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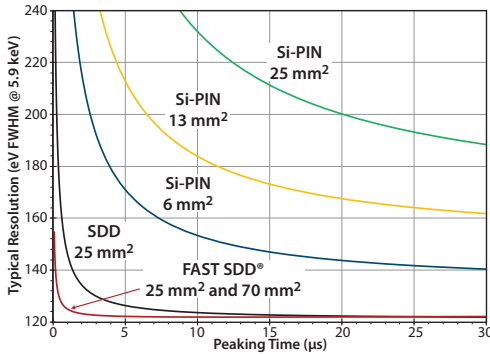
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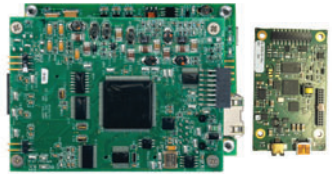
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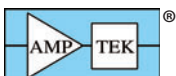


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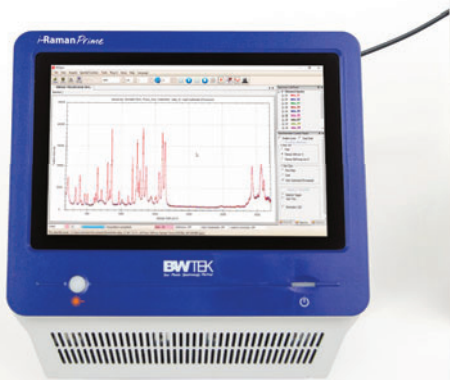
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# Introduction to the Guide

Jerome Workman, Jr.

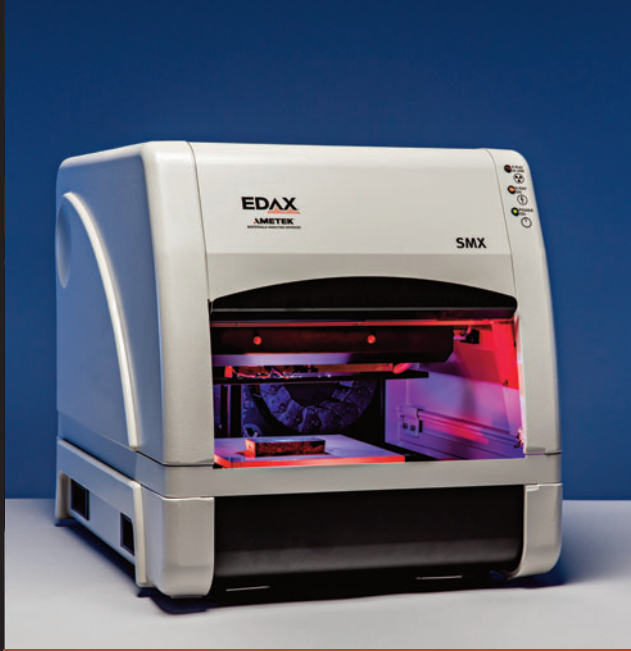
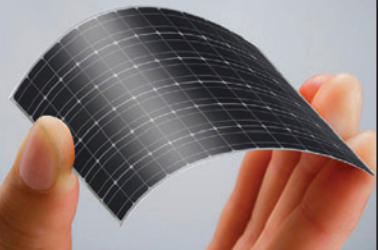
A few years ago, our sister publication, *LCGC*, published a terminology guide, and copies flew off the stand all year at conferences. That response made the editors of *Spectroscopy* consider that it might be worthwhile to develop a similar guide, initially focusing on terms specifically related to molecular spectroscopy. Such a guide would include a comprehensive set of definitions for topics of interest to molecular spectroscopists and those using molecular spectroscopy in their daily work. This would include the types of molecular spectroscopy methods and many terms related to spectrophotometers, spectrometers, and the many applications of these instruments. In addition, it would include some data and computer terms, some statistical data analysis terms, and the essential chemometric terms for typical data preprocessing and calibration.

This terminology guide includes definitions for over 250 molecular spectroscopy terms in sufficient detail to provide readers with a reasonable understanding of the concepts covered. In deciding which terms to include, we first identified specific terms, like *hotband*, *isotope shift*, and *hydrogen bonding* that directly affect the appearance of spectra, as well as many general terms more familiar to our readers. We noted that if the scope was “molecular spectroscopy,” then we needed to add nuclear magnetic resonance and possibly other methods, but, if we narrowed that to “vibrational spectroscopy,” then NMR could be dropped. Cavity ring down (CRD) spectroscopy and surface plasmon resonance (SPR) would be borderline cases, with fluorescence as a must-have addition.

After considering these issues carefully, we decided to be more comprehensive and added more terms to the list.

In addition to using this guide, spectroscopists may also wish to know the definitions given by various organizations for many spectroscopic terms; for these, one may refer to *The ACS Style Guide*, the American Society for Testing and Materials (ASTM) terminology guides, United States Pharmacopeia (USP) documents, or the International Union of Pure and Applied Chemistry (IUPAC) guidance documents. All of these reference sources will provide additional terms and updates on periodic changes in definitions as might occur over time. We have included many topical terms that are not mentioned in those standard definitions and nomenclature guides, so that our guide is complementary to those official publications.

This terminology guide is not intended to be highly mathematical, theoretical, or all-inclusive in its coverage. For example, we have elected not to cover every possible term used in spectroscopic instrumentation, measurement, data handling, and validation, but have chosen instead to use most terms that may be encountered in everyday laboratory work where ultraviolet (UV), fluorescence (FL), visible (Vis), near-infrared (NIR), infrared (IR), Fourier transform infrared (FT-IR), Raman, or terahertz (THz) spectroscopy are in general use. This glossary should be helpful to both novice and advanced users in spectroscopy, and can also serve as a useful reference guide to even the most experienced in the field.



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**A** **Abscissa:** Designates the horizontal (x) axis of a graph and, typically, the wavelength or wavenumber scale of a spectrum.

**Absorbance:** Measure of the amplitude of absorbed energy in a spectrum related to the concentration of an analyte. This term is also referred to as the negative log (base 10) of Transmittance ( $-\log_{10} T = \log_{10} [1/T]$ ). This is also represented as the product of absorptivity (extinction coefficient), pathlength, and concentration, written as  $A = \epsilon bc$ . Absorbance =  $\log_{10} (1/\text{reflectance})$  or absorbance =  $\log_{10} (1/\text{transmittance})$ .

**Absorptivity:** Probability of energy absorbing at a particular wavelength for a specific analyte under specific conditions (that is, a specific combination of pH, solvent, and temperature). Thus, a specific amount of material at specified measurement conditions will absorb a specific fraction of the energy striking it. Absorptivity is generally signified by either a lower case epsilon ( $\epsilon$ ) or  $a$ . It is defined as:

$$\epsilon = \frac{A}{cl} \quad [1]$$

Where  $\epsilon$  is the molar absorptivity in units of  $L \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ;  $c$  is the concentration of molecules in the spectrometer beam in units of  $\text{mol} \cdot L^{-1}$ ; and pathlength ( $l$ ) is the thickness of the sample in units of cm; and  $A$  is the measured absorbance.

**Accuracy:** A measure of the agreement between the amount of a substance as determined by an analytical procedure and the “true” amount of that substance in the sample. Since the “true” value may be unknown, it is approximated by determining it using a reference analysis method—that is, a method whose accuracy can be estimated. If enough determinations are averaged, improved approximations of the “true” analyte concentrations can be made. In spectroscopic calibrations, the accuracy is usually expressed as the standard error of estimate (SEE) or the standard error of prediction (SEP) as statistics that measure agreement between the

spectroscopic analysis and the reference value determined by a reference method. This error is usually ascribed to the instrument, although, in fact, it is due to the error variances of both the instrument and reference methods. Accuracy, with respect to an instrument performance calibration, is the agreement of a measurement parameter (for example, wavelength, photometric value, or linearity) to the certified values of a reference standard.

**Acousto-optical tunable filter (AOTF):**

A bandpass filter, also known as a Bragg cell, that uses sound waves to electronically change the bandpass and angle of transmitted energy through the device. The device uses acoustic diffraction of light with a broadband detector if the filter is rotated, or with an array detector if no rotation of the AOTF optical element occurs. This device is generally made using a tellurium dioxide ( $\text{TeO}_2$ ) crystal in combination with a piezoelectric detector. A radio frequency pulse is applied to the device, which changes the index of refraction within the crystal, and, therefore, its light diffraction or transmittance characteristics. A change in radio frequency causes a change in the transmitted wavelengths and the exit angle of the diffracted light. The typical spectral ranges for AOTF devices are from near 390 nm to above 4400 nm with a typical spectral resolution of 0.5% of the transmitted wavelength.

**Active detector:** A photon detection system requiring electronic power that will detect photons at various frequencies and create a change in an electronic signal based on the photon or electromagnetic energy flux striking the active detection element. The detector elements include photocathodes, photodiodes, photodetectors, and charge-coupled devices (CCDs). Materials include silicon (Si), cadmium zinc telluride (CdZnTe), mercury cadmium telluride (MCT, HgCdTe), indium gallium arsenide (InGaAs), lead sulfide (PbS), light-emitting diodes (LEDs), indium antimonide (InSb), and germanium (Ge).



**Analog:** A term used to describe or represent continuously variable physical quantities. Analog data has continuity as contrasted to digital data, which is in discrete reporting states. Analog signals are continuously variable quantities that contain information resolution dependent only upon the magnitude of the signal.

**Analysis:** The determination of the quantity of a particular substance (that is, analyte) contained within a sample, usually expressed as weight percent of an analyte. Note that spectroscopy directly measures a volume fraction unit, not a weight fraction unit. One may also perform analysis on the optical performance of a spectrometer for its optical, mechanical, and electronic performance levels.

**Analysis of variance (ANOVA):** A mathematical or statistical procedure for determining the contributions that various phenomena make to the total variation in a set of measurement data. Variance is defined as the standard deviation squared, and follows the F-distribution for statistical purposes. Variances are additive terms and allow arithmetic operations.

**Angle of incidence:** The angle between the incident radiation beam with respect to a normal (perpendicular) surface angle. For a plane and specular surface, the incident and reflected angles for a beam of light are equivalent.

**Anisotropy:** A reflection property where the energy is not equivalent for all positive angles of reflection; therefore, reflected energy is different for different reflection angles from a surface.

**Anti-Stokes shift:** See *Raman effect*.

**Apodization or apodization function:** A function used to remove the “ripple” effect on either side of spectral peaks or bands following the application of the Fourier transform to an interferogram. These ripples are minimized by applying a function to spectral data to produce smaller ripples and slightly broadened peak widths.

**Array detector:** A photoelectric detector that includes multiple, evenly spaced lines or rectangles of detectors (or pixels), each of which

may independently detect a broad wavelength range of energy. These detectors may be flat or curved to accommodate a multiwavelength beam of diffracted light. They may be a linear array, such as in a charge-coupled device (CCD), or a rectangular array where different pixels form a mosaic of smaller pixels capable of collecting and reporting multidimensional images.

**At-line:** A term used to describe instrumentation that chemically quantifies or qualifies materials in near real-time (as they are produced) near a production line. Generally, a sample aliquot is taken from the production line and moved to an analysis station for manual sample presentation to a nearby instrument.

**Attenuated total reflectance (ATR):** A sampling device used for surface analysis with infrared spectra where physical contact of the ATR crystal occurs with the sample surface. ATR crystal materials include diamond (Di), germanium (Ge), silicon (Si), and zinc selenide (ZnSe). ATR measurements can yield excellent quality spectra, provided that the contact pressures of the ATR crystal and the sample are held constant. By applying an ATR correction algorithm, ATR spectra may be compared qualitatively with transmission spectra.

**Attenuated total reflection (ATR) correction:** This is also known as “attenuated total reflectance correction.” A conversion function to compare transmission spectra to ATR spectra for infrared spectroscopy. The functional conversion depends upon the refractive indices of the ATR crystal and the sample, the angles of incidence and collection for the infrared beam, and the number of bounces for the beam with the ATR crystal. The conversion is important for quantitative and qualitative comparisons between ATR spectra and transmittance spectra.

## B

**Bandpass filter:** A filter that is designed to provide transmission for a particular band of

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frequencies, but to attenuate (reduce) transmission of frequencies above (or above and below) the specified transmission band. Specifications include a half width or full width at half-maximum (FWHM) of the transmission band, the transmission peak position, and the attenuation transmission specifications with respect to frequency or wavelength.

**Bandwidth:** This term refers to the full width at half-maximum (FWHM), the line width, or the spectral resolution, of a spectrophotometer. It also refers to the range of frequencies (wavelengths) over which a particular instrument is designed to function within specified performance limits. Also, it refers to the limits or extreme difference between the specified frequencies of a measured spectral range (that is, high versus low frequencies over a spectral range).

