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Raman instruments calibration and verification protocols

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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.

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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