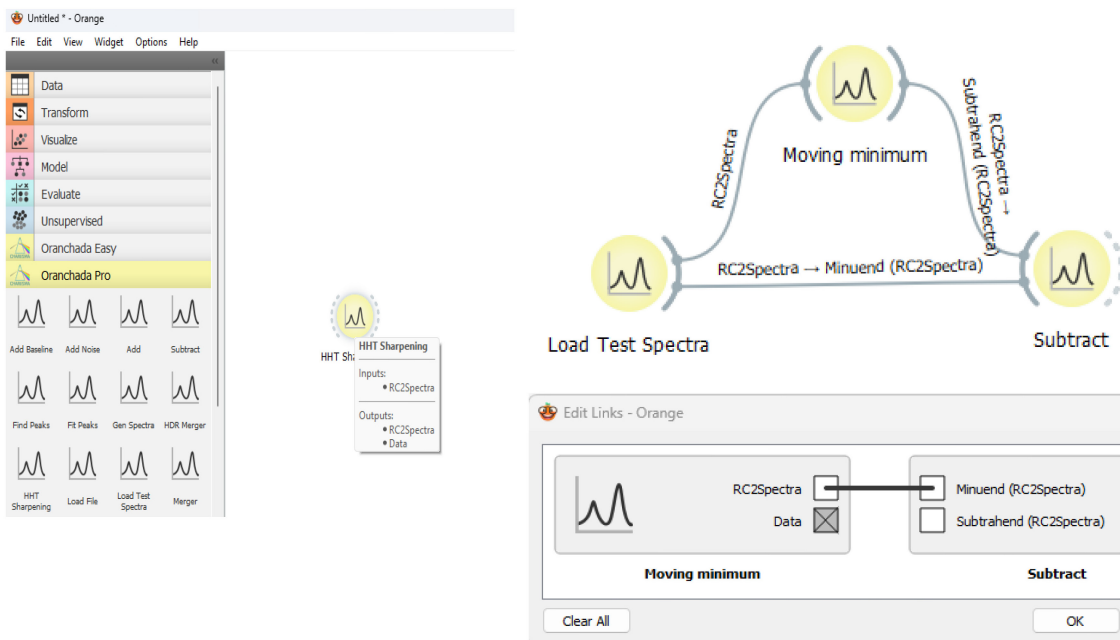


Figure 6 — Widgets have input and output channels

C.1.1 Spectral import

Spectral import is done by using the load file widget (Figure 7). Various spectral file formats are supported. After a spectrum is loaded, it can be visualized by clicking the Plot button.

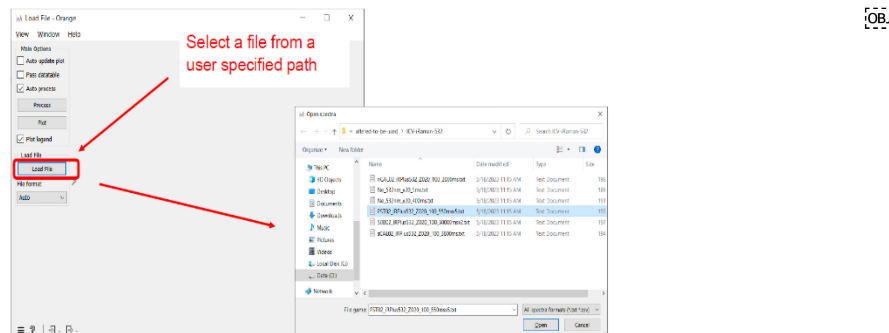


Figure 7 — Load file widget allows selecting, loading and visualize one or more spectra in supported formats

C.1.2 Calibration

Orange workflow implementing the calibration protocol is available as .ows file at <https://github.com/h2020charisma/oranchada/tree/main/examples>.

The pending Oranchada release will feature a single widget for calibration.

The calibration can also be done by Python code using ramanchada2 library.

