

Interpretive spectroscopy for near infrared

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Why interpretive spectroscopy?

To begin this discussion a clear definition of two terms is required, first a *spectrum* is the convolution of the measuring instrument function with the unique optical and chemical characteristics of the sample being measured. Second, the *reference values* are those chemical or physical parameters *to be predicted using spectroscopic measurements*; a spectrum may, or may not, contain information related to the sample chemistry measured using a reference method. Interpretive spectroscopy provides a scientific basis for the establishment of a known cause and effect relationship between instrument response (spectral) and reference (analyte) data. Probability and statistics cannot be used as a direct metric for the determination of cause-effect. Interpretive spectroscopy is a key intellectual process for achieving an analytical understanding of near infrared measurements.

Introduction to near infrared spectroscopy

The discovery of the infrared region in 1800 is credited to William F. Hershel's familiar work, "Experiments on the Refrangibility of the Invisible Rays of the Sun", read April 24, 1800 at the Royal Society, *Phil. Transact. Roy. Soc.* **90**, 284–292.

O.W. Wheeler¹ describes the near infrared region as extending "from about 2 μm into the visible at about 0.7 μm " in a general discussion article (with 11 references). He also noted that "the term "near infrared" formerly was used to denote the infrared spectrum to 23 μm , and to distinguish this region from that of the far infrared above 23 μm ". Wheeler credits Rawlins and Taylor² with this early use of the term near infrared. Using a variety of instrumentation, the author identifies near infrared bands (in micrometres) in tabular form as follows. For C–H stretch, the fundamental occurs at 3.5, the 1st overtone at 1.8, 2nd overtone at 1.2, 3rd overtone at 0.85, and 4th overtone at 0.7 μm . The author identifies band positions for both O–H and N–H stretch as occurring near 2.8 for the fundamental, 1.4 for the 1st overtone, 0.95 for the 2nd overtone and 0.7 μm for the 3rd overtone. R.F. Goddu and D.A. Delker³ provide two detailed tables showing (i) the spectra–structure correlations and average molar absorptivity for a number of functional groups for the NIR region (1.0 to 3.1 μm), and (ii) maximum recommended pathlengths for twelve solvents (useful for NIR spectroscopy) over the wavelength region 1.0 to 3.1 μm . The authors cite two references in this helpful article.

Early reviews

Professor J.W. Ellis⁴ has reviewed work below 3 μm for absorption of organic liquids. The review cites 44 separate works related to studies made prior to June 1929. In 1929, Professor Joseph W. Ellis wrote, "The region of the spectrum below 3 μm , although representing a relatively

small portion of the total infrared spectrum, is nevertheless quite significant in the study and interpretation of the absorption spectra of molecules. In particular, the absorption spectra of organic liquid molecules shows numerous bands in this region.” He goes on to cite work by Coblentz and Raman related to the observations of bands in the infrared region due to infrared absorptions and the Raman effect. Ellis goes on to refer to earlier work by Puccianti in 1900 with respect to the presence of specific near infrared bands associated with, “molecules [having] a hydrogen atom combined with a carbon atom.” Ellis reports that bands relating to “the carbon–hydrogen linkage” were observed at 2.3–2.2, 1.7, 1.4, 1.2, 1.0 and 0.9 μm . With this work, and the work of other investigators, the modern science of near infrared spectroscopy was underway.

W. Kaye⁵ provides a summary review of the work in near infrared spectroscopy from the late 1920s to April 1954. The author draws information from 106 references for this review. The author refers to the term “hydrogenic” stretching vibrations as CH, NH and OH. Work involving measurements in the region of 0.7 to 3.5 μm is reviewed. The author presents a Colthup-type chart of characteristic NIR bands, and the accompanying references. R.F. Goddu⁶ provides an extensive review of near infrared spectrophotometry prior to 1960. The author cites 110 literature sources of information for this review. K.B. Whetsel⁷ reviews the significant work in near infrared spectrophotometry prior to 1968. The review contains 336 references covering aspects of theory, instrumentation and sampling techniques. Stark *et al.*⁸ review work related to near infrared (NIR) analysis prior to 1986. The review, containing 300 references, describes the history, instrumentation, computations related to qualitative and quantitative analysis, and applications for NIR analysis. The authors cite the classical reviews of W. Kaye, O. Wheeler, R. Goddu, R. Goddu and D. Delker, K. Whetsel and C. Tossi and A. Pinto, briefly describing each work.

SW–NIR as a separate topic

Schrieve *et al.*⁹ discuss applications for the short-wave near infrared (SW–NIR) region, referring to synonyms such as “the far-visible”, the “near, near infrared”, or the “Herschel-infrared” to describe the range of approximately 700–1100 nm of the EMS (electromagnetic spectrum). The authors cite the increased interest of this spectral region to spectroscopists, particularly those involved with implementing process near infrared measurements.

Spectroscopy in the near infrared region

Since 1912, research investigations into the molecular structures of organic compounds using infrared spectroscopy has grown. This early work by W.W. Coblentz reported on the IR absorption of water. Coblentz used the spectral region from 1 to 8 μm . The new decade of the 1960s brought about a prolific series of papers related to “direct determination,” and the measurement of light transmittance and reflectance properties of intact biological materials.^{10–22} A summary of the most notable review papers describing the history of NIR interpretive spectroscopy would include the References 8 and 23–34.