**Baseline correction:** Spectra taken with different instruments or with varying sample conditions, such as particle size or turbidity, may have a different baseline offset and curvature. Visually or mathematically comparing such spectra may require a baseline correction. These corrections are generally a single point or multipoint offset, a linear correction, or various first- or second-order polynomial corrections. The single- and multipoint correction involve the addition or subtraction of one or more points from the baseline. Linear or polynomial corrections involve fitting such a mathematical function to the baseline, and then subtracting the fitted line or curve from the spectrum, transforming the comparative spectra to have a similar amplitude scale and shape.

**Beamsplitter:** An optical element that is coated in such a way that approximately 50% of the energy striking the element is reflected and 50% is transmitted; these optical elements are often referred to as half-mirrors. A Michelson interferometer comprises a beamsplitter, which is an active optical element, along with one fixed and one moving mirror. Dual-beam instruments exhibiting simultaneous sample and reference beams also use a beamsplitter

to separate the beams used to measure ratioed spectra as the sample and reference beams.

**Beer's law (Beer-Lambert law):** A linearization algorithm to convert transmission or reflection spectra to absorbance. The transmission or reflection spectral responses are not considered linear with concentration, whereas the logarithmic absorbance conversion is assumed linear with changes in analyte concentration. It is strictly defined for transmission or transmittance spectroscopy. Beer's law relates the amount of electromagnetic radiation that passes through a sample to the composition of that sample. For the case of a single absorbing species, it is often written as follows:

$$A = abc = \epsilon bc \quad [2]$$

Where  $A$  = measured absorbance =  $-\log_{10}(I/I_0)$ ;  $I$  = intensity of radiation through the measuring system in the presence of the sample;  $I_0$  = intensity of radiation through the measuring system in the absence of the sample;  $a = \epsilon$  = the absorptivity of the sample at the wavelength of measurement; an intrinsic property of the molecular species (also known as the extinction coefficient in physics);  $b$  = the pathlength through the sample; and  $c$  = the concentration of the sample for a single absorbing species. If all the physical parameters (particularly the pathlength) are kept constant, then the measured absorbance ( $A$ ) is directly proportional to the concentration (as weight per unit volume) of the analyte species of interest. This principle is the basis of absorption-based spectroscopic quantitative analysis.

**Bias:** The average difference between a set of instrumental analyses and the corresponding set of laboratory reference values; or, a set of samples measured using a comparison instrument or analytical method. More generally, it is the average difference between two sets of measurements on the same sample or samples.

**Bit:** Abbreviation of binary digit. A bit is the value of the least significant place of a number

in the binary number system. It is the smallest unit of information a traditional computer can handle. A bit corresponds to the output of a solid-state device, which is either the "0" state (usually 0 V), or the "1" state (usually +5 V). In traditional computer circuits, intermediate states are not defined.

**Blind duplicate:** Reference laboratory data used for calibrating instruments are generally analyzed using primary analysis methods—that is, methods that depend only on fundamental physical laws and well-determined physical constants, such as molecular weight. Thus, the accuracy of such laboratory data cannot be measured by comparison with reference data, since there is, theoretically, no more accurate technique. Nevertheless, error does exist in such data; the magnitude of the error can be assessed by comparing the laboratory with itself, or by comparing the values reported on multiple independent analyses of the same sample. To ensure that the analyses are independent, the test samples should be randomized so that the laboratory analyst cannot detect the repeat aliquots of the same sample. If several samples are replicated, then it suffices to send each one in only twice, because this approach will provide data to calculate an estimate of laboratory accuracy.

**Boxcar apodization:** The apodization function applied to Fourier-transformed interferogram spectra that maximizes both peak height and resolution (band half width) as compared to other apodization functions. It is the apodization function most often used for gas-phase infrared spectrophotometry. It is a square waveform apodization function, in contrast to a triangular or Happ-Genzel (smoothed triangular function) apodization function.

**Brewster angle:** When a light beam at a specific wavelength passes through one medium (for example, air) and reflects or interacts with another medium (for example, glass, plastics, or other dielectric materials), the angle where the p-polarized light does not reflect (that is, the p-

polarization light reflection equals 0) is termed the Brewster angle. It is also the angle that constitutes perfect or 100% of the light transmitted through the dielectric.

**C** **Calibration:** Most often defined as determining the response of an analytical method to known amounts of pure or reference analyte. *Instrument calibration* refers to measuring and aligning the *x*- and *y*-axis measurements of a spectrophotometer with respect to a reference material of standard and known characteristics, such as in wavelength or photometric accuracy calibration. *Product calibration* is the process of computing an equation or model to fit reference laboratory readings to instrument readings for product calibrations. In spectroscopy, product calibrations are usually performed by linear or nonlinear multiple regression techniques.

**Calibration curve:** The results of a calibration when graphed, usually with Cartesian coordinates, with a parameter such as concentration (in molarity) on the *x*-axis, versus absorbance or instrument response on the *y*-axis. Developing a calibration curve or line often involves the application of statistical regression methods.

**Calibration set:** A collection of samples containing varying amounts of the analyte used to calibrate an instrument. This collection is also referred to as the learning set or teaching set.

**Centerburst:** An interferogram has a centerburst, also referred to as the "zero-path-difference" (ZPD) location. When the optical path distance of the fixed and moving mirror are identical in the interferometer, the interferogram is at maximum interference; this is referred to as the centerburst position.

**Chalcogenide:** These materials contain a Group XVI element from the periodic table. The main use in spectroscopy is for infrared-range transmitting optics such as fiber optics and optical lens elements. The most common materials in this category include cadmium sulfide (CdS), cadmium selenide (CdSe), cad-

mium telluride (CdTe, formerly marketed as IRTRAN-6), Cleartran (water clear zinc sulfide), zinc selenide (ZnSe, formerly marketed as IRTRAN-4), and zinc sulfide (ZnS, formerly marketed as IRTRAN-2).

**Chemometrics:** A subdiscipline of analytical chemistry involving complex overlapping molecular patterns from a sample chemistry (that is, chromatography or spectroscopy); and the interpretation of these signal patterns (for example, chromatograms or spectra), using a series of multivariate mathematical techniques in the usable form of computer algorithms.

**Chopper:** A device used for modulating or interrupting a current or light beam at regular intervals. This form of modulation is often used to convert signals into resolvable segments for measurement when using slower response detectors.

**Christiansen effect:** An effect where a nonlinear distortion occurs for strong absorption bands transmitting or reflecting energy through, or from, crystalline particles that are slightly larger than the measuring wavelength of energy.

**Circular dichroism:** For an optically active molecule, left or right circularly polarized energy will produce different absorption spectra. The circular dichroism spectrum for optically active molecules changes with the wavenumber of the incident energy. The technique is used to determine the structures of certain types of bioorganic molecules, such as DNA or nucleic acids, and for secondary structure estimation of proteins. It is often performed using the ultraviolet or infrared spectral regions.

**Coherent anti-Stokes Raman spectroscopy (CARS):** A measurement where two lasers are used as a near-infrared pump beam and a longer wavelength Stokes beam. These lasers are used to excite molecules to their virtual state; the molecules then return to their vibrational state. Tuning of the excitation pump laser allows excitation of specific molecules at specific spatial locations with a  $10^5$  signal enhancement over conventional Raman. CARS imaging may

be completed in real time for specific molecular vibrations at known planar locations for image reconstruction without the use of excitation dyes.

**Color measurement:** A measurement of a physical sample is made with appropriate illumination and measurement geometry. For color measurement, a variety of color coordinates are computed from the visible spectrum to approximate and define colors to simulate human vision. To compute the color coordinates for any sample requires three vectors or tables of values: the spectral power distribution of the illuminant (usually either Standard Illuminant D65 or Standard Illuminant A); the color matching functions representing the human eye sensitivity to red, green, and blue (RGB) as the  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$  coordinates; and the visible spectrum of the sample in the appropriate measurement geometry.

**Colorimetry:** The techniques for the measurement of color (in the visible region) and for the interpretation of the results of such measurements as they correspond to universal mathematical color scales. There are many color scales used to report color vision in a digital format. See also *color measurement*.

**Combination band:** An absorbance band arising from the interaction of two or more vibrations of a molecule—for example, stretching and bending. The new frequency for the combination band is calculated as the sum of the vibrational frequencies of the coupled (interacting) bands ( $\nu$  combined =  $\nu_1 + \nu_2$ ). In the near-infrared region, C-H stretch combination bands occur four times, and the O-H combination bands occur three times. For example, in the NIR region the first combination region for C-H stretching occurs from  $4550\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  or 2200 nm to 2500 nm; the second combination region occurs from  $7400\text{ cm}^{-1}$  to  $6666\text{ cm}^{-1}$  or 1350 nm to 1500 nm.

**Combination search:** A method of selecting a subset of variables from a larger set by performing trial calibration using different combinations of variables to form each subset, then

selecting that subset giving the most accurate calibration. This concept is usually extended to trying all possible combinations of variables. It was most often applied to selecting appropriate wavelengths for multiple linear regression calibrations.

**Compression:** A term used to describe a method of minimizing repack variation in spectral data by averaging several aliquot scans of each sample before calibration development. Thus, all repeated scans for a sample are averaged to a single scan or spectrum, and the variation in repacks is removed from the data. The resulting calibration will be more accurate, but, statistically, will require that future predictions also be averaged.

**Concentration:** The amount of analyte in a given volume of sample—for spectroscopy, this is in moles per liter or mass per unit volume.

**Confocal optics:** The term is defined as two optical elements with an identical focal length or focus, such as a pair of matched spherical mirrors with a distance equal to their respective radii of curvature, a set of pinholes with the same foci, or a pair of matched lenses with the identical foci. For confocal microscope optics, the sample and the condenser optics are at the same focus. Greater resolution is possible when confocal pinhole apertures are used as in confocal microscopy; this technique is also useful for three-dimensional structure rendition.

**Constituent:** Any discrete component of a sample; more specifically, a component for which an instrument can be calibrated. Also referred to as *parameter* or *product constituent*.

**Correlation:** The tendency of two sets of numbers to follow one other; that is, to increase or decrease together. This tendency is usually expressed numerically by the *correlation coefficient*. In some fields, this term is commonly referred to as Pearson's *r* or Pearson's correlation, named after Karl Pearson (1837–1936).

**Correlation coefficient:** The numerical measure of correlation as described above. The correlation coefficient must always lie between

-1.0 and +1.0. For instrument calibrations the correlation coefficient should be positive (+). The correlation coefficient is calculated from the following expression, where there are two variables compared, namely *X* and *Y* with *n* being the number of data-point pairs.

$$r = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2} \cdot \sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2}} \quad [3]$$


**Correlation transform:** A term used to describe the process of using correlation statistics with multilinear regression analysis to select the optimum regression equation for the sample, based on the correlation between the analyte concentration and a change in spectral response for a particular wavelength or wavenumber data point, or wavelength or wavenumber region.

**Counts:** The measured raw signal used in photon detection electronics relating to the analog-to-digital (A/D) converter signal. Most modern photodetectors use a 16-bit A/D electronics converter corresponding to a maximum signal count of  $2^{16} = 65,536$  counts for full-scale detection, having a full range of 0 counts to 65,536 counts.

**Curve resolution:** One of several methods of deconvoluting severely overlapped complex spectra. Resolution algorithms reveal the individual absorbance bands that make up the spectrum. Various functions are used to approximate the shapes of the component spectra, including normal and Lorentzian curves.

**Cuvette (also cuvet):** Transparent receptacle in which sample solutions are introduced into the light path of spectrometers. Usually, the two sides are equal (for example, 1-cm square) while the third dimension (height) is elongated, possibly as long as 15 cm. For UV work, the window material is generally low-OH quartz. For visible spectroscopy, some polymers are used, such as polystyrene (PS) or polymethylmethacrylate (PMMA). The *z*-dimension is the distance from

the bottom of the cuvet holder to the center of the transmission beam of the spectrophotometer. See *Window* for additional information of materials used for sample holders.

**D**  **Data:** The collection of numbers representing the direct results from actual measurements, and upon which calculations are to be performed to determine the quantities of interest. Common data file formats for analytical spectroscopy include AB SCIEX Data Explorer (.pkm), ASCII Table (.csv), Bruker (.XML), Excel (.xls), Finnegan (.asc), JCAMP-DX (.dx), MatLab (.mat), mzData (.XML), PerkinElmer (.sp), Plain Text (.txt), Spectra-Calc, Archival, fixed point (.spc), Thermo Galactic (.spc), Thermo Scientific Nicolet (.SPA), and XLM marked-up text (.XML).

