NEAR-INFRARED SPECTROSCOPY IN FOOD SCIENCE AND TECHNOLOGY

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CONTENTS

PREFACE

Near-infrared (NIR) spectroscopy has recently become increasingly important in food science and technology as a non-destructive analytical technique. An enormous number of articles and research papers are published every year that deal with applications of NIR spectroscopy in this important field. Search for a comprehensive book describing both basic principles and modern application of NIR spectroscopy food science and technology proved fruitless. This book, *Near Infrared Spectroscopy in Food Science and Technology*, fills the void. It covers principles of molecular vibrations, spectral analysis, and instrumentation for NIR spectroscopy as well as its novel applications within food science and technology. It is written to be appreciated by food and agricultural scientists and engineers as well as molecular spectroscopists. The aim of this book is to provide a basic understanding of techniques and applications that demonstrate the potential of NIR spectroscopy for researchers and users in food science and technology.

The book is suitable for students at graduate level as well as researchers and engineers in academic and industry. It may be used as a textbook for a graduate course in food science and technology or agricultural science and technology and for short courses. We hope you enjoy this book and that it will inspire you and other readers to adapt the principles and techniques discussed herein to your particular area and interests.

Yukihiro Ozaki
W. Fred McClure
Alfred Christy

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CHAPTER 1

Introduction

W. FRED MCCLURE

WORLD FOOD PRODUCTION

The industrialized world consists of about 59 countries, all with a total populations of about 0.9 billion people, about one-sixth of the total world population. In contrast, about 5 billion people live in approximately 125 low- and middle-income countries. The remaining 0.4 billion live in countries in transition, which include the Baltic states, eastern Europe and the Commonwealth of Independent States (1). Today, our world produces food for 6.39 billion people (Fig. 1.1). Yet statistics show that many people go to bed hungry every night. Each year the food crisis intensifies and more and more people go hungry.

Shockingly, the push to produce more and more food is thwarted by diminishing arable land suitable for food production. Plant yields have been maximized for many crops, leaving few options for increasing food production. In the face of these seemingly insurmountable problems, scientists are beginning develop technology for maximizing *food potential*, a philosophy that calls on any means that will reduce waste.

The philosophy for maximizing food for fresh foods potential goes something like this.[1] Time of harvest for plant-based foods must be optimized in order to maximize food potential. If harvested too early, both yield and quality are reduced: Again, if crops left too long in the field, both yield and quality fall. Furthermore, between the time of harvest and the time of consumption fresh foods undergo a decaying process called senescence. Senescence can reduce food potential by 7–12%, depending on how

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[1] "Maximizing food potential" was first introduced by W. Fred McClure at the International Conference on Planning for the Future, Newcastle University, Newcastle, UK in W. F. McClure. 1995. Biological measurements for the 21st Century. In *New Horizons*, *New Beginnings*, ed. Staff, 1:34–40. Newcastle University, Newcastle, UK: Newcastle University.

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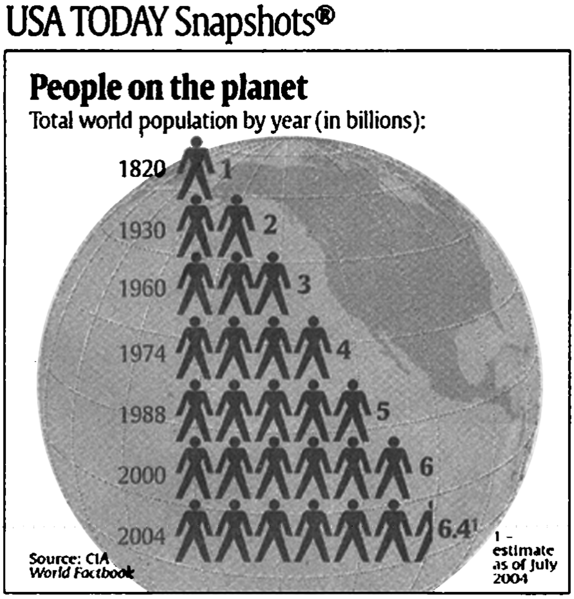

By Shannon Reilly and Adrienne Lewis, USA TODAY

Figure 1.1. World population statistics for the USA, 1820–2004 published in CIA World Fact Book (USA Today Snapshots, July 2004).

quickly the food is made ready for consumption.[2] The potential exists for reducing losses if appropriate tools are made available for measuring the quality of fresh food.