Flour and grain analysis

In 1973, P. Williams reported the use of a commercial NIR grain analyzer for analyses of cereal products following the pioneer work of Norris and others. Later, Williams and Karl Norris would edit a comprehensive text³⁵ on the subject of NIR analysis for commercially important biological materials. The book includes an exhaustive set of references (986) covering the early aspects of NIR in food and agricultural products analysis. Additional key references are given in References 36–40. B.G. Osborne *et al.* presented a detailed description of research into NIR analysis of wheat flour. He reported measurements for protein, moisture, ash, alpha-amylase, starch damage, water absorption, grain texture, particle size, loaf score and pentosans, in wheat flour used in the baking

industry at the 65th AACC meeting, Chicago, Illinois, USA, in September 1980. The information in this presentation was later included in a textbook written by B. Osborne and T. Fearn.⁴¹ References 42 and 43 describe the early work, most of which used multiple linear regression to identify key calibration wavelengths relating NIR instrument response to reference analytical data. P. Williams and co-workers⁴⁴ described the work in flour milling using near infrared spectroscopy for the determination of moisture in cereals and cereal grains. The authors describe the uses of NIR for protein and moisture analysis in hard and soft wheat flours. Additional references describing wavelength selection and methodology for flour applications are presented in References 45–47.

Forage analysis

Forage analysis using NIR measurement has been a major application of the technique largely due to the work of J.S. Shenk, M. Westerhaus, W. Barton, G. Marten, N. Martin and a host of others who improved upon the technique and worked toward its widespread use and acceptance among scientists as a valid analytical technique. One could not mention NIR and forage analysis without listing the primary reference source in the field since August 1985. The handbook edited by G.C. Marten, then of the University of Minnesota; J.S. Shenk of The Pennsylvania State University, and F.E. Barton of the Richard Russel Research Center, USDA; has become the most used handbook for NIR forage analysis.⁴⁸

A second comprehensive information source for NIR analysis of forages is a book chapter containing 106 references by Shenk, Workman and Westerhaus.⁴⁹

Other key initial references for this application are found in References 50–61.

Hydrocarbon analysis

The text below points to only a few of the myriad references available that give key or important wavelengths for the designation of hydrocarbon groups, as well as outlines references giving the general procedures that are universally followed for multivariate calibration of near infrared instruments. Infrared spectroscopy, including the narrower term near infrared spectroscopy, does not directly measure hydrocarbon classes such as olefins or naphthenes, as such, but rather it measures functional group absorptions such as methyl, methylene, methine and aromatic stretching and deformation vibrations. The ratios of these various absorptions, when correlated (using a variety of well described multivariate calibration techniques) to known physical or compositional parameters, for a learning or teaching set, provides a correlation estimate of the hydrocarbon class composition from various unknown complex mixtures. References 62–84 describe classic and multivariate spectroscopic measurements of hydrocarbons.

Interpretive NIR spectroscopy

Molecules that absorb NIR energy vibrate in two fundamental modes; *stretching* and *bending*. Stretching is defined as a continuous change in the interatomic distance along the axis between two atoms, and bending is defined as a change in the bond angle between two atoms. Near infrared (0.78 to 2.5 μm) spectral features arise from the molecular absorptions of the overtones (0.78 to 1.8 μm) and combination (1.8 to 2.5 μm) bands from fundamental vibrational bands located at frequencies within the mid-infrared region. For fundamental vibrations, a series of overtones exist with decreasing intensity as the transition (overtone) number increases. Combination bands arise as the summation of fundamental bands, their intensity decreasing with an increase in the summation frequency. Most near infrared absorptions result from the harmonics and overtones of X–H fundamental stretching and bending vibrational modes. Other important functional groups,

relative to near infrared spectroscopy, include hydrogen bonding, carbonyl carbon to oxygen stretch, carbon to nitrogen stretch, carbon to carbon stretch and metal halides.

Precise band assignments are difficult in the near infrared region due to the fact that a single band may be attributable to several possible combinations of fundamental and overtone vibrations, all severely overlapped. The influence of hydrogen bonding results in band shifts to lower frequencies (higher wavelengths); a decrease in hydrogen bonding due to dilution and higher temperatures results in band shifts to higher frequencies (lower wavelengths). Band shifts of the magnitude of 10 to 100 cm^{-1} , corresponding to a range from a few nm to 50 nm, may be observed. The substantial effect of hydrogen bonding should be kept in mind when composing calibration sample sets and experimental designs using near infrared measurements.

Near infrared spectra contain information relating to differences in bond strengths, chemical species, electronegativity and hydrogen bonding. For solid samples, information with respect to scattering, diffuse reflectance, specular reflectance, surface gloss, refractive index and polarization of reflected light are all superimposed on the near infrared vibrational information. Information related to hydrogen bonding and hydronium ion concentration are also superimposed upon a near infrared spectrum.