**Degrees of freedom:** A measure of the number of independent measurements in a data set. In a data set to be used for calibrating an instrument, the degrees of freedom are equal to the number of reference laboratory measurements against which the instrument is calibrated. The final results contain fewer degrees of freedom than this number of measurements, because the calibration process creates some dependence between the results; there is a loss in 1 degree of freedom for every calculated parameter.

**Derivatives:** In spectroscopy, it is used to indicate first through fourth derivative or difference functions of the absorbance spectrum with respect to wavelength. Generally, the Savitzky-Golay algorithm is used to create derivative spectra.

**Detector:** A device sensitive to electromagnetic radiation at the wavelength region of interest. The output of the device is usually an electrical signal proportional to the intensity of the electromagnetic energy input. The detector generally produces an analog signal proportional to the radiation striking the detector element. This analog signal is converted into a digital signal by means of an analog-to-digital (A/D) converter

and amplifier circuit. Usually, a simple silicon diode, a more sensitive photomultiplier tube (PMT), or various photodetector systems are used to detect the light energy. See also *passive detector* and *active detector*.

**Detrend:** A general term used to describe the removal of a basic trend from data to more closely determine the signal attributes associated with analyte concentration or basic information content within a signal. To perform detrending, the data in a time series are subjected to a linear least squares fit, and then the fit function is subtracted from the data. For unusual curved shapes in the baseline of spectra, a polynomial function of a selected order is fit to all the data points in the spectrum, and this fit function shape is subtracted from the spectrum. The polynomial is used to fit all data points in the spectrum. This technique will remove large background interferences, or specific background trending variations, and is often used in combination with the standard normal variate (SNV) preprocessing function. A detrend algorithm consists of a polynomial or linear fit to each spectrum and a subtraction function of the fit function from the spectrum. The remaining spectrum is used for multivariate calibration or qualitative comparison.

**Difference bands:** Similar to combination bands in that two or more absorbance bands are involved. In difference bands, the observed frequency of two interacting bands is the difference in frequency between the two bands, as defined in equation 4:

$$(\nu \text{ difference} = \nu 1 - \nu 2) \quad [4]$$

**Difference spectroscopy:** In difference spectroscopy, two spectra are subtracted one from another to determine spectral differences. This technique is quite powerful for determining slight variations in composition when interpreting spectra; it also assists in identifying low levels of individual compound differences in mixture spectra.

**Digital:** Refers to the behavior of certain devices (such as computers) that can only be in one of a finite number of discrete states. Computers can only be in the states associated with the output of the various electronic components exhibiting voltage levels corresponding to the 0 state or the 1 state. Each such solid-state device contains the information for one binary digit. See also *bit*.

**Digital light processing (DLP):** A digital light processing device is a microelectromechanical system (MEMS) device also known as a digital micromirror device (DMD). This stationary fixture consists of many thousands or millions of micromirrors used in a DLP spectrophotometer. The micromirrors move in series to capture the diffracted light from a fixed diffraction grating onto a set of collimation optics guided to a detector to create a full spectrum in microseconds. The solid-state DLP spectrometer yields fast, high-resolution spectroscopy, particularly for the visible and near-infrared regions.

**Dipole moment:** Any covalent, intermediate, or polar molecule containing opposite charges ( $+q$  and  $-q$ ) separated by a distance of  $d$ ; the magnitude of the moments are reported in Debye units. The permanent electric dipole moment is equal to the vector  $p = qd$ . If the charges ( $q_i$ ) are located at points  $a_i, b_i, c_i$ , the magnitude of the dipole moment ( $P_a$ ) is equal to

$$P_a = q_i d_i \text{ where; } d_i = a_i b_i c_i \quad [5]$$

**Discriminant analysis:** A mathematical technique for identifying or classifying data according to previously defined patterns. This technique is sometimes referred to as qualitative analysis or classification analysis.

**Double (dual) beam:** This term is applied to the simultaneous measurement of optical data from both a sample beam and a stable reference beam. Although the optical radiation used to obtain the measurements may share part or all of the optical path, there must be a separation either in space or in time between the two

measurements; thus, two beams of optical radiation must be used. One beam is used as a reference and the other as sample measurement. The ratio of the sample to the reference beams, respectively, provide the  $I/I_0$  spectral measurement for use in absorbance (A, Au) as  $-\log_{10}(I/I_0)$  computations.

**Double-sided interferogram:** An interferogram has a “center-burst,” also referred to as the zero-path-difference (ZPD) location. When the path of the fixed mirror and the moving mirror are identical in the interferometer, the interferogram is at maximum interference. The centerburst may be placed anywhere along the recorded data for the interferogram. When it is placed in the center of the interferogram, it is termed a double-sided interferogram (also known as an asymmetric interferogram).

## E

**Eigenvector:** A nonzero vector used for the dot product solution in a matrix multiplication. For example, principal components are eigenvectors, as is a regression or b vector.

**Electromagnetic spectrum:** The continuum of frequencies that contains electromagnetic radiation (EMR). Instruments measure the intensity of radiation within a defined range of the spectrum, and usually present the results of their measurements as a set of values of some function, or the measured intensity at (usually) evenly spaced intervals within the range. The energy throughout the electromagnetic spectrum ranges from gamma radiation (most energetic and highest frequency) to radio waves (least energetic and lowest frequency). The spectrum is expressed in terms of wavelength, wavenumber, frequency, or energy. See also *unit conversions for photon energy*.

**Etendue:** The etendue is the relative throughput advantage for an optical system. It is calculated as the product of the potential illuminated surface area times the solid angle of the optical system. It is an indicator of the relative efficiency of an optical system.

**Extinction and extinction coefficient:**

Words sometimes substituted for absorbance and absorptivity, respectively. They are generally considered physics terms.

**F**

**Far infrared (far-IR):** The spectral region representing molecular vibration from  $400\text{ cm}^{-1}$  to  $10\text{ cm}^{-1}$ , or  $2.5 \times 10^4\text{ nm}$  to  $10^6\text{ nm}$ .

**Fermi resonance:** In its simplest definition, for infrared and Raman spectroscopy, it is a fundamental vibration coupled with an overtone (harmonic) band or combination band at the same frequency to create two strong bands where only the fundamental band is anticipated. These two strong bands occur at both higher and lower frequencies than the fundamental band. Only certain combinations are allowed and are, for example, observed in carbonyl (C=O)-containing compounds. Fermi resonance causes the splitting of two vibrational bands having nearly identical symmetry and energy, such as the fundamental with overtone or combination bands. This resonance causes a change in wavelength (or frequency) and amplitude (or intensity) of the resulting spectral bands. The strong and weak bands thus combine into two strong bands.

**Field:** In database management, a section of a record in a file that contains the same type of information as the corresponding section in other records in the same file. The term also refers to a variety of fields in physics such as electronic, magnetic, and gravitational. According to Merriam-Webster's definition, a "field" is "a region or space in which a given effect (such as magnetism) exists."

**Filter:** A device used to attenuate particular wavelengths or frequencies while passing others with relatively little change. There is electronic filtering (digital signal processing [DSP]), and physical optical filters. Optical filters include interference filters with narrow or broadpass bandwidths, as well as filters that pass high-range wavelengths (high pass) or low-range

wavelengths (low pass). There are also special filters, such as linear variable filters (LVFs), which pass specific bandwidths of energy simultaneously. Another optical filter type is multivariate optical element (MOE) regression filters, which are special filters that resemble the regression b vector from a calibration and thus produce a final prediction of a constituent from an optical signal.

**Filter spectrophotometer:** A spectrophotometer that uses filters to isolate narrow bands of the spectrum.

**Filter transform:** A mathematical operation that converts data collected with a monochromator-based instrument to mimic the corresponding data that would have been collected from an instrument containing interference filters, taking into account the differences in characteristics between the two types of devices.

**Fingerprint region:** The infrared spectral region from  $1500\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  often attributed to bands from the bending molecular vibrations. The bands in this spectral region represent the C-C, C-N, C-O, and C-X stretching vibrations, as well as the C-H and C-S scissoring, bending, and rocking vibrations.

**Fixed filter:** A spectrophotometer characteristic where narrow-band interference filters are mounted on a rotating turret. The turret is rotated so as to align the different filters between the incident radiation and the sample. Thus, this instrument design produces a different wavelength light of incidence on the sample for each rotation of the turret. See also *near-infrared filters*.

**Fluorescence:** Photons with energies in the ultraviolet (that is, 190–360 nm) to the blue-green visible (that is, 350–500 nm) spectral regions will excite an electronic transition for atoms in molecules that fluoresce (that is, fluorophores). Fluorescence is an electronic transition from a ground state to the excited state with the emission of a photon to return to the ground state. After the molecule is excited, it relaxes (Stokes shift) to the ground state while emitting a pho-

ton within a femtosecond ( $10^{-15}$  s) to picosecond ( $10^{-12}$  s) timeframe. The Stokes shift indicates a lower energy of the fluorescence photons than the energy of the excitation photons. The fluorescence typically has a lifetime (or duration) of nanoseconds ( $10^{-9}$  s) per transition. A fluorescence spectrophotometer normally has an excitation monochromator that defines the excitation energy, and an emission monochromator that provides a full spectrum of the fluorescence emission.

**Fourier transform:** A mathematical operation in which a curved repetitive function is described in terms of the sum of sine and cosine waves. A conversion from a time domain interferogram to a frequency spectral domain occurs when using this transformation. In spectroscopy, an interferogram is taken from a sample measurement in the time domain and converted into a spectrum in the frequency domain. This conversion is completed for both sample and reference interferograms, which are then processed and ratioed to produce an  $I/P$  spectrum.

**Fourier transform infrared (FT-IR):** A means of measuring the electromagnetic spectrum using an interferometer; the desired spectrum is then obtained by performing a Fourier transform on the resulting interferometric data. Other Fourier transform measurements include Fourier transform near-infrared (FT-NIR) and Fourier transform ultraviolet (FT-UV).


**Frequency:** Frequency as  $\nu$  (Greek: nu) is the frequency of light, also known as Hertz (Hz) or the number of vibrations per second, in units of  $s^{-1}$ . It is defined by the following expression:

$$\nu = \frac{c \cdot n^{-1}}{\lambda} \quad [6]$$

Where  $\nu$  (nu) is the frequency of light,  $n$  is the refractive index of the medium the light is passing through (for example, the refractive index of air is 1.0003),  $\lambda$  (lambda) is the wavelength in units of cm, and  $c$  is the velocity of light in a vacuum (or  $2.9979 \times 10^{10}$  cm/s).

**Fundamental region:** The lowest frequency corresponding to a given molecular vibration. Fundamental group frequency vibrations for molecular bands are within the infrared spectral region of  $4000\text{--}1500\text{ cm}^{-1}$ . The bands in this spectral region represent the asymmetric and symmetric stretching of C-H, O-H, N-H, Ar-H,  $>\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}\equiv\text{C}$ , and other bonds. Note that overtones are derived from fundamental absorption frequencies as equal to integer multiples of 2 (first overtone), 3 (second overtone), 4 (third overtone), and 5 (fourth overtone).

**F-value:** A ratio of variances, usually used to determine if one of the variances is due to the same cause as the other. In regression analysis, a particular  $F$ -value (that is, the mean square due to regression divided by the mean square due to error) has the secondary meaning of giving an indication of the robustness of the regression. The  $F$ -value is testable against a critical value of the  $F$ -distribution to determine if the result is significant or not.

**G**  **Graphical user interface (GUI):** A term invented by Xerox in Palo Alto, California in the early 1970s that refers to a software interface between the user and the operational software code. Today, it may involve touch-screen icons and graphics that are easy to activate and understand.

**Grating:** A reflective surface covered with evenly spaced, microscopic grooves, whose purpose is to separate individual wavelengths from broadband energy. The distance between grooves and the angle of the faces is determined by the wavelengths to be separated. The grating (except for diode arrays) is rotated at a set angle and speed, and the desired wavelength is diffracted through an exit slit onto the sample and detector (or detectors). It is used to disperse light of various wavelengths and orders from its surface. It disperses zero order as specular reflected light, and first, second, and higher

orders as diffracted light. When the diffracted light interacts in a phonon effect it decreases the energy dispersed from the surface, resulting in a phenomenon termed *Wood's anomalies* (see this term for more information).

**Grating spectrometer:** A spectrometer that uses a grating for the diffraction and resulting resolution of light of various wavelengths. This is often termed a monochromator when one grating system is involved.

