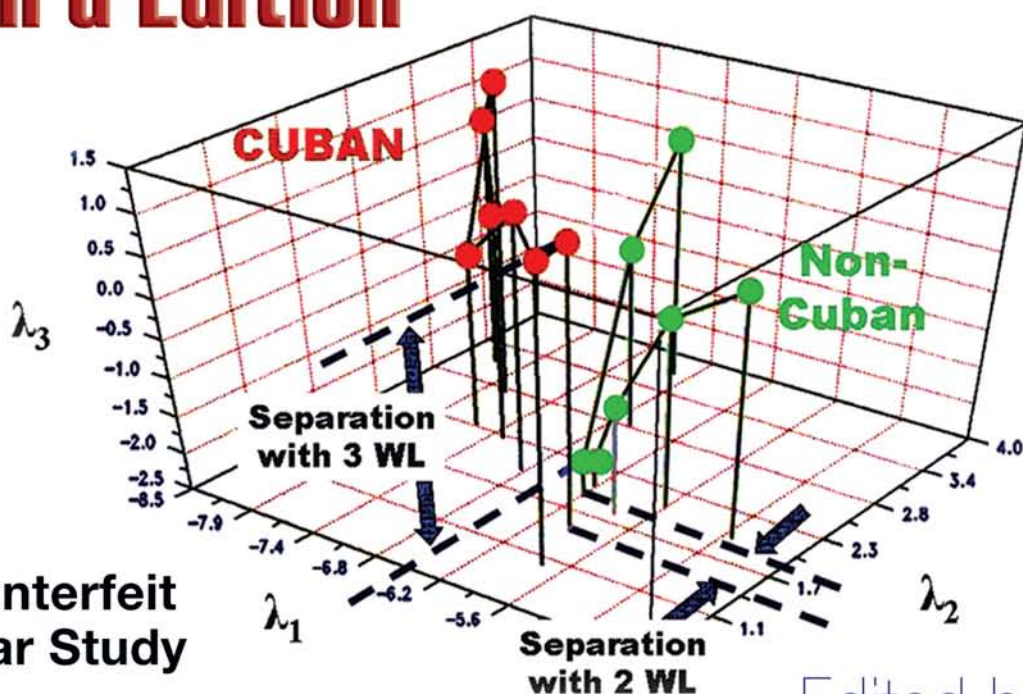


Handbook of Near-Infrared Analysis

Third Edition



Counterfeit
Cigar Study

Edited by

Donald A. Burns
Emil W. Ciurczak

**Handbook of
Near-Infrared
Analysis
Third Edition**

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We are delighted to dedicate this third edition of the *Handbook of Near-Infrared Analysis* to our good friend and colleague, Karl H. Norris.

Karl is regarded as the “father” of modern near-infrared spectroscopic analysis. He was a major force in the development of the *near-infrared reflection* technology for the simple, accurate, rapid, and inexpensive testing of many quality characteristics of food and grains. This technology has now been widely accepted and has revolutionized the way many chemical analyses are performed. As one can see in the *applications* chapters that follow, the *near-IR* approach to the determination of sample composition now permeates nearly every industry.

After nearly 40 years as an internationally recognized authority in this field, Karl was awarded a well-deserved honorary doctorate by Wilson College on August 10, 2006. This came as a surprise during the 25th anniversary celebration of the *International Diffuse Reflectance Conference* in Chambersburg, PA, before a crowd of nearly 150 colleagues.

Dr. Norris is now retired as leader of the *Instrumentation Research Laboratory* of USDA's *Agricultural Research Service*. He holds several patents, and is the author or co-author of more than 100 research papers.

Way to go, Karl. Keep it up!

Donald A. Burns

Emil W. Ciurczak

Preface

Near-Infrared (NIR) spectroscopy is a technique whose time has arrived. And for good reason — it is unusually fast compared to other analytical techniques (often taking *less than 1 s*), it is nondestructive, and as often as not, no sample preparation is required. It is also remarkably versatile: if samples contain such bonds as C—H, N—H, or O—H, and if the concentration of the analyte exceeds about 0.1% of the total composition, then it is very likely to yield acceptable answers, even in the hands of relatively untrained personnel.