C.1.3 Applying calibration to acquired data

Guideline how to run and apply calibration using Python code (ramanchada2) and GUI (oranchada) can be found at

<https://github.com/h2020charisma/ramanchada2/blob/main/CALIBRATION.md>

C.2 Altaxo

Altaxo is an open source, general purpose graphical data analysis and plotting program developed since 2002 by one of the consortium members.^{15,16} It is a project-oriented program. This means that everything is stored in one project file, which is a .zip file containing the project items. There are different types of project items. The most relevant are tables, in which the data are stored, 2D and 3D graphs for the visualization of the data, and notes using the Markdown language syntax. The project items can be organized in a hierarchical way, i.e. they can be organized in folders and subfolders. In this way, even very large projects (in the GB range) can be realized without losing overview.

There are special menu points for treating repeating task: project items and entire folders can be moved and copied. Data can be mass imported. Project items can be mass exported in various formats, including to Excel format for tables, Word format for Notes, and various image formats for 2D and 3D graphs. By utilizing data sources for each table, tables remember where the data has come from. In this way, data analyses can be repeated by executing the data source again.

If the built-in menus are not appropriate, tasks can also be scripted. There is a built-in script editor for C# with syntax highlighting and code completion. This makes scripting really easy. Altaxo has a huge mathematical and signal processing library. Vector and matrix operations are accelerated by the Intel Math Kernel library.

The main window of Altaxo is shown in Figure 8. The structure of the program windows is flexible, i.e. both document windows and toolbar windows can be docked to every side, stacked, and even moved outside of the main window.

Installation of Altaxo is easy: use the graphical installation with a .msi installation file. In fact, no installation at all is necessary, because Altaxo runs on all computers with Windows 7, Windows 10 and Windows 11 out of the box, simply by expanding a provided .zip file into a folder on the computer or even a USB memory stick. Details on how to install Altaxo can be found on the homepage [13].

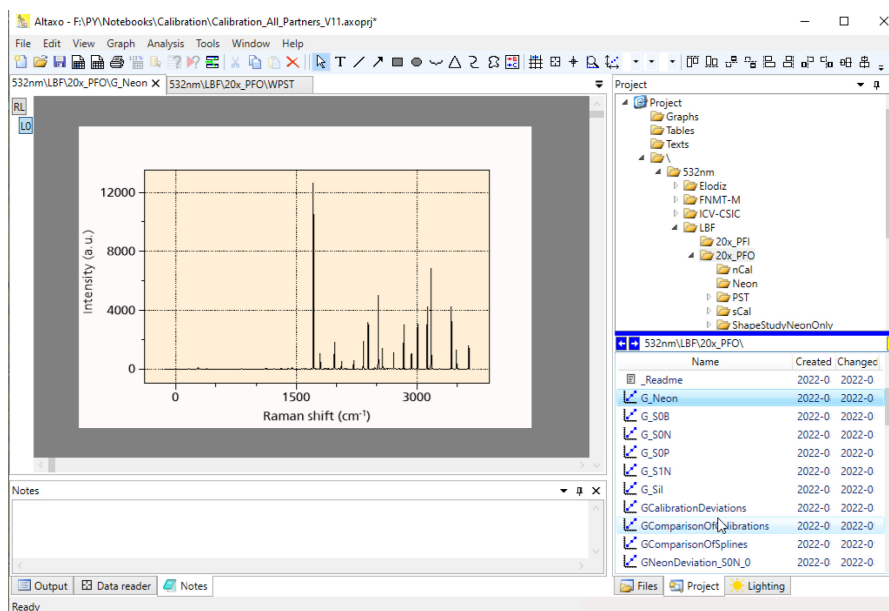


Figure 8 — Main window of Altaxo. On the left side, the document area shows the currently visible documents. On the right side, the project explorer shows the content of the project

For the CHARISMA project, some features were added to Altaxo, which are described in the following sections.