## H

**Harmonic bands:** A synonym for *overtone*. These bands represent multiple harmonics of the fundamental vibrations for molecular bonds and are found at integral multiples of the fundamental band frequencies. For example, a first overtone band occurs at twice the frequency of the fundamental band, and the second overtone at three times the frequency of the fundamental band. Harmonic bands in the infrared and Raman regions are found as multiples of the fundamental frequency according to the harmonic oscillator approximation, with a proportional higher shift in frequency and reduced amplitude in the spectrum with an increase in harmonic number. Within the near-infrared region these harmonics are known as the first overtone ( $2\nu$ ), second overtone ( $3\nu$ ), third overtone ( $4\nu$ ), and fourth overtone ( $5\nu$ ).

**Highpass filter:** A dielectric composite filter that enables energy above a certain cut-on wavelength or frequency to pass at nearly 100% transmission, whereas energy at wavelengths or frequencies below the cut-on wavelength will not pass or is nearly 0% transmissive.

**Histogram:** A plot of the frequency of occurrence of sample values within the subranges of the range of values of the data. Histogram bars touch (are adjacent), whereas bar graph bars do not touch (are not adjacent).

**Holographic grating:** A grating made by using a holographic process where a photoresist is placed on an optical surface such as a glass blank. A series of interference fringes corre-

sponding to the grooves of the desired grating model are recorded on this photosensitive layer by projecting a hologram of light and dark lines. Subsequent chemical treatments are used to erode either the exposed or unexposed photoresist material (there are different types of treatments such as positive and negative photoresist processes) on the surface to produce a grooved diffraction grating of specified groove shapes and lines per millimeter.

**Hotband:** A hotband results when an already excited vibrational band is further excited, often related to a change in temperature; the intensity of a hotband is proportional to the temperature. At room temperature, the ground state of a molecular vibration is the most common as defined using the Boltzmann distribution. The Maxwell-Boltzmann distribution law further states that the distribution of these hotband transition bands is dependent upon the Boltzmann constant and the temperature in degrees kelvin.

**Hydrogen bonding:** Hydrogen bonding within a molecule and between a solvent and a solvated molecule manifests as changes in the force constants of the X-H bonds. Generally, molecular bands will shift in frequency and broaden as a result of the formation of hydrogen bonds. Since combination bands result as the summation of two or more fundamental vibrations, and overtones occur as the result of the multiples of fundamental vibrations, frequency shifts related to hydrogen bonding have a greater relative effect on combination and overtone bands than on their corresponding fundamentals. The reason for this greater effect is that harmonics have weaker bond energies relative to the hydrogen bonding and have greater anharmonicity. This feature of vibrational spectra alerts one to the importance of the relative hydrogen bonding effects brought about by solvent and temperature variations.

**Hyperspectral imaging:** The collection of multiple spectra into a three-dimensional data hypercube consisting of wavelength, amplitude, and either time or spatial dimension scanning

(as the third dimension). For example, a moving sample may be measured by having a fixed linear array sensor with the third dimension being the sample measured over time. The data cube may also be constructed by moving the sensor over a stationary surface to gather a set of spectra for each line area of a surface. Array detection is often involved in generating hyperspectral images; either by means of linear arrays or by using rectangular arrays.

**Indicator variable:** A variable used in regression analysis to allow the inclusion of information that cannot otherwise be expressible numerically. Generally, they are assigned a 1 or a 0 to indicate the presence or absence of a particular condition. Examples could include which of two operators prepared a sample, what instrument was used to measure the sample, the type of solvent used, average particle size range of sample, and so forth.

**Infrared absorption bands:** A bond within a molecule that is infrared active or capable of absorbing infrared radiation. When the radiation striking an infrared-active molecule matches the natural vibrational frequency of the various bonds within the molecule, the radiation is absorbed. When absorption takes place at a specified frequency, an absorption band at that frequency is observed. For an infrared-active molecule, the dipole must change as the frequency of the infrared radiation changes for it to absorb infrared energy or scatter Raman energy. Dominant infrared absorption bands include the C-H (methyl, methylene, aromatic, methoxy, and carbonyl) fundamental stretching and bending molecular vibrations, the O-H (hydroxyl) stretch fundamental vibrations, the N-H (amine) stretching, the C-F (fluorocarbon) stretching, the  $\text{-C}\equiv\text{N}$  (nitrile) stretching, the  $\text{-C=O}$  (carbonyl) stretch from esters, acetates, and amides, the C-Cl stretch from chlorinated hydrocarbons, and  $\text{-NO}_2$  from nitro-containing compounds.

**Infrared (IR) spectroscopy:** *Infrared* refers to that portion of the electromagnetic spectrum containing radiation with wavelengths longer than those visible to the human eye, and extending to approximately  $30\ \mu\text{m}$ . A broad definition of the infrared region is subdivided into the near-infrared ( $0.75\text{--}2.5\ \mu\text{m}$ ), mid-infrared ( $2.5\text{--}30\ \mu\text{m}$ ) and far infrared or terahertz ( $30\text{--}300\ \mu\text{m}$ ). Mid-infrared spectroscopy provides a measurement technique for intense, isolated, and reliable absorption bands of fundamental molecular vibrations from polymers and other organic compounds.

**Infrared windows:** See *Window*.

**Integrating sphere:** A hollow sphere, coated with a diffuse reflecting material and provided with openings for incident beam, specimen, and detector. It is primarily used for measuring the most accurate diffuse reflectance or transmittance of objects. In most versions, the sample is measured outside of the sphere.

**Intensity correction:** A correction of the y-axis (intensity) for Raman spectra in which a standard lamp or a standard reference sample is used in combination with a polynomial fit across the entire wavenumber axis to standardize the intensity measurements of any Raman spectrometer. It is analogous to a photometric correction accomplished for absorption spectroscopy. It is also used to correct and measure the output of spectrometer lamps.

**Interface:** A junction or connection. For example, a computer input-output (I/O) interface. Also, the junction between air or sample and an optical element.

**Interference filter:** A filter that controls the spectral composition of radiant energy passing through it by the effects of interference. Frequently, these filters are made up of thin layers of metals and dielectrics, and provide narrow bandpass and high transmittances.

**Interferogram:** A wave pattern created using an interferometer where waves are superimposed and later interpreted to compute a pattern of amplitude versus frequency for a

measurement of light interaction with materials. This interferometer pattern is interpreted using a Fourier transform to compute a Fourier transform near-infrared (FT-NIR), FT-infrared or FT-Raman spectrum.

**Interpolation:** A method used to provide a specified number of data points for a spectrum. Generally, a cubic spline interpolation method is used to change the number of data points for sparse data to a greater fixed data resolution. For example, a spectrum of 500 data points may be adjusted to 1000 data points by interpolation. Note that the interpolation may provide fixed data intervals, but the missing data points cannot be reconstructed, and peak positions may be quite different for sparse interpolated data versus the denser higher resolution data.

**Interval:** The difference in wavelength between two adjacent wavelengths over which optical data are collected.

**Isotope shift:** The change or displacement in position of vibrational bands resulting from the different masses of the isotope atoms in a molecule. A commonly used example is to compare the spectra of hydrogen and deuterium within a molecule. The isotope shift is directly related to the isotope mass number differences between the atoms involved.

**Isotropic:** A reflection property for which the energy is assumed equivalent for all positive angles of reflection.

**Kramers-Kronig transformation:** A mathematical transform to adjust infrared absorbance spectra from reflectance into absorbance spectra generated using transmission spectroscopy. This transformation is required for quantitative or qualitative comparison of reflection and transmission spectra. In general, the Taylor series or Maclaurin series is used to compute the Kramers-Kronig transformation.

**Kubelka-Munk function:** A series of mathematical expressions derived to relate absorbance and scattering properties of a reflecting medium

to the concentration of an absorbing material in that medium. The original work was begun by A. Schuster in 1905 in the *Astrophysical Journal*.

**Laser:** An abbreviation for *light amplification by stimulated emission of radiation*. Lasers are used in a variety of ways for molecular spectroscopy, including diode lasers for alignment of Michelson interferometers, for spectrometer sources, and for fluorescence or Raman excitation. For Raman spectroscopy, lasers are used to produce the Raman effect as inelastic scattering collisions of light energy with the various atoms forming chemical bonds in molecular structures. The excitation laser sources used may be gas lasers or diode lasers of relatively low power and constant frequency. Common laser wavelengths include 532 nm, 785 nm, and 1064 nm, although multiple lasers are available for wavelengths ranging from the ultraviolet through the near-infrared regions.

**Learning set:** See *teaching set*.

**Least squares fit:** A descriptive name for regression analysis. A mathematical technique used for choosing the coefficients of a linear equation—that is, one of the form

$$Y' = B_0 + B_1X_1 + \dots + B_nX_n \quad [7]$$

Where  $Y'$  is the dependent or estimated variable (that is, analyte or parameter concentration for a sample spectrum),  $B_0$  is the intercept, the  $B_n$  variables are the regression coefficients, and the  $X_n$  variables are the independent variables (that is, spectral data). For this equation, the sum of the squares of the differences between the reference values ( $Y$ ) and the estimated values ( $Y'$ ) into the resulting equation is minimized.

**Limit of detection:** Lowest amount of analyte that may be seen above the noise the level of the instrument; it is generally estimated at three times the root mean square (RMS) noise level above the zero signal for specific measurement conditions.

**Linear:** Straight line. In context, a linear relationship means that, for a doubling of the analyte concentration, the signal will double. This relationship allows the most accurate prediction of unknown analyte composition from spectral measurements.

**Linear response:** Straight-line response between concentration and measured signal. In context, a linear response means that, for a doubling of the analyte concentration, the detectable and measurable signal will double. This type of response allows a linear calibration model or equation to be used to determine the accurate concentration of analyte through a range of absorbance or intensity levels.

**Linearity:** An experiment demonstrating that the response of an instrument changes in a predictable and linear fashion with increasing analyte concentration.

**Linear variable filter (LVF):** A dichroic filter that produces a full spectrum when light is directed orthogonally to the filter without physically tilting the filter. It is used in combination with an array detector to capture a full spectrum rapidly, without requiring the movement of any spectrometer components.

**Liquid crystal tunable filters (LCTFs):** A liquid crystal tunable filter is a bandpass optical filter based on the use of liquid crystal elements that are electronically activated to transmit a specific wavelength range of light, while excluding other wavelengths; the working principle is based on the Lyot filter concept. The useful spectral measurement range for LCTFs is from 400 nm to 2450 nm, with spectral resolution of approximately 1% to 2% of the transmitted or measured wavelength; LCTFs are useful for hyperspectral and multispectral imaging.

**Log(1/R):** An analogy to Beer's law, this function of measured reflectance is often used to relate sample reflectance to constituent composition of a substance. It is analogous to the  $\log(1/T)$  for transmittance measurements; these equations are equivalent to  $-\log R$  and  $-\log T$ , respectively.

**Lowpass filter:** A dielectric composite filter that enables energy below a certain cut-off wavelength or frequency to pass at nearly 100% transmission; energy from wavelengths or frequencies above the cut-off wavelength will not pass where the filter is nearly 0% transmissive.

## M

**Mass storage:** Used to refer to information storage devices other than the internal memory of the computer. Usually means disk, solid-state drive (SSD), or cloud storage.

**Mathematical pretreatments:** Mathematical procedures used to relate spectral data to concentration in an attempt to produce results deemed "improved." These treatments empirically are used before multivariate variable selection and equation-solving algorithms. Kubelka-Munk,  $\log(1/R)$ , standard normal variate reduction, normalization, mean centering, and difference (derivative) math are the most common pretreatments in use.

**Matrix:** Any rectangular array of numbers. By predefining certain types of mathematical operations such as matrix operations, complicated algebraic manipulations can be expressed in a simple notation of rows and columns.

**Mean:** The algebraic average ( $\bar{X}$ ) of a list of numbers. The sum of:  $X_i$  for  $i = 1$  to  $n$  divided by  $n$ .

$$\bar{X} = \frac{\sum_{i=1}^n X_i}{n} \quad [8]$$

**Mean corrected standard error of prediction (SEP):** A measure of the accuracy of a set of instrumental analyses after correcting for bias between the set of instrument predictions and the corresponding set of reference laboratory results. This measurement involves a set of samples with known reference data, but that were not included within the calibration teaching set. The mean corrected SEP may be calculated as the standard deviation of the differences between the predicted results and reference laboratory results.

**Mean drift:** The average systematic (unidirectional) change over time of an instrument measurement of a primary standard (or known) reference material.

**Mean subtracted spectrum:** For a set of two or more spectra, the mean spectrum of the set is subtracted from each spectrum leaving a residual spectrum for each spectrum. This process centers the data or spectra—that is, it gives a residual spectrum relative to the average spectrum. Thus, those spectra most different from the mean spectrum will stand out as having the largest residual spectra with the most different features. The process uses vector operations.