Quality measurements made early in the production cycle, when fresh products are still edible, can determine whether the product goes to fresh market or to processing. The fresh market fraction with optimized quality factors is sent to fresh market; the remaining fraction is sent to facilities for further processing to make pop-tarts, jams, cooked meals and/or soups. Thus the food potential is maximized by minimizing waste.

NEAR-INFRARED SPECTROSCOPY

Near-infrared (NIR) spectroscopy has taken its place among other proven spectroscopic tools, especially for determining chemical and physical properties of foods and food products. Covering the small region of the electromagnetic spectrum from 780 to 2500 (nm) (Sheppard, 1985 #354), producing spectra with only 860 data points spaced 2 nm apart, NIR spectroscopy has experienced phenomenal growth over its short history from 1905 (the year Coblentz produced the first official NIR publication) to the

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[2] Based on a survey taken of six major grocery chains in the USA in Ibid.; reported at the conference in Newcastle, UK.

TABLE 1.1. Major Constituents/Properties in Foods Determined with Near-Infrared Spectroscopy

Number	Constituent	Comment	References
1	Water	Water was the first constituent to be studied with near-infrared spectroscopy.	49
2	Protein	Williams, Norris and Kays studied of protein, oil, water and starch in pulverized wheat and foods.	10–15
3	Fats (Oils)	Fats (or oils) were in foods has become a routine NIR measurement today.	16–19
4	Cereals: Dietary Fiber	Dietary and health issues have been studied extensively.	20–23
5	Scattering Properties	Any solid material demands an understanding of the scattering properties in order to obtain robust calibrations.	24, 25
6	Sucrose	Sucrose is a critical constituent in health issues.	26
7	Carbohydrates	Dietary matters call for NIR analyses of carbohydrates.	10
8	Energy	Energy content of food determined by NIR spectroscopy	27
9	Homogeneity	Homogeneity is critical to robust calibrations.	28
10	Condiments Sucrose, Starch, Flour	Osborne has studied the combination of these constituents in processed cereals.	29
11	Meats: Beef, Poultry, Fish	Beef, poultry and fish are analyzed using NIR by a number of researchers.	30–39
12	Fresh Foods: Fruit, Nuts	Once thought to be a very difficult determination, Kawano, Saranwong and others have demonstrated that NIR is useful for the analyses of high-moisture products.	40–50
13	Honey, Corn Syrup, Molasses	Even amorphous sugars in honey and other products can be measured.	51–57
14	Candy, Chocolate, Caramel	The same is true for candies, plus the nicotine related components in chocolates.	54, 58–60

(*Continued*)

TABLE 1.1. (*Continued*)

Number	Constituent	Comment	References
15	Sweets: Sucrose, Saccharin, Honey, Corn Syrup, Molasses	The spectra of sucrose and saccharin are strikingly similar.	54, 61–65
16	Beverages: Milk, Soft and Hard	In particular, ethanol in beer, wines and spirits is easily determined with near-infrared spectroscopy.	66–78
17	Bread	Osborne has been the leader in the analysis of bread using NIR spectroscopy.	79–81

present. Its sensitivity to the CH, NH, and OH absorptions related to food components, its speedy response time, the simplicity of sample preparation involved, the fact that the measurement is nondestructive, and its low instrumentation cost have fixed its position along side other spectroscopies, including ultraviolet, visible, mid-infrared, Raman and others. Its expansion into the field of food production and processing is undeniable. (2–11)

NIR technology cuts across many fields (agriculture, textiles, pharmaceuticals, cosmetics, medicine, and others), with demonstrated success in all areas published in the literature. This book is not intended to address all the above areas. Rather, this book is intended to provide the reader an opportunity to understand something of the impact NIR spectroscopy has had on food science and technology. Expectedly, it does include basic principles of NIR spectroscopy (Chapter 2), characteristics of the NIR spectra (Chapter 3), instrumentation (Chapter 4), sampling techniques (Chapter 5), and chemometrics (Chapter 6). The remainder of the book discusses numerous applications of NIR technology in the food science field [agricultural and Marine (Chapter 7), food and food products (Chapter 8)] and some specialized applications (Chapter 9). The Editors and Authors all hope you will find this book to be helpful in your work.