C.2.1 Spectral import

Spectral data can be imported into Altaxo in various formats:

- ASCII format. This is the most flexible option. Altaxo is able to recognize the structure of most of the ASCII files, including different separation strategies (separation by tabs, spaces, columns with fixed width etc.) and different cultures (numbers with dot or comma as decimal separator). There is a menu point to import multiple ASCII files in one table, which is useful when having multiple spectra belonging together, for instance a time series of spectra.
- .SPC files. This is a binary file format, developed by Thermo Galactic, for containing the spectral data to be processed in GRAMS (a spectral software). .SPC files can contain multiple spectra. Currently, most of the spectrometers are able to export spectra using this format.
- JCamp-DX files. It is a text-based file format for storing spectroscopic data, originally for infrared spectroscopy.
- Renishaw Wire .wdf files. This is a binary, vendor specific file format from Renishaw.
- Import using an import script. Arbitrary other file formats can be imported by writing an import script in C#.

In Figure 9, the import menu points of Altaxo are shown.

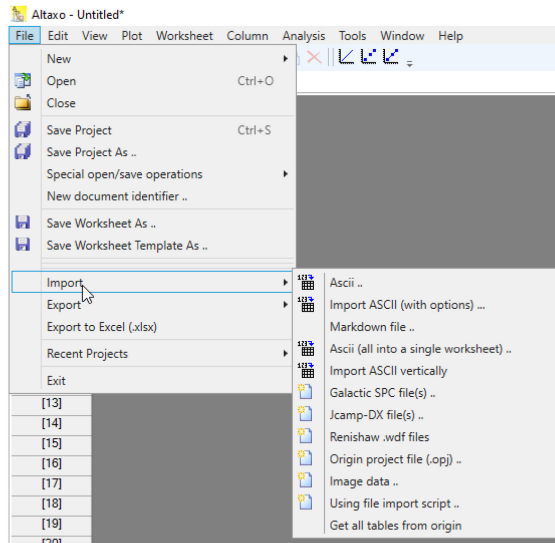


Figure 9 — Import menu of Altaxo

C.2.2 Calibration

Altaxo contains fully automated routines for performing x-axis calibration as well as y-axis calibration of a Raman instrument. In order to perform an x-axis calibration, a spectrum of neon (obtained by using a neon lamp) and a Raman spectrum of a silicon sample are necessary.¹⁷ After both spectra are imported into Altaxo, the user first chooses the neon spectrum, then uses the menu point Analysis- > Spectroscopy- > Raman- > Neon calibration. The neon calibration dialogue opens (Figure 10). Almost all options available can be left to their default value. Only the approximate wavelength of the laser shall be entered.