**Menu:** A method of presenting the computer's requirements for operator input that presents the available choices to the operator, and asks for the selection of choices desired. It is a portion of the graphical user interface.

**Micrometer:** A unit of length in the metric system equal to  $10^{-6}$  meter, abbreviated  $\mu\text{m}$ . The term is used in place of "micron." Wavelength is most often expressed as in units of nanometers ( $10^{-9}$  m) for ultraviolet through near-infrared spectroscopy. The use of angstrom ( $\text{\AA}$ ,  $10^{-10}$  m) is uncommon in modern spectroscopic terminology.

**Molecular vibration:** Molecules do not remain still; the atoms composing a molecule are in continuous motion with respect to one another. These movements can be classified into distinct categories, and the net molecular motion can be shown to be the sum of the separate vibrational modes. These vibrations are approximated by the resonant frequencies of a macroscopic mass-and-spring model for each molecule and bond type, approximating Hooke's law.

**Monochromator:** An instrument used to provide an incident light beam with a narrow wavelength range. A monochromator becomes a spectrophotometer when it is combined with a light source, slits, grating,

detectors, an amplifier, and an output energy measuring device.

**Multifile:** A single file that incorporates multiple spectra used with some software packages, such as Grams and eFTIR.

**Multiplicative scatter (or signal) correction (MSC):** This correction method provides some mitigation of the reflection scattering phenomenon by regressing the individual spectrum to the mean spectrum for a collection of spectra, for both calibration and prediction data sets. The identical mathematical treatment must be completed for both the calibration and the prediction sets. When conditions or data sets are changed, the algorithm is recomputed for the entire sets. The algorithm assumes that the ideal spectrum is the mean spectrum. MSC approximates a regression estimate of the mean spectrum with the remaining unexplained residual spectrum representing the spectral differences between the spectra within a set. This residual difference is assumed to contain much of the chemical information differences between samples in the spectrum set.

**Multivariate mathematics:** The branch of mathematics that deals with data that change in multiple ways (that is, multiple variables or response factors) with respect to a single dependent variable (reference analyte value). Multivariate methods include regression (multiple linear regression [MLR], principal components regression [PCR], and partial least squares regression [PLSR]), variance analysis (VA), factor analysis (FA), component analysis, cluster analysis, neural networks analysis (NNA), support vector machines (SVM), classification, and discriminant analysis [DA].

## N

**Nanometer:** Unit of measurement for wavelength, abbreviated as nm; as one-billionth of a meter ( $10^{-9}$  m).

**Near-infrared filters (traditional):** Near-infrared (NIR) spectroscopy using special

wavelengths with filters was traditionally used in agricultural product analysis during the late 1960s for lignin polymers (2270 nm), paraffins and long alkane chain polymers (2310 nm), glucose-based polymers such as cellulose (2336 nm), amino acid polymers as proteins (2180 nm), carbohydrates (2100 nm), and moisture (1440 and 1940 nm). A reference position was often located at 1680 nm.

**Near-infrared relative band intensities:**

Relative intensities of C-H stretch bands for infrared and the various NIR overtone regions are shown in the table below.

Band Type	Wavelength Region (nm)	Relative Intensity
Fundamental ( $\nu$ )	3380–3510	100
First overtone ( $2\nu$ )	1690–1755	1
Second overtone ( $3\nu$ )	1127–1170	0.1
Third overtone ( $4\nu$ )	845–878	0.01
Fourth overtone ( $5\nu$ )	690–780	0.005

**Near-infrared spectral features:** NIR spectral features include the methyl C-H stretching vibrations, methylene C-H stretching vibrations, aromatic C-H stretching vibrations, O-H stretching vibrations, methoxy C-H stretching, and carbonyl-associated C-H stretching. In addition, N-H from primary amides, secondary amides (both alkyl, and aryl group associations), N-H from primary, secondary, and tertiary amines, and N-H from amine salts predominate near-infrared spectral features of polymers, natural products, and synthetic organic compounds.

**Near-infrared spectroscopy:** The NIR portion of the electromagnetic spectrum; comprises those wavelengths between the visible region and infrared region or 0.75  $\mu\text{m}$  to 2.5  $\mu\text{m}$  (750 nm – 2500 nm). NIR spectra consist of overtones and combination bands of the funda-

mental molecular absorptions found in the mid-infrared region. More complete harmonic and combination band information is found from approximately 680 nm to 2600 nm.

**Noise:** The random component of a set of measurement data, caused by the uncontrollable phenomena that affect all parts of the experimental setup. Random (or white) noise is reduced by a factor equal to the square root of  $r$ , where  $r$  is the number of repetitive measurements.

**Normalization:** This term has at least two distinct meanings in spectroscopic methodology. The first meaning refers to division of each point in a spectrum by the spectrum  $y$ -axis standard deviation so that each spectrum is given the same weight when used for calibration. In this first definition, normalization refers to division of each data point in the spectrum by a correction factor (for example, pathlength, area, standard deviation, reference band, or multiplicative signal correction). The second meaning refers to the use of spectra for discriminant analysis, and is the method used to make the multidimensional size of the data from each sample type the same.

**Nuclear magnetic resonance (NMR):**

NMR is a method for determining precise molecular structure or chemical composition based on the nuclear spin of atoms in a molecule. All atoms are electrically charged and have a spin profile. When an external magnetic field is applied to matter an energy transfer may occur from the ground energy state to a higher energy state for each nucleus (the ground and excited energy states are the two spin states for an atomic nucleus). This specific energy transfer occurs for each type of atomic nuclei at a radio frequency, and when the atomic nuclei return to the ground energy state a signal is emitted. The resulting signals for a specified magnetic field strength (for example, 1–21 tesla [T]) applied to a molecule is an NMR spectrum with the abscissa as frequency (usually as 20–900 MHz) and the ordinate as amplitude for number of

different types of nuclei. NMR spectra are also displayed as the chemical shift in parts per million (ppm) as the abscissa, versus signal intensity as the ordinate. The chemical shift is the change in frequency between the two spin states (that is, ground state and excited state) at a given magnetic field strength for each nuclei ratioed to the reference frequency (rf). For example, a change in frequency of 2000 Hz for a 100-MHz rf would be 2000/100 MHz = 20 ppm. NMR spectra are able to measure quantitative (composition) values for known materials or to identify molecular structures, diffusion rates, and other molecular details. NMR is termed magnetic resonance imaging (MRI) for medical use.

**Online:** A term used to describe instrumentation that chemically quantifies or qualifies materials in real time (as they are produced).

**Order-sorting filter:** A diffraction grating creates multiple orders of spectra from its surface. As more than one spectrum is created, those spectra beyond the first order (that is, second order and higher) overlap with one another. Order-sorting filters remove the wavelengths above and below the desired measurement wavelength. They are also termed high-pass and low-pass filters as the designation for which wavelength region they are transparent to. The filter is placed in front of a broadband detector, and only the wavelengths permitted through the filter are measured. The other dispersion orders are eliminated.

**Ordinate:** A term used to refer to the vertical (y) axis of a graph.

**Orthogonal signal correction (OSC):** The purpose of OSC is to remove variation from the spectral data,  $X$ , that are orthogonal to the reference data,  $Y$ . This orthogonal variation is modeled by additional components for  $A$  and results in the following decomposition:

$$X = t \times p' + t_o p_o' + e \quad [9]$$

Where  $t_o$  and  $p_o$  represent the scores and loadings for the orthogonal component, respectively and  $e$  the residual. By removing the  $Y$ -orthogonal variation from the data via  $X - t_o p_o'$ , OSC maximizes correlation and covariance between the  $X$  and  $Y$  scores to achieve both good prediction and interpretation. There are several OSC algorithms that have been reported in the literature.

**Outlier:** A data point representing a sample that does not conform to the properties defining the rest of the samples in a data set; it is essentially from a different population. There are statistical tests to examine suspected outliers, such as Dixon's Q test.

**Overtone:** A term used to describe those absorbance bands found at multiples of the fundamental frequency. They are usually close to, but, for quantum mechanical reasons, not exactly integer multiples of the fundamental frequency. Also see *harmonic bands*.

**Parity:** An extra bit added to a group of data bits as an error-detection scheme. The parity bit is set to either 0 or 1 so that the total number of bits in the group (including the parity bit) that is set to 1 is either even or odd. Any error that occurs will most likely affect only one bit; thus after the error occurs, the wrong number of bits will be set to 1.

**Passive detector:** A sensor that detects infrared energy when present. It consists of a front face and an internal pyroelectric thin film material that generates an electronic signal when exposed to radiant energy or heat. Typical materials for passive detectors include cesium nitrate, cobalt phthalocyanine, gallium nitride, and polyvinyl fluoride.

**Pathlength:** The distance the light passes through the sample in its holder. In practical terms, the inside dimension of the cuvette or sample holder. For transmittance, the optical pathlength is 2.5 to 3 times the mechanical pathlength. In Raman measurements, the

physical pathlength is considered infinite, because the Raman intensity is determined by the matrix chemistry and its scattering properties relative to the excitation laser wavelength and power.

**Peak position:** The peak position is the center wavelength or frequency position (that is, center of mass or maximum transmittance or absorbance for a spectral band or a band created using an interference transmittance filter). It is most often the center of the band of frequencies transmitted by a bandpass filter or the center wavelength of an absorbance band.

**Phase correction:** An interferogram inherently contains out of phase portions because of the optical path variation within an instrument. If these portions are not corrected, the photometric intensity of the spectrum will not be accurate. A phase correction using the Mertz method is often applied to correct the phase and make the spectrum accurate in the photometric axis.

**Photon energy:** Photon energy as  $E_p$  is given by  $E_p = h\nu$  or  $E_p = hc\bar{\nu}$ . In this notation,  $h$  is Planck's constant (or  $6.6256 \times 10^{-27}$  erg-s; and  $\nu$  (nu) is the frequency of light, also known as hertz (Hz) or the number of vibrations per second, in units of  $s^{-1}$ ;  $\bar{\nu}$  is the wavenumber units as  $cm^{-1}$  (that is, the number of waves per centimeter), and  $c$  is the velocity of light in a vacuum (or  $2.9979 \times 10^{10}$  cm/s).

**Plasmon:** Plasmons are described as a charge-density oscillation occurring in a plasma. This can also be described as a quantum oscillation of free electrons with respect to the positive ions in a metal. Plasmons are active in demonstrating the optical properties of metals and semiconductor material physics. Frequencies of light below the plasma frequency are reflected by a metal, whereas frequencies above the plasma frequency are transmitted by the metal. In most metals, the plasma frequency resides in the ultraviolet frequencies, a property which makes metals reflective or shiny in appearance within the visible spectral region.

**Precision:** A measure of the agreement of multiple readings (measurements) of a sample with each other, generally expressed as the standard deviation of multiple readings under the specific measurement conditions.

**Prediction:** The measured value of a constituent or parameter in a sample, most often not included within the calibration (teaching) sample set.

**Procrustes analysis (PA):** In analytical chemistry, it is necessary to form instrument-dependent calibration models. Problems such as instrument drift, repair, or use of a new instrument create a need for recalibration. Calibration transfer using PA methods require translation (as mean-centering), rotation, and stretching of the instrument spectral response. The standard PA steps include translation, uniform scaling, rotation, and fine adjustments to superimpose the signals or spectra.

## R

**Raman effect:** Also known as *Raman scattering*, the Raman effect is demonstrated when a high flux of photons strikes an atom or molecule and an inelastic collision between the photons and the atom (or atoms) occurs. This collision causes both an increase (anti-Stokes shift) and decrease (Stokes shift) in photon-radiated (or scattered) energy. This shift in energy is proportional to the vibrational energy (that is, frequency) of the vibrations in the molecules the photon flux collided with and produces a Raman spectrum of the molecular bands.

**Raman spectroscopy:** Raman spectroscopy can be used for a variety of measurements on samples that are aqueous in nature or where glass sample holders are present. Carbon dioxide, water, and glass (silica) are weak scatterers and thus generally no interference is encountered in analyzing samples having these properties. Typically no sample preparation is required in Raman measurements. Raman spectroscopy is complementary to mid-infrared spectroscopy in the direct measurement of fundamental mo-

lular vibrations. The typical spectral range for laboratory Raman spectroscopy is  $3800\text{ cm}^{-1}$  to  $200\text{ cm}^{-1}$ , with the Stokes shift region specifically denoted as the region from  $3500\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ .

**Range:** The difference between the highest and lowest values of a constituent in a sample set, or between highest and lowest values of a data set or spectral region.