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CHAPTER 2

Principles of Molecular Vibrations for Near-Infrared Spectroscopy

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INTRODUCTION

The fundamental vibrations of molecules lead to absorption in the infrared (200–4000 cm^{-1}), while their overtones and combination tones appear in the infrared and in the near infrared. The highest wavenumber associated to an infrared active fundamental vibration appears at 3998 cm^{-1} for HF; therefore 4000 cm^{-1} is somehow the border of the infrared and the near infrared. The near-infrared spectrum is located between the infrared and the visible, from 2500 nm to 800 nm or from 4000 cm^{-1} to 12,500 cm^{-1}. It is sometimes called the overtone region, but, naturally, the first overtone of vibrations of lower wavenumber are in the mid-infrared. As a rule overtones and combination tones are much weaker than the fundamentals, the first ones usually by a factor of 10 to 100. Second and higher overtones and combination tones are even weaker. The near-infrared absorption of polymers, especially in the region from 4000 to 9000 cm^{-1}, originates from the overtones of OH, NH, CH, and SH stretching vibrations as well as from stretching-bending combinations involving these groups. The overtones and combination tones are most often affected by hydrogen bond formation, certain aspects of which can be monitored to advantage in the near infrared (1). In addition, a few electronic transitions may appear in the upper range of the near infrared, close to the visible, especially in the range of 9000 cm^{-1} to 15,000 cm^{-1}. For example, electronic transitions of oxyhemoglobin and deoxyhemoglobin give rise to a band around 13,160 cm^{-1} (760 nm). Because most of the analytical applications of near-infrared spectroscopy on polymers and biomolecules are centered in the 4000-cm^{-1} to 9000-cm^{-1} region, the present review focuses on overtones and combination tones of molecular vibrations.

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Two languages are available for the treatment of overtones: the language based on normal coordinates (2–5) and the more recent treatment based on local coordinates (6–9). Whereas the latter appears to be better adapted to higher overtones, especially when kinetics of chemical reactions are concerned, the first overtones are treated well on a normal coordinate basis. In what follows, normal coordinates will be used; then we discuss the approach based on local coordinates.

THE DIATOMIC OSCILLATOR

The simplest possible assumption about the form of the vibrations in a diatomic molecule is that each atom moves toward or away from the other in a simple harmonic motion (2–5). Such a motion of the two atoms can be reduced to the harmonic vibration of a single mass point about an equilibrium position. In classic mechanics a harmonic oscillator can be defined as a mass point of mass m that is acted upon by a force F proportional to the distance Q from the equilibrium position and directed toward the equilibrium position:

$$F = m\frac{\partial^2 Q}{\partial t^2} = -kQ \tag{2.1}$$

where the proportionality factor k is called the force constant and depends only on the strength of the chemical bond. The solution of the differential equation is:

$$Q = Q_0 \sin(2\pi \nu t + \phi) \tag{2.2}$$

Q_0 is the amplitude of the vibration, ϕ is a phase constant dependent on the initial conditions, and ν is the vibrational frequency. The displacement of the point mass from the equilibrium position is a sine function of time. By substituting Equation 2.2 into Equation 2.1, it follows that:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{2.3}$$

Because the force is the negative derivative of the potential energy U, using Equation 2.1 one obtains that:

$$U = \frac{1}{2}kQ^2 = 2\pi^2 m\nu^2 Q^2 \tag{2.4}$$

The potential energy of a harmonic oscillator is proportional to the square of the displacement from the equilibrium position. The restoring force exerted by the two atoms of a molecule on each other when they are displaced from their equilibrium position (r_e) is approximately proportional to the change of internuclear distance

$(r - r_\mathrm{e})$. For the first atom, of mass m_1:

$$m_1 \frac{\partial^2 r_1}{\partial t^2} = -k(r - r_e) \tag{2.5}$$

For the second atom of mass m_2:

$$m_2 \frac{\partial^2 r_2}{\partial t^2} = -k(r - r_e) \tag{2.6}$$

where $Q = (r - r_\mathrm{e})$ is the displacement from the equilibrium position, r_1 and r_2 are the distance of the two atoms from the center of gravity, r is the distance of the two atoms from each other, and r_e is the equilibrium distance. For a dumbbell model of a diatomic molecule:

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r \tag{2.7}$$

By substituting Equation 2.7 into either Equation 2.5 or Equation 2.6 one can obtain:

$$\begin{aligned} f &= \frac{m_1 m_2}{m_1 + m_2} \frac{\partial^2 Q}{\partial t^2} = -kQ \\ \mu &= \frac{m_1 m_2}{m_1 + m_2} \end{aligned} \tag{2.8}$$

μ is so-called reduced mass.