The types of vibrations found in near infrared and infrared spectroscopy are designated by ν (Greek letter nu) with a subscript denoting the vibration as stretching (s) or bending (b), e.g., stretching is designated as $\tilde{\nu}_s$, and bending vibrations as $\tilde{\nu}_b$. Combination bands resulting from the sum of stretching and bending modes are designated as $\tilde{\nu}_b + \tilde{\nu}_s$; and harmonics are designated as $k\tilde{\nu}_s$, where k = an integer number as 2 (first overtone), 3 (second overtone), ..., k ($k-1$ th overtone), and $\tilde{\nu}_s$ is the frequency of the fundamental stretch vibration for a specific functionality.

Group frequencies

Group frequencies are characteristic absorptions of vibrational or bending modes from groups of atoms (termed functional groups). The common infrared and near infrared groups are listed in Table 1 and are described in References 85–89. These groups exhibit characteristic absorption frequencies within the near infrared region. The group frequencies are given as those bands occurring below 6667 nm; whereas fingerprint frequencies are those above 6667 nm. Thus, for the near infrared region (below 2500 nm) fingerprint frequencies do not occur. The group frequencies usually demonstrate bands of reasonable intensity, with somewhat reliable interpretation based upon frequency (wavelength) position. Dominant near infrared spectral features include: methyl C–H, methylene C–H, methoxy C–H, carbonyl C–H, aromatic C–H, hydroxyl O–H; 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. The identification and discussion of each group frequency is beyond the scope of this paper and will be addressed later in a review of the subject. References 1–7, 71, 76, 81, 86 and 89 provide further information on the location of NIR group frequencies.

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Table 1. Common infrared and near infrared groups.

$-\text{OH}$	hydroxyl	$\text{R}-\text{CH}_3$	methyl C–H
$\text{R}-\text{OH}$	alcohols	$\text{R}-\text{CH}_2\text{R}'$	methylene C–H
$-\text{CH}_2-\text{OH}$	primary alcohols	$\text{R}-\text{CHR}'\text{R}''$	methine C–H
$\text{R}'\text{R}''\text{CH}-\text{OH}$	secondary alcohols	$\text{C}=\text{C}$	olefinic group (or alkenes)
$\text{R}'\text{R}''\text{R}'''\text{C}-\text{OH}$	tertiary alcohols	$-\text{CH}=\text{CH}_2$	vinyls
$\text{Ar}-\text{OH}$	phenolics (or phenols)	$\text{R}'\text{R}''\text{C}=\text{CH}_2$	vinylidenes
$-\text{OCH}_3$	methoxy (or ether group)	$>\text{C}=\text{C}=\text{CH}_2$	allenes
$\text{C}-\text{O}-\text{C}$	ethers	$-\text{C}\equiv\text{C}-$	acetylinics
$\text{R}-\text{C}=\text{O}-\text{H}$	aldehydes	$\text{R}-\text{C}\equiv\text{N}$	nitriles
$\text{R}-\text{C}=\text{O}-\text{R}'$	ketones	$\text{C}_\text{N}\text{H}_\text{N}$	aromatics
$\text{C}=\text{C}=\text{O}-\text{R}'$	ketenes	$\text{C}_\text{N}\text{H}_{2\text{N}}$	naphthalenes (or cycloalkanes)
$\text{R}-\text{C}=\text{O}-\text{OR}'$	esters	$\text{C}-\text{NO}$	nitroso- group
$\text{S}-\text{C}=\text{O}-\text{O}-\text{R}'$	thiol esters	CONO	nitrites
$\text{R}-\text{C}=\text{O}-\text{C}=\text{O}-\text{R}$	anhydrides	$\text{R}'\text{R}''\text{NNO}$	nitrosamines
$-\text{C}-\text{O}-\text{O}-\text{C}-$	peroxides	$\text{R}-\text{NO}_2$	nitro- group
$-\text{O}-\text{C}=\text{O}-\text{C}=\text{O}-\text{O}-$	oxalates	$\text{R}-\text{NH}_2$	primary amines
$-\text{O}-\text{C}=\text{O}-$	carboxy–	$\text{R}'\text{R}''\text{NH}$	secondary amines
$-\text{C}=\text{O}-$	carbonyl group	$\text{N}=\text{N}$	azo- group
$-\text{C}=\text{O}-\text{NH}_2$	primary amides	$-\text{N}=\text{N}^+=\text{N}^-$, $-\text{N}^--\text{N}^+\equiv\text{N}$	azides
$-\text{C}=\text{O}-\text{NHR}$	secondary amides	NNO	azoxy group
$-\text{C}=\text{O}-\text{NR}'\text{R}''$	tertiary amides	$\text{R}-\text{O}-\text{N}-\text{N}=\text{O}$	organic nitrites
$-\text{C}\equiv\text{N}$	nitriles	$-\text{NO}_3$	nitrates
$\text{C}-\text{C}$	paraffinics (or alkanes)	$\text{ON}=\text{NO}$	nitrates
$\text{CH}_3-(\text{CH}_2)_\text{N}-\text{CH}_3$	normal paraffins	$\text{H}_3\text{N}^+-\text{CH}-\text{COO}^-$	amino acids

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