**Rapid scan:** A mode in which an instrument achieves a full scan in a few milliseconds, and repeats the scan many times in order to average out random noise or error. By contrast, some instruments require several seconds for a full scan, but still average multiple readings at each point to reduce random noise.

**Rayleigh scattering:** Rayleigh light scattering is an elastic (that is, nonreactive) scattered light interaction between energy of a given frequency and particles. When this effect occurs, the intensity of the scattered energy (as  $I_{RS}$ ) is inversely proportional to the fourth power of the incident light wavelength ( $1/\lambda^4$ ) in nanometers, micrometers, or meters.

**Reference set:** A collection of samples for which primary reference laboratory data are available for the constituent composition, and thus can be used to calibrate an instrument for multiple products and constituents.

**Reference spectrum:** In context, a reference spectrum is generated using everything that is in the sample light path except the analyte of interest—that is, the cuvette, solvent, and any buffer or matrix used to prepare the sample. For reflectance spectra, the reference is a nearly 100% reflector; for transmission spectra, the reference is dry air. For a traditional dual-beam spectrum, the reference is the sample holder containing the solvent without the analyte.

**Reference standard:** Analyte wherein the purity is documented and used to construct a calibration curve. The calibration may be either of the instrument performance, or for the analytical determinations of an analyte.

**Reflectance:** Reflectance ( $R$ ) refers to the measured ratio of the quantity of electromagnetic energy reflected from a sample ( $I$ ) to the quantity of energy reflected from a reference material ( $I_0$ ), so  $R = I/I_0$ . The R scale may be expressed as 0% to 100% or 0 to 1.0. This term is also defined as the measured fraction of electromagnetic radiation striking a surface that remits, or returns, from that surface. At any wavelength, the reflected light can be considered as having two major components. One is the diffuse component, resulting from the light penetrating into the material and having a scattering interaction with it so as to reemerge at an altered angle relative to the incident angle. The other is the specular component, resulting from mirror-like elastic reflections at the sample surface.

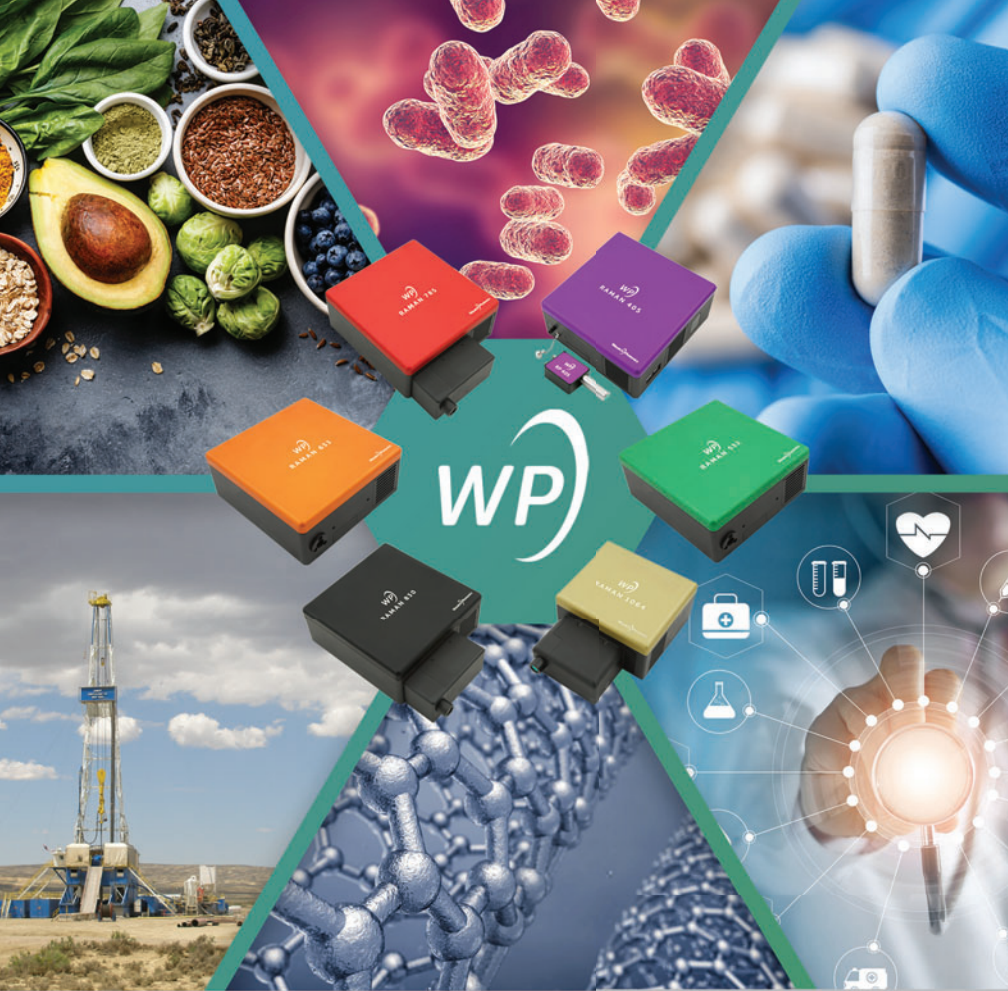
**Reflection:** Reflection refers to the act or phenomenon of reflecting, which is the change in direction of electromagnetic energy at the interface between two different media, such as air and quartz.

**Regression:** Another name for the process of generating a least-squares fit in an equation to a set of  $X$  (spectral signal) and  $Y$  (reference analyte concentration) data. Multivariate regression is performed on multiple  $X$  independent variables on the  $Y$  dependent variable. The types of regression most common to spectroscopy calibration work include multiple linear regression (MLR), principal components regression (PCR), and partial least squares regression (PLSR).

**Regression coefficient:** The regression coefficient is denoted in a general form by the following equation:

$$(Y = B_0 + B_1X_1 + \dots + B_nX_n) \quad [10]$$

Where the regression coefficients are the variables labeled  $B_i$ . These coefficients are the parameters that are calculated by regression analysis, and are the necessary calibration constants that determine the sensitivity of an instrument to the optical readings at the various



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wavelengths included in the calibration. See also *least squares fit*.

**Relative standard deviation (RSD):** The standard deviation of a set of data divided by the mean value of that set of data. May also be referred to as the coefficient of variation. It is reported directly as a ratio value or as a percentage.

**Repack:** Removing a sample from the measuring cup, and replacing it with a different aliquot of the same sample. Measurements made on several repacks of a sample allow an estimate to be made of the contribution of the sampling error to the total measurement error.

**Reread:** The process of taking multiple readings on a single pack of a sample. Multiple rereads of a sample allow an estimate to be made of the contribution of electronic noise to the total error. The replicate measurements are made without changing or moving the sample holder or sample.

**Resonance Raman spectroscopy (RRS):** In this approach, the laser excitation wavelength is matched to the specific electronic transition associated with a molecular vibration mode of interest within a sample. This technique provides a method for “isolation” of specific molecular vibrational modes for the Raman structural studies of particular vibrational bands of large molecules.

**Residual:** The statistical nomenclature for the difference between the value reported by the reference laboratory for a sample and the value as determined by the calibration equation being used for the spectroscopic or analytical method. This is the difference for predicted minus “true.”

**Reststrahlen bands (or effect):** This is the cause of “inverted” peaks observed when measuring infrared reflection. When the frequency band of incident electromagnetic radiation normally strikes a material and is strongly or completely reflected from the surface of the material because of the refractive index of the material, the phenomenon is referred to as the reststrahlen effect (German: meaning “residual rays”). The spectral regions exhibiting the strong reflection

are termed the reststrahlen bands. Note that the refractive index ( $n$ ) of a material describes how light absorbs or reflects from a material and is defined as  $n = c/v$ , where  $c$  is the velocity of light in a vacuum and  $v$  is the velocity of light in the medium; this ratio is a dimensionless number.

**Retardation:** Retardation is defined as the optical path difference between the two beams in the interferometer. Higher retardation gives better resolution, increases the number of data points, and results in larger spectral data files.

**R<sup>2</sup>:** The square of the *correlation coefficient*. Also called the *coefficient of determination*, which represents the total explained variance from a fitted regression in terms of 0 to 1, or 0% to 100%.

## S

**Sample:** A uniform lot of material that is to be analyzed. In spectroscopic quantitative analysis, samples are divided into two categories: *calibration* samples and *prediction* samples. Calibration samples are split into at least two aliquots, one of which is sent to a reference laboratory and the other read by the instrument; these are then combined into a calibration set for determining the regression coefficients or calibration model. Prediction samples are any samples not included in the calibration set. They may also be sent to a reference laboratory for analysis if the purpose is to check the accuracy of the calibration.

**Sample ID:** An identifier that can be entered into the appropriate field of a data record to label the sample whose data is in the same record. May be alphanumeric.

**Sample number:** A second identifier that can be included in a data record. Sometimes a sample number is automatically provided and updated by the computer if the operator fails to enter a sample number. A sample number must be numeric.

**Scale:** A mathematical method or software tool used to perform arithmetic operations on a spectrum, such as multiplication, addition, subtraction, or division using a scalar (constant) or vector operation.

**Scan:** The process of measuring a spectrum at uniform wavelength or wavenumber intervals throughout the spectral range of interest. The interval should be small compared with the width of the absorbance bands of the sample in order to produce a quasi-continuous approximation of the sample's absorbance band characteristics. It consists of measuring the transmittance, reflectance, absorbance, scattering, and so forth with respect to wavelength or wavenumber for any material.

**Scanning:** The process whereby the optical data signal is measured and recorded with respect to the wavelength or wavenumber range of the spectrometer. The wavelength range is measured in order, usually from lowest to highest wavelength for ultraviolet, visible, and near-infrared measurements. For infrared and Raman instruments the wavenumber range of the spectra is viewed from larger to smaller wavenumber—that is, highest to lowest frequency—respectively. For a monochromator this process occurs when a grating is precisely rotated about its axis or projected onto a single or array detector. For FT-IR and FT-Raman instruments an interferometer is sequenced for scanning an interferogram and converting the signals to a spectrum. Some microelectromechanical systems (MEMS) devices move a micromirror reflecting the beam from a fixed grating onto the detector to produce a spectrum.

**Search strategy:** The sequence of steps followed to find the set of wavelengths producing the most accurate calibration equation for a multiwavelength calibration model. It is also a term used for searching or comparing a test spectrum against a library of reference spectra to find a qualitative match for identification.

**Sensitivity:** See *limit of detection*.

**Signal:** The output of the detector resulting from its response to light emerging from the sample holder or reference cell. It consists of an analog signal converted to a digital signal and then converted to units such as counts, reflec-

tance, transmittance, or absorbance, depending upon the measurement geometry and precise computational methods.

**Signal-to-noise ratio (S/N):** The ratio of the value of the signal (intelligence, message, or effect to be transmitted) to that of the noise (random variation or disturbance of the signal). A measure of performance for a measurable characteristic of a device which includes a level of disturbance to the desired characteristic. In spectrometers it is often measured by taking the amplitude of the signal for 100% transmittance or 100% reflectance and dividing it by the root mean square (RMS) deviation of the repetitive measurements of that sample. The numerical ratio of the total signal  $I/I_0$  to the noise of the instrument as RMS deviation of repeated signal measurements. The RMS is the standard deviation of the photometric measurements at a set of wavenumbers or wavelengths.

**Single-sided interferogram:** An interferogram has a “center-burst,” also referred to as the zero-path-difference (ZPD) location. When the path of the fixed and moving mirrors are identical in the interferometer, the interferogram is at maximum interference. The centerburst may be placed anywhere along the recorded data for the interferogram. When it is placed near the start of the interferogram it is termed a single-sided interferogram (also known as a symmetric interferogram).

**Skew:** A term used to refer to a systematic variation of instrument readings when they are compared to the reference laboratory, to the extent that samples near the low end of the range read low and samples near the high end of the range read high, or vice versa. It is also a term for slope change in  $X$  and  $Y$  comparative data.

**Slit:** An aperture, usually rectangular in shape with a large length-to-width ratio, and a fixed or adjustable shape through which radiation enters or leaves a monochromator-based instrument. The slit aperture is usually quite small relative to the light source. For monochromators, there is an entrance and exit slit for each

grating; for interferometers there is a J-stop aperture, which in effect acts as a slit adjusting the effective resolution.

**Slit width:** The size of opening of slit through which light passes. The slit width depends on the wavelength range, separation ability of the wavelength selector (for example, grating), and desired isolation of the specific wavelength (that is, line width). Slits are either fixed or automatically programmed for width variation.