Equation 2.8 is identical to Equation 2.1 of the harmonic oscillator, except that Q is replaced by $Q = (r - r_\mathrm{e})$. The vibration of the two atoms of a molecule is reduced to the vibration of a single mass point of mass μ. From Equation 2.8 it follows that:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{2.9}$$

Usually, the wavenumber ($\bar{\nu}$) is used in infrared and near-infrared spectroscopy. Equation 2.9 is often written as:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \tag{2.10}$$

The frequency of the vibrational mode depends on two parameters: the reduced mass μ and the force constant k. It follows from this equation that isotopic labeling is a powerful tool to assign bands in infrared and near-infrared spectra. For example, the CH_2 symmetric stretching of lipid is located at 2851 cm^{-1}, whereas the C^2H_2 symmetric stretching of perdeuterated lipid is at 2070 cm^{-1} (10). Assuming that k

is not affected during the isotopic substitution and assuming that CH_2 and C^2H_2 symmetric stretching modes behave like vibrational modes of a diatomic molecule, by using Equation 2.10 and computing the reduced mass of CH and of C^2H, the theoretical ratio of the two wavenumbers $\bar{\nu}(\mathrm{CH})/\bar{\nu}\,(\mathrm{C^2H})$ can be obtained:

$$\mu(\mathrm{CH}) = \frac{12 \times 1}{12 + 1} = 0.923$$

$$\mu(\mathrm{C^2H}) = \frac{12 \times 2}{12 + 2} = 1.714$$

$$\bar{\nu}(\mathrm{CH})/\bar{\nu}\,(\mathrm{C^2H}) = (\mu(\mathrm{C^2H})/\mu(\mathrm{CH}))^{1/2} = 1.36$$

For comparison, the ratio of the two measured wavenumbers is $2851/2070 = 1.38$. Although the lipid is not a diatomic molecule, the CH vibrational mode behaves almost like a diatomic molecule. Some vibrational modes in polymers that are very well localized can be considered as vibrational modes of a diatomic molecule. Fortunately, most of the first overtones and combination tones in the near infrared arise from well-localized vibrational modes such as OH, NH, CH, and SH stretching modes. The force constant k depends on the strength of the chemical bond, which is mainly controlled by the electronic environment surrounding atoms in molecules. Electrostatic interactions or formation of hydrogen bonds alter the force constant k and therefore can shift the frequency. It is well established that infrared and near-infrared spectroscopies are very sensitive in detecting the formation of hydrogen bonds. For example, a change in hydrogen bonding distance of only 0.0002 nm shifts the wavenumber of the stretching vibration of NH of a peptide backbone by approximately 1 cm^{-1}. This shift is well within the experimental limit. In contrast, X-ray crystallographic results rarely have a resolution below 0.1 nm (11). Classically, only one vibrational frequency is possible according to Equation 2.9, whereas its amplitude and its energy can assume any value.

ENERGY LEVELS

In quantum mechanics, the vibration in a diatomic molecule may also be reduced to the motion of a single point mass of mass μ, whose displacement Q from its equilibrium position corresponds to $(r - r_e)$. Assuming that the potential is that of a one-dimensional harmonic oscillator (4), the Hamiltonian H becomes:

$$H = \frac{h^2}{8\pi^2\mu}\frac{\partial^2}{\partial Q^2} + \frac{1}{2}kQ^2 \tag{2.11}$$

Using the Schrödinger equation:

$$\left(\frac{h^2}{8\pi^2\mu}\frac{\partial^2}{\partial Q^2} + \frac{1}{2}kQ^2\right)\psi(Q) = E\psi(Q) \tag{2.12}$$