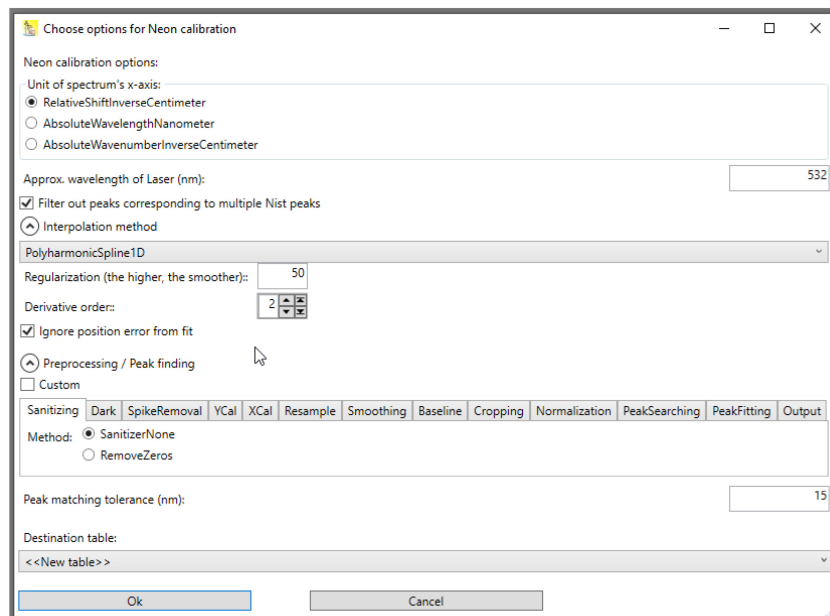


Figure 10 — Neon calibration dialogue of Altaxo

After confirming the dialogue with OK, a new calibration table is created, in which the results of the neon calibration are stored. The results already allow to assign each point of the spectrum, which usually has shift as its x-value, an absolute wavelength value. But the calibration is not yet complete, because the exact laser wavelength is still unknown. In order to get this, the user chooses the silicon spectrum, and by using the menu Analysis- > Spectroscopy- > Raman- > Silicon calibration opens the silicon calibration dialogue (Figure 11). Again, the option can be left to their defaults. If the temperature of the measurement (of the silicon wafer) is known, it can be entered in the dialogue box. The destination table is set to the same table as where the neon calibration is already stored.

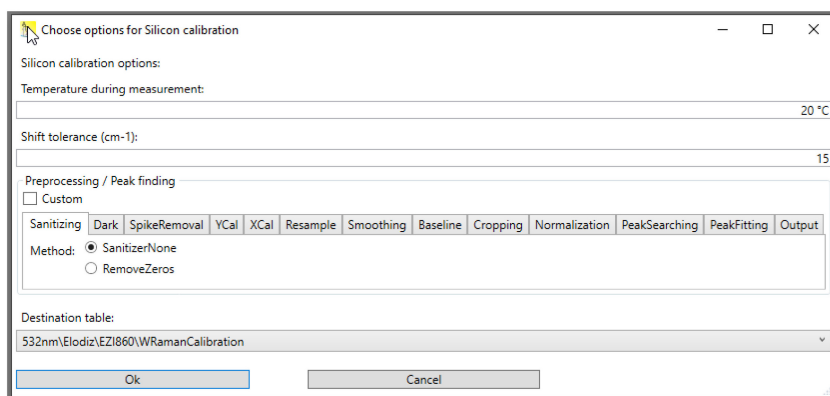


Figure 11 — Silicon calibration dialogue of Altaxo

By confirming with OK, the silicon calibration is executed, and the calibration table is amended with the results of the silicon calibration. The calibration table now contains all information in order to map the uncalibrated shift values of the experimental spectra to calibrated shift values. Additionally, it contains the calibrated laser wavelength.

The y-calibration is done with a spectrum of a calibrated LED or the Raman spectrum of a NIST calibration standard. After the spectrum is imported, the intensity calibration dialogue (Figure 12) can be opened by using Analysis- > Spectroscopy- > Intensity calibration.