**Slope:** Another term for skew; the use of the term “slope” implies that the amount of skew is known.

**Smoothing:** Smoothing may be applied to spectroscopic data for a several purposes—for example, to improve the quality of the spectral appearance, to remove apparent noise, to decrease spectral resolution to match bandwidth between two spectra measured at two resolutions, and to remove apparent random and structured variation in signals. Smoothing allows enhanced manual viewing and multivariate processing by eliminating spectral variation caused by random measurement noise. The most common applications of smoothing within spectroscopy include boxcar smoothing, Fourier-domain (fast Fourier transform [FFT]) smoothing, and Savitzky-Golay smoothing.

**Solvent:** Liquid used to dissolve the sample analyzed. Commonly water or methanol of high purity. Usually designated as specially purified for ultraviolet work—for example, “Spectrophotometer Quality,” “Spectro-Quality,” or “Spectro-Grade.”

**Solvent cutoff:** The wavelength at which the solvent absorbs a significant portion of the light, causing a loss of signal and inability to perform an analysis in that spectral region. In other words, the solvent becomes opaque to the wavelengths being used acting as a cutoff filter. This phenomenon is common in ultraviolet spectroscopy, and is much more rare in the visible and higher wavelength spectral regions.

**Source:** An electromagnetic energy generating supply to make the measurement for an

optical spectrometer system. The source is the origin of the light used in the spectrometer; also known as the “lamp” (UV-Vis-NIR), or Globar (IR), or laser (Raman). The source may also be an enclosed incandescent wire for visible light, a deuterium gas discharge lamp for ultraviolet spectroscopy, or an excitation laser for Raman spectrometers. Note that multiple types and wavelengths of lasers are used for Raman measurements.

**Spatially offset Raman spectroscopy**

**(SORS):** For this measurement technique, Raman scattering is measured at a surface point and also at a point deeper into the sample. The two resulting spectra are scaled and subtracted to yield a difference spectrum representing a depth-profiling Raman spectrum. Multiple offset spectra may be combined with multivariate analysis to determine the spectrum of various depths in the sample.

**Spectral energy units:** Spectral energy for molecular and electronic spectroscopy is described in terms of units of wavelength—for example, micrometers ( $\mu\text{m}$ ) as  $10^{-6}$  m, or nanometers (nm) as  $10^{-9}$  m, or angstroms ( $\text{\AA}$ ) as  $10^{-10}$  m. Energy is also expressed as frequency (cycles per second or  $\text{s}^{-1}$ ) termed hertz (Hz), as wavenumbers ( $\text{cm}^{-1}$ ), and as electron volts (eV).

**Spectral matching:** One of several procedures of identifying alike spectral patterns for the purpose of sample identification, classification, or subgrouping. The matching is performed using a spectral library of various materials combined with computer algorithms. To match an unknown spectrum found in the library, the computer compares each known spectrum to the unknown spectra of the library to locate a probable match.

**Spectral reconstruction:** A mathematical technique for recreating the spectrum of any of the constituents in a mixture provided the concentration of the constituent is known for several different samples. The technique works well, and reconstructed spectra of pure compounds in mixtures have been shown to com-

pare favorably with spectra obtained directly from the pure compound as long as two conditions are met: 1) the constituent concentration is expressed as weight percent (this is mathematically necessary, because the algorithm depends on the fact that all constituents add up to 100% for proper operation); and 2) the constituents are uncorrelated. A constituent that is correlated with the one whose spectrum is being reconstructed will have its absorbance bands appear within the reconstructed spectrum.

**Spectrophotometer:** A device used to measure and record the spectrum of a material at uniform, usually closely spaced, wavelength or wavenumber intervals. This type of instrument is sometimes referred to as a spectrometer, although correct terminology is spectrophotometer. It is specifically designed to measure the ratio of the sample signal ( $I$ ) versus the reference signal ( $I_0$ ) as the ratio  $I/I_0$ .

**Spectrum:** An abbreviated form of “electromagnetic spectrum.” It is a series of wavelengths of radiation, belonging to a specific portion of the electromagnetic continuum—for example, the visible spectrum, where the “colors” are viewed in increasing wavelength. For the visible portion of the continuum, the colors in order of increasing energy frequency are red, orange, yellow, green, blue, indigo, and violet. For other spectroscopy it is the absorbance (computed from transmittance or reflectance) as a response of the instrument to a sample and reference measurement ( $I/I_0$ ) with respect to wavelength or wavenumber. For a Raman shift spectrum, the Stokes scattering of a sample measurement is recorded with respect to wavenumber position.

**Spontaneous Raman spectroscopy (SRS):** SRS is a revised name for the phenomenon of Raman spectroscopy using continuous wave (CW) laser excitation. It is classic Raman spectroscopy, where approximately 0.001% of incident laser energy is translated into Raman signal intensity.

**Standard deviation:** A measure of the spread of a set of numbers that are the same units as the

numbers themselves. The standard deviation of a number of measurements is computed for any variable set of data points,  $X_i$  from the following formula, where  $n$  is the number of data points:

$$s_i = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X}_i)^2}{n-1}} \quad [11]$$

### Standard error of cross validation

**(SECV):** A measure of the standard error of estimate determined by using a portion of the calibration set to generate the calibration and a portion of samples to validate the calibration. This operation is generally an automated process in which some samples are “left out” of the calibration to use in a computation of prediction error. SECV is typically a low estimate of the true prediction error (standard error of prediction) since in this procedure most of the samples in the set used for calibration and validation are quite similar.

**Standard error of estimate (SEE):** A standard deviation measure of the difference between the reference laboratory values for a set of samples and the values determined by the instrument, in which the calibration resulting from a regression equation is applied to the very samples used to derive that equation.

**Standard error of prediction (SEP):** A standard deviation measure of the accuracy of an instrumental measurement compared to a reference laboratory using a set of samples that were not included in the calibration.

**Standard normal variate (SNV):** The SNV data reprocessing method partially compensates for some spectral slope and particle size differences within a series of spectra measured using diffuse reflection. The algorithm is applied individually to each spectrum for both calibration and prediction spectra. This processing step is applied to each data point for each spectrum using the mean and standard deviation of the spectrum in absorbance space (units). The mean absorbance difference for each data point

is compared to the mean absorbance of the spectrum ratioed to the standard deviation of the absorbance for the spectrum. The computation formula is as follows:

$$a_{ij}(SNV) = \frac{(a_{ij} - \bar{a}_i)}{\sqrt{\frac{\sum_{j=1}^n (a_{ij} - \bar{a}_i)^2}{n-1}}} \quad [12]$$

Where  $a_{ij}(SNV)$  is the computed standard normal variate for the data point (element)  $a_{ij}$  and  $\bar{a}_i$  is the mean of the spectrum  $i$ , and  $n$  is the number of data points or elements in the spectrum.

**Standard reference material (SRM):**

These registered trademark materials are provided by the National Institute of Standards and Technology (NIST), which is a non-regulatory agency of the United States Department of Commerce. Standard reference materials are carefully measured and are used for calibration of spectrophotometers and other analytical instruments as a means of near first principles traceable calibration.

**Standardization:** Direct standardization (DS) and piecewise direct standardization (PDS) are the general and most common methods used for instrument standardization. The DS and PDS approaches are also often combined with small adjustments in bias or slope of the predicted values to compensate for small differences not accounted for by using standardization algorithms. The algorithm in effect introduces an offset (bias) and general slope change of the spectra to more closely map one instrument to another.

**Step-up search:** One strategy in identifying the most useful wavelengths for multiple linear regression wavelength calibration modeling searches. See also *combination search*.

**Stimulated Raman:** A dynamic technique whereby two different-wavelength laser pulses are applied to a sample simultaneously using polarization (that is, parallel or perpendicular).

When the difference frequency of the excitation lasers matches a particular molecular vibrational frequency of the sample, amplification of the Raman signal occurs. The polarization of the laser pulses effectively determines the molecular alignment and orientation properties of the sample.

**Stimulated Raman spectroscopy (SRS):**

By applying a relatively high energy pulse, as contrasted to traditional continuous wave (CW) lasers, pulsed lasers have an enhanced effect on the Raman scattering signal by as much as 40–50% of the excitation laser energy. The overall Raman signal is enhanced by  $10^4$  over traditional spontaneous Raman spectroscopy, with the resultant significant increase in effective signal-to-noise ratio for the produced spectra.

**Stokes shift:** See *Raman effect*.

**Stray light :** Any radiation reaching the detector that is not remitted or transmitted from, or through, the sample at the selected measurement wavelength.

**Striking a sample:** Leveling off the top of a powdered or ground sample in an open cup to present a constant surface geometry and sample thickness to the instrument.

**Structured query language (SQL) database:**

SQL database is a specialized computer programming language designed for managing data held in a relational database. It allows the use of a single command for access to data records and allows a data record to be accessed without indexing.

**Sum of squares:** Literally just that; the sum of squares of a set of numbers representing some quantity in a mathematical equation. The concept is useful because it can be shown that some sums of squares are the combination of other sums of squares. For example, in a regression calculation:

$$(\text{total sum of squares}) = (\text{sum of squares due to regression}) + (\text{sum of squares due to error})$$


[13]

**Surface-enhanced Raman spectroscopy (SERS):** In SERS, a sample is placed within a gold or silver colloid, and the electric field for the molecules within the sample increases and causes the Raman scattering signal to be enhanced by a factor approximating  $10^{10}$ .

**Surface-enhanced resonance Raman spectroscopy (SERRS):** This Raman technique combines surface-enhanced Raman spectroscopy and resonance Raman spectroscopy; the Raman excitation laser is matched to the maximum absorbance of the molecular vibration of interest. This technique enhances the signal of a specific vibration under study.

**Surface-enhanced spatially offset Raman spectroscopy (SESORS):** This technique uses imaging techniques to collect multiple surface measurements combining multiplexed surface-enhanced Raman scattering signals and spatially offset Raman spectroscopy (SORS) as a noninvasive measurement technique for depth profiling multiple layers of samples.

**Surface plasmon polariton enhanced Raman spectroscopy (SPPERS):** A small cylindrical lens is used for near-field excitation of tiny samples or films deposited on the lens surface. For this technique, measurement areas as small as  $100 \mu\text{m}^2$  in size with the thickness of a molecular monolayer are possible. The technique uses special excitation and collection optics to enable an enhanced small spatial signal.

**T**   
**Teaching set:** Another name for a *calibration set*.

**Terahertz:** See *far infrared*. This term is also represented by the region of  $1.2 \times 10^{13}$  to  $3.0 \times 10^{11}$  Hz ( $\text{s}^{-1}$ ).

**Tilting filter:** An interference filter, when tilted, produces wavelengths different from those produced when the light is normal or perpendicular to its surface. Controlled tilting can produce a known band of wavelengths. This approach is

the basis of both near-infrared and infrared instrumentation intermediate between less-expensive fixed interference filters and more expensive grating or interferometer based instruments.

**Tip-enhanced Raman spectroscopy (TERS):** TERS combines Raman spectroscopy with scanning probe microscopy, such as atomic force microscopy (AFM). AFM uses scanning probe tips as small as 10–20 nm, and an enhanced Raman signal is collected simultaneously with the AFM profile of a sample surface. The Raman signal is combined with the AFM topography to create a detailed three-dimensional image of the nanoscale spatially related composition of a sample.

**Transflectance:** The process of measuring a liquid in which an optical beam passes through the sample, reflects off a highly reflective backing, and then passes through the liquid again before detection. This approach allows the absorbance of a clear transmitting liquid to be measured in a reflectance mode measurement geometry. It also allows the source and the detector to remain on the same side of the sample (as in measuring the reflectance of solids).

**Transform:** A mathematical procedure for converting a function of one variable into a unique function of another variable. Some well-known transforms are the Laplace and Fourier transforms.

**Transmission:** Transmission refers to the act or phenomenon of transmitting energy, which is the phenomenon of electromagnetic energy passing through a material from one refractive index to another, generally air to glass or quartz.

**Transmittance:** Transmittance ( $T$ ) refers to the fraction of electromagnetic energy that passes through a sample ( $I$ ), relative to the total amount quantity of energy that strikes the sample ( $I_0$ ), so it is represented by the ratio of  $T = I/I_0$ . The  $T$  scale may be expressed as 0%–100% or 0–1.0. In transmittance measurements, dry air is used as the typical reference.

**Truncate:** A technique of selecting only a portion of a spectrum with which to perform calibration or mathematical processing.

**t-test:** Also known as Student's *t*-test. The ratio of a difference between a single measurement or estimate and the parameter being estimated to the standard error of that parameter. It is used to determine whether a specific measurement variation is random or determinate when its *t*-test is compared to a *t*-distribution value. A statistical quantity that in the case of regression analysis allows the determination of whether a particular wavelength and coefficient are significant to the model.