The Hermite polynomials are the wavefunctions that satisfy Equation 2.12. For a diatomic molecule the Hermite polynomials have the form (5):

$$\psi_v = N_v e^{\frac{1}{2}Q^2} H_v(\sqrt{\alpha}Q) \tag{2.13}$$

where $\alpha = \frac{4\pi^2}{h}\mu\nu = \frac{2\pi}{h}\sqrt{\mu k}$, μ is the reduced mass, h is the Planck constant, k is the harmonic potential constant, and N_v is the normalization factor. Then for successive values of the vibrational quantum number v we have with $\sqrt{\alpha}Q = z$

$$\begin{aligned}
H_0(z) &= 1\\
H_1(z) &= 2z\\
H_2(z) &= 4z^2 - 2\\
H_3(z) &= 8z^3 - 12z\\
H_4(z) &= 16z^4 - 48z^2 + 12\\
H_5(z) &= 32z^5 - 160z^3 + 120z
\end{aligned}$$

The solution of Equation 2.12 indicates that the vibrational energies $E(v)$ have discrete values (4).

$$E(v) = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \tag{2.14}$$

$$E(v) = \left(v + \frac{1}{2}\right)h\nu \tag{2.15}$$

where the vibrational quantum number v can take only integral values, 0, 1, 2.... These values are the only energy values allowed by theory for the harmonic oscillator. ν is the vibrational frequency of the diatomic molecule as defined in Equation 2.9. The lowest energy ($v = 0$) has $E(0) = (1/2)h\,\nu$. Thus even in the lowest state, the vibrational energy of a molecule is not zero, in contrast to the result of classic mechanics. Equation 2.14 is often written in wavenumber units as:

$$G_v = \frac{E(v)}{hc} = \left(v + \frac{1}{2}\right)\omega_e \tag{2.16}$$

SELECTION RULES

If the diatomic molecule in its equilibrium position has a dipole moment as in heteronuclear diatomic molecules, it will in general change if the internuclear distance varies. To a first approximation it may be assumed that the change of dipole moment with internuclear distance is linear. Therefore the dipole moment changes with a frequency equal to the frequency of the mechanical vibration. On the basis of classic electrodynamics, this would lead to the emission of light of frequency ν. Conversely, the oscillator could be set in vibration by absorption of light of frequency ν. In quantum mechanics, emission of radiation takes place as a result of a transition of the oscillator from a higher to a lower state, and absorption is the reverse process (2). The wave number of the emitted or absorbed light is given by:

$$\nu^{v'v''} = \frac{E(v'')}{hc} - \frac{E(v'')}{hc} \tag{2.17}$$

where v' and v'' are vibrational quantum numbers of the upper and the lower states, respectively. To determine which particular transitions can occur, the transition moment that corresponds to the probability of the transition from an initial to a final state must be evaluated. The transition moment for a vibrational transition is given by (2–5, 12):

$$R^{v'v''} = \int \psi_{v'}^{*} M \psi_{v''} \partial\tau \tag{2.18}$$

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions for the upper and lower vibrational states with their respective quantum numbers v' and v'' and M is the variable dipole moment. The well-known selection rule is $\Delta v = \pm 1$, that is, only quantum jumps by 1 are allowed. Therefore fundamental vibrations are allowed while overtones are not. This selection rule is based on the properties of the harmonic oscillator wave functions that are the normalized Hermite polynomials (Equation 2.13). Thus it only applies to the harmonic oscillator that is ruled by a quadratic potential, that is, as long as the wave functions are the exact Hermite polynomials. These conditions are never exactly met; overtones and combination bands do appear in the spectra. It is instructive to remember how this selection rule is obtained. The variable dipole moment is, if we neglect higher terms:

$$M = M_e + M_1 Q = M_e + \left(\frac{\partial M}{\partial Q}\right)_e Q \tag{2.19}$$

where $\left(\frac{\partial M}{\partial Q}\right)_e$ is taken at the equilibrium geometry. So the transition moment becomes:

$$R^{v'v''} = M_e \int \psi_{v'}^{*} \psi_{v''} \partial Q + \left(\frac{\partial M}{\partial Q}\right)_e \int \psi_{v'}^{*} Q \psi_{v''} \partial Q \tag{2.20}$$

The first term is zero because of the orthogonality of the harmonic oscillator wave functions, and the integral in the second term is, because $\partial z = \sqrt{\alpha}\partial Q$:

$$\int \psi_{v'}^{*} Q \psi_{v''} \partial Q = \frac{N_{v'} N_{v''}}{\alpha} \int H_{v'}(z)\, z\, H_{v''}(z) e^{-z^2} \partial z \tag{2.21}$$