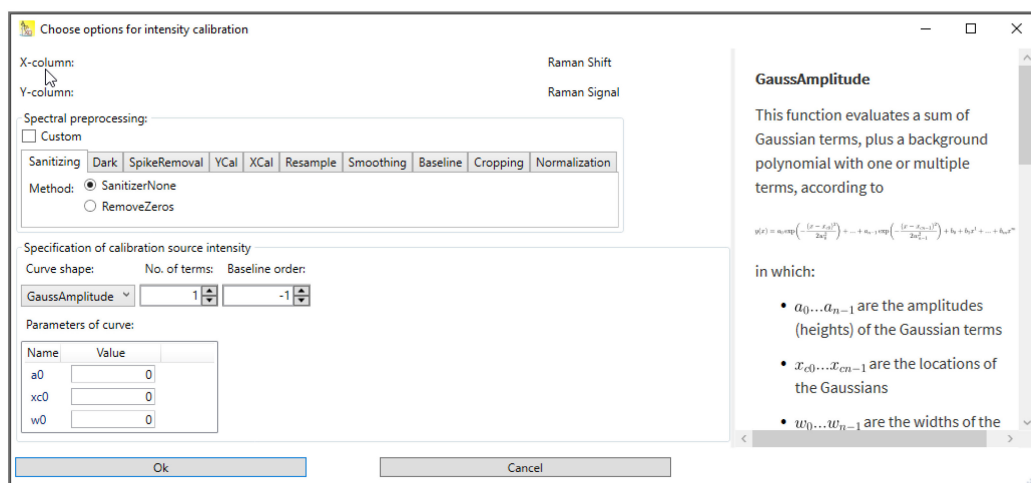


Figure 12 — Intensity calibration dialogue of Altaxo

In the upper part of the dialogue, the pre-processing options can be chosen. For intensity calibration to be performed, it is important to have a spectrum for which the dark spectrum is already subtracted. If this is not yet the case, it can be done here by choosing the appropriate pre-processing option. In the lower part of the dialogue, the calibrated curve shape of the LED or NIST standard can be entered. In the case above, a Gaussian shape is chosen, for which the parameters amplitude, position, and sigma can be entered. Other shapes, more peak terms, and parameters for a polynomial baseline can be entered as well. After confirming the dialogue with OK, a new calibration table will be created, which contains factors by which the y-values of the spectrum will be multiplied with in order to obtain an intensity calibrated spectrum.

C.2.3 Applying calibration to acquired data

If a calibration was successfully performed, it can be applied to other uncalibrated spectra, in order to get a calibrated spectrum. This can be achieved by first import the spectrum or the spectra for which the calibration should be applied into a worksheet. Then a preprocessing is applied to those uncalibrated spectra. Select the y-columns of all spectra for which the calibration should be applied, then choose from the menu Analysis- > Spectroscopy- > Preprocess. In the spectral preprocessing dialogue, go to the tab "XCal", choose "XCalibrationByDataSource", and then choose in "Tables containing calibrations" the table which contains the x-calibration that should be applied to the spectrum or spectra (Figure 13).

Likewise, in order to apply the y-calibration, go to the tab "YCal", choose "YCalibrationByDataSource", and then choose in "Tables containing calibrations" the table which contains the y-calibration that should be applied to the spectrum or spectra (Figure 14).

In the other tabs of the preprocessing dialogue, choose the additional options that you want to apply to the spectrum or spectra. Since the spectral preprocessing dialogue is also used for peak analysis, you can also apply a x- and y-calibration before making a peak analysis of spectra. You can find it using the menu Analysis- > Spectroscopy- > Peak finding and fitting.