**Turret-mounted filters:** See *fixed filter*.

**Two-dimensional (2D) correlation spectroscopy:** The combination of two dimensions of spectra to be processed into a 2D correlation spectrum. These spectra have an increased rank of information content and are most often determined by a change in mechanical strain or temperature between one spectrum and the second spectrum used for the two dimensions. It may also be formed using two spectra from different spectral ranges, such as a near-infrared spectrum combined with an infrared spectrum.

## U

**Ultraviolet (UV) spectroscopy:** Spectroscopy using the portion of the electromagnetic spectrum generally from 190 to 400 nm, and most often from 190 nm to 360 nm for the majority of ultraviolet laboratory measurements. The types of electrons that can be excited by UV-Vis light are few in number: nonbonding electrons, electrons in single bonds, and electrons involved in double bonds.

**Unit conversions for photon energy:**

The conversions between wavelength, wavenumbers, frequency and photon energy are as follows:

Wavenumbers (cm<sup>-1</sup>) to wavelength (in nanometers):

$$\lambda_{nm} = \frac{10^7}{\bar{\nu}_{cm^{-1}}} \quad (14)$$

Wavelength (in nanometers) to wavenumbers (cm<sup>-1</sup>):

$$\bar{\nu}_{cm^{-1}} = \frac{10^7}{\lambda_{nm}} \quad (15)$$

Wavelength (in nanometers) to frequency (in Hz):

$$\nu_{cm^{-1}} = \frac{2.9979 \times 10^{17} \text{ nm} \cdot \text{sec}^{-1}}{\lambda_{nm}} \quad (16)$$

Wavelength (in nanometers) to photon energy (in eV):

$$E_{P_{eV}} = \frac{1240}{\lambda_{nm}} \quad (17)$$

## V

**Variable:** Any quantity in a mathematical equation that is subject to change. In spectroscopic calibration involving regression, two types of variables are of interest: the independent variables (*X*), which consist of the optical readings and any auxiliary or indicator variables; and the dependent variables (*Y*), which consist of the constituent or analyte quantity information.

**Variance:** The square of the standard deviation. An important concept in statistics, because, like sum of squares, the total variance can be shown to be composed of the sum of the individual variance (or error) contributions. Arithmetic operations such as addition and subtraction may be performed on variances.

**Visible spectroscopy:** Spectroscopic measurement using that portion of the electromagnetic spectrum detectable by human eyes—that is, the portion of the spectrum from 360 to 780 nm. This portion is sometimes referred to as 350 nm to 770 nm spectral region. This region is used for color measurements. Colors are produced by electrons in a material moving from one orbital

transition to another orbital around the atoms within the molecules of the colored substance.

## W

**Wavelength:** Electromagnetic energy is transmitted in the form of a sinusoidal wave; the wavelength is the physical distance covered by one cycle of this wave. It is defined as the distance from one crest of an electromagnetic wave to the same position on the subsequent wave. Peak-to-peak distance is generally measured in nanometers or wavenumbers for use in molecular spectroscopy.

**Wavenumber:** The number proportional to the inverse of the wavelength in a harmonic wave; the number of waves per unit length (centimeter), or  $\text{cm}^{-1}$ . For infrared spectroscopy, the wavenumber represents the number of waves (cycles) occurring per centimeter. It is equivalent to  $1 \times 10^7/\text{wavelength}$  in nanometers; for example, 2500 nm is equivalent to  $4000 \text{ cm}^{-1}$ . For Raman spectroscopy, the wavenumber represents the number of waves (cycles) occurring per centimeter for the Raman shift corresponding to the molecular vibrational frequency for measured materials. It is also equivalent to  $1 \times 10^7/\text{wavelength}$  in nanometers. Note the relationship of wavenumber photon energy and wavelength from the following equations:

$$\bar{\nu} = \frac{E_p}{hc} \Rightarrow \frac{1}{\lambda} = \frac{E_p}{hc} \Rightarrow \lambda = \frac{hc}{E_p} \quad [18]$$

Where  $\bar{\nu}$  is the wavenumber units as  $\text{cm}^{-1}$  (that is, the number of waves per centimeter);  $h$  = Planck's constant (or  $6.6256 \times 10^{-27}$  erg-s; and  $c$  is the velocity of light in a vacuum (or  $2.9979 \times 10^{10}$  cm/s);  $\lambda$  (Greek: lambda) is the wavelength in units of cm; and  $E_p$  is the energy of a photon of light, where  $E_p = hc\bar{\nu}$ .

**Wavenumber correction:** The process of aligning the X-axis or wavenumber axis for a Raman spectrometer. It is accomplished by measuring a standard reference material with carefully known wavelength or wavenumber peak positions, and making adjustments to

align the instrument to these reference standards. Wavenumber correction is essential for high quality infrared and Raman spectra.

**Window:** A transparent material with plane parallel surfaces used to admit light into an optical system and exclude contaminants such as dirt and moisture. Windows are used within an instrument and for holding samples. For UV work, the window material is generally low-OH quartz ( $\text{SiO}_2$ ), and, for visible spectroscopy, some polymers are used, such as polystyrene (PS), or polymethylmethacrylate (PMMA). Generally windows for near-infrared or Raman spectroscopy are low-scattering quartz ( $\text{SiO}_2$ ); and for infrared a variety of salts are used, such as sodium chloride (NaCl), potassium bromide (KBr), calcium fluoride ( $\text{CaF}_2$ ), magnesium fluoride ( $\text{MgF}_2$ ), barium fluoride ( $\text{BaF}_2$ ), cadmium telluride (CdTe), silver chloride (AgCl), germanium (Ge), or zinc selenide (ZnSe), zinc sulfide (ZnS), AMTIR (GeAsSe), and thallium bromide-iodide (KRS-5).

**Wood's anomalies:** A variety of surface plasmon polariton (phonon or light interaction effects) where a diffraction grating will change its efficiency relative to specific angles of incidence and the frequency (wavelength) of light interacting with the grating. A diffraction grating will dramatically change (generally decrease) the amount of energy (photon flux) dispersed from its surface, based upon the interaction of p-polarized light from the spectrometer source with the physical groove period of the grating surface (the groove or grating period of a grating is equivalent to  $1/\text{groove density}$ ). The decrease in energy dispersed from the grating is present only for p-polarized light at specific angles of incidence; noting that for p-polarized light the magnetic field of the energy is parallel to the grooves on the grating surface. Efficiency curves may be plotted for any wavelength of light incident to a diffraction grating such that the angle of incidence (x-axis) is plotted against the diffracted light flux (as percent efficiency) to yield a graphic showing the Wood's anomaly region(s).

**XYZ**

**x-axis**: The Cartesian coordinate system horizontal reference axis. In spectroscopic instruments it refers to the wavelength or wavenumber axis.

**x-shift**: When spectra are measured from two or more instruments, there may be differences between the x-axis of the spectra when trying to compare them. In this case, the wavelength or wavenumber scale is shifted or different between instruments. An x-axis correction shift will move one spectrum to better line up with another spectrum along the x-axis for improvements in accuracy for quantitative or qualitative analysis.

**x-unit conversion**: Conversion of one x-axis spectral data type to another, for example, wavenumbers ( $\text{cm}^{-1}$ ); wavelength (nm) or  $10^{-9}$  m; wavelength ( $\mu\text{m}$ ) or  $10^{-6}$  m, energy (eV), or frequency (Hz) as  $\text{s}^{-1}$ .

**y-axis**: The Cartesian coordinate system vertical reference axis. In spectroscopic measurements it refers to the intensity, reflectance, transmittance, scattering, amplitude, or absorbance axis.

**y-unit conversion**: Conversion of one y-axis spectral data type to another—for example, absorbance, transmittance, Kubelka-Munk,  $\log(1/T)$ ,  $\log(1/R)$ , reflectance, attenuated total reflectance (ATR) correction, or some other amplitude function.

**Zap tool**: This software feature allows the selection of a specific spectral region as delineated by the x-axis for manipulation of that specific region. A certain zapped region is changed, while the remaining spectrum remains unaltered.

**Zero filling**: Is a process of adding a number of data points consisting of amplitude values located between corresponding interferogram data points to increase the number of data points. This action is completed before applying the fast Fourier transform (FFT) to the interferogram to produce a spectrum. Zero-filling adds interpolated points that lie between the real interferogram data points. The resultant data

are smoother in appearance, and more suitable for application of the FFT algorithm (proper number of data points). The appearance and photometric accuracy of the spectrum is improved, but there is no improvement in the line width resolution of the spectrum.

**z-dimension**: See *cuvette*.

**Zero order pulse (ZOP)**: The mirror reflection position from a grating system indicating precise positioning of the grating for calibration of a monochromator encoder alignment.

**Zero path difference (ZPD)**: An interferogram has a centerburst, also referred to as the zero-path-difference location. When the path of the fixed and moving mirror are identical within the interferometer, the interferogram is at maximum interference; there is zero path difference between the light traveling through the two channels of the Michelson interferometer.

### References and Further Reading:

- (1) J. Workman, *The Concise Handbook of Analytical Spectroscopy* (World Scientific Publishing-Imperial College Press, New Jersey and Singapore, 2016). ISBN-13: 978-9814508056.
- (2) J.M. Chalmers and P.R. Griffiths, *Handbook of Vibrational Spectroscopy* (John Wiley & Sons, New York, New York, 2002). ISBN: 978-0-471-98847-2
- (3) ASTM (American Society for Testing and Materials) ASTM Volume 03.06, "Molecular Spectroscopy and Separation Science; Surface Analysis" (ASTM International, West Conshohocken, Pennsylvania, 2017).
- (4) N.B. Colthup, L.H. Daly, and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press/Elsevier, Boston, Massachusetts, 3rd Ed., 1990). ISBN: 9780121825546

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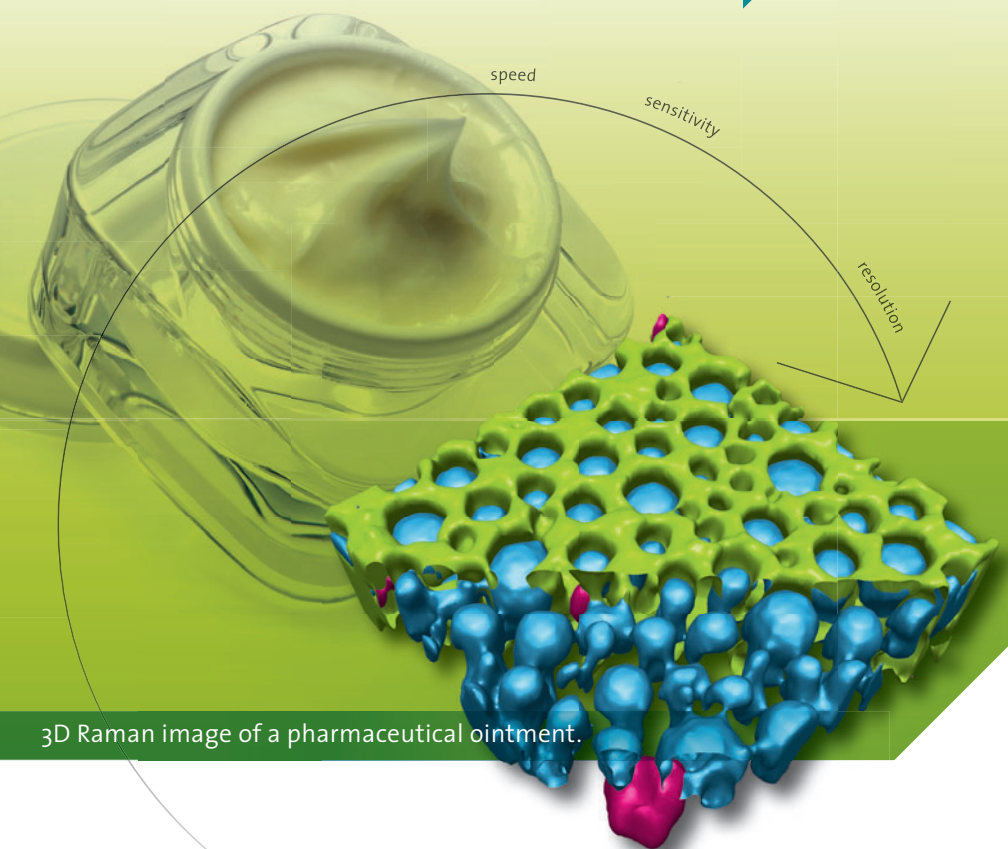


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