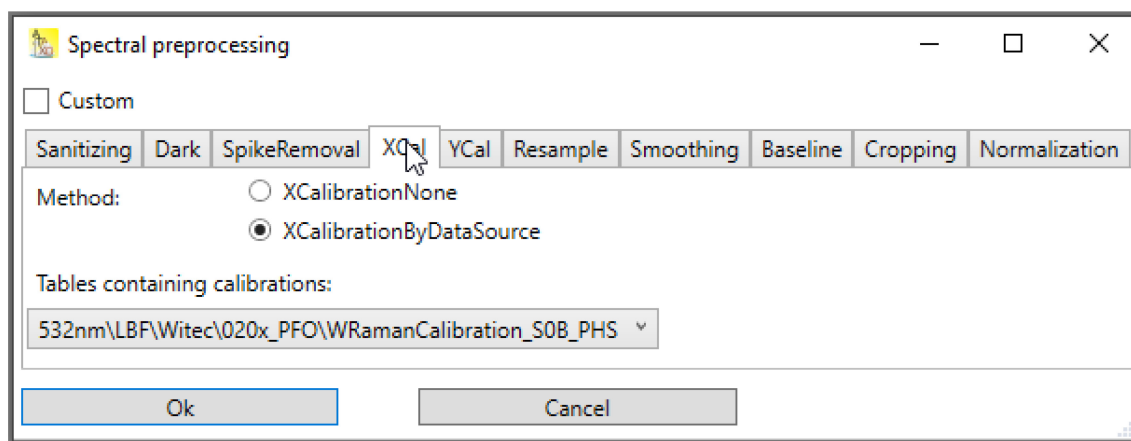


Figure 13 — Spectral preprocessing dialogue showing the "XCal" tab

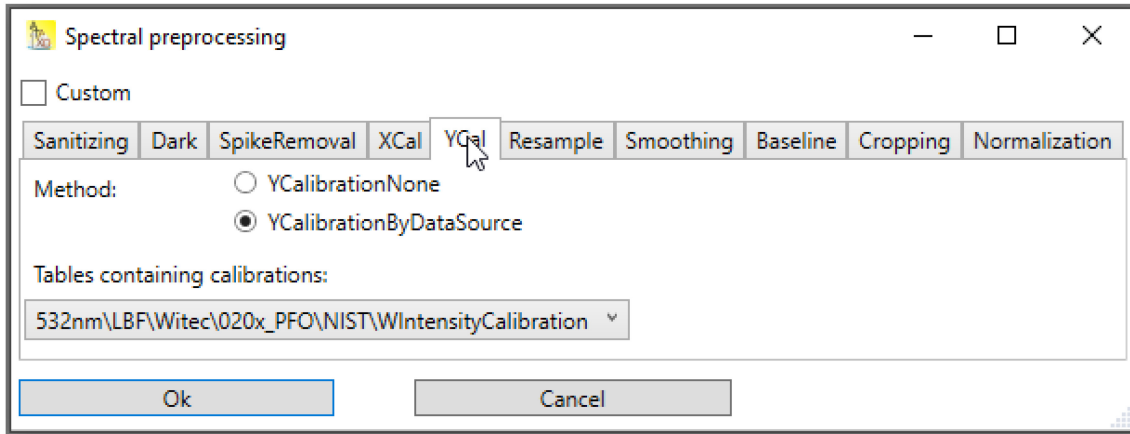


Figure 14 — Spectral preprocessing dialogue showing the “YCal” tab

Annex D (informative)

Correlation with theoretical methods

Peak position and relative peak intensity can be obtained by theoretical calculations and used to validate Raman spectra. Calculations can be performed by widely used *ab initio* techniques such as density functional theory (DFT) without the input of experimental data, with robust implementation in materials science codes (VASP, CRYSTAL etc). The following issues should be considered:

- Experiment-free Raman spectra do not depend on measurement conditions (hardware, software, cosmic rays, operator). Their accuracy relies on: i) the physico-chemical laws included in the theoretical protocol followed: electronic interactions such as exchange, correlation or dispersion, laser and temperature corrections, computational algorithms used to compute frequency (harmonic approximation) or polarizability (DFPT, finite differences, AIMD). Typically fluorescence and resonance are not included in regular codes, nor overtones. ii) the structural model as a representation of the real sample. Well-characterized crystalline materials such as calcite can be properly represented by its corresponding lattice parameters and atoms Wyckoff positions, whereas polymers need a proper sampling of molecular models. Impurities or mixtures need to be included in the structural model to assess their impact in the computed spectrum. The computed Raman spectra should be carefully analysed before comparison with measurements.
- The computational protocol should be adjusted to provide the closest results to the observations. This is particularly important for calibration purposes. Note that the computational protocol is very sensitive to the nature of the material: simple ionic crystals and polymers will not necessarily need the same computational protocol.
- CHARISMA protocols for computed Raman spectra (2 MODA sheets available, for static and dynamic approaches) were developed and tested. Besides the peak position and intensity, which defines the spectra shape, static approaches can be used to assign vibrations to each peak, providing valuable information on the nature of the signal by identifying vibrations (stretching, bending, collective). This may be used for calibration purposes to assess the robustness of a peak. For instance, several polystyrene models (finite, infinite, syndiotactic, atactic, helicoidal) show very robust peaks for vibrations associated with phenyl C-H stretching, whereas other peaks appear within a larger range of Raman shift because of their backbone nature (they are thus sensitive to the polymer structure and chain end). A document summarizing the main results of computed polystyrene Raman spectra can be found here <https://hal.science/hal-04344053>.

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