The price to be paid, however, is the preliminary work, which is typical of any chemometric method. The instrument/computer system must be “taught” what is important in the sample. While this task may be time-consuming, it is not difficult. Today’s sophisticated software offers the user such choices of data treatments as multiple linear regression (MLR), partial least squares (PLS), principal components regression (PCR), factor analysis (FA), neural networks (NN), and Fourier transform (FT), among others. The trade-off is a good one: even after several hours (or days) of calibrating, the multiple advantages of analysis by NIR far outweigh the time required for method development.

This book is divided into four parts. Following the Introduction and Background, there is a general section on Instrumentation and Calibration. This is followed by Methods Development, and the depth of NIR’s utility is covered by a broad (if not comprehensive) section on Applications.

The *Handbook of Near-Infrared Analysis* was written for practicing chemists and spectroscopists in analytical, polymer, forage, baking, dairy products, petrochemicals, beverages, pharmaceutical, and textile chemistry who are responsible for methods development or routine analyses where speed, accuracy, and cost are vital factors.

Chapters 2 and 3 have been replaced (Basic Principles and Theories of Diffuse Reflection), several chapters (4,19,25,26,29, and 37) have been updated (Commercial Instrumentation, Analyses of Textiles and of Baked Products, Advances in the Petrochemical Industry, Polymers, Pharmaceutical Applications, and Process Analysis), and some new chapters (12,18,21,28,29,31,32,33,35, and 38) have been added (Process Sensors, Agro-Forestry Systems, Gas Analysis, Use of NIR at the Bowling Alley, PAT in the Pharmaceutical Industry, Nutraceuticals, Detection of Counterfeit Drugs (e.g., Viagra), NIR Photography in Medicine, Biomedical Components in Blood and Serum, and The Detection of Counterfeit Currency and Turquoise).

All this should enable you to assess the potential of NIR for solving problems in your own field (and it could even lead to becoming a hero within your organization). You will discover the relative merits of on-line, in-line, and at-line analyses for process control. You will see how interferences can be removed spectrally rather than physically, and how to extract “hidden” information via derivatives, indicator variables, and other data treatments.

Thanks are due to many people in our lives (i) Linda Burns, who put up with the disappearance of all flat surfaces in our house for those weeks (or was it months?) when piles of papers were everywhere, awaiting some semblance of organization into a book, (ii) the publisher, whose prodding was minimal and whose patience was long, (iii) *the special people in my (Emil’s) life: Alissa, Alex, Adam, Alyssa, and Button (the Wonder Dog)*, and (iv) the many contributors, both original and new. We hope that this general book will be useful to those already using

NIR as well as to those just entering the field and having to make important decisions regarding instrumentation, software, and personnel. Suggestions for improving the next edition are most welcome.

Donald A. Burns

Emil W. Ciurczak

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Part I

Introduction and Background

1 Historical Development

Peter H. Hindle

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1.1 THE DISCOVERY OF NEAR-INFRARED RADIATION

The interaction of light with matter has captured the interest of man over the last two millennia. As early as A.D. 130, Ptolemaeus tabulated the refraction of light for a range of transparent materials, and in 1305, Von Freiburg simulated the structure of the rainbow by using water-filled glass spheres.

By the mid-eighteenth century, through the work of great scientists such as Snell, Huygens, Newton, Bradley, and Priestly, the laws of reflection and refraction of light had been formulated. Both the wave and corpuscular nature of light had been proposed along with measurement of its velocity and adherence to the inverse square law. For the student of the infrared, it is Herschel's discovery of near-infrared (NIR) radiation that is probably of the greatest significance.

Sir William Herschel was a successful musician turned astronomer. Without doubt, he was one of the finest observational astronomers of all time. In 1800, he wrote two papers [1] detailing his study of the heating effect in the spectrum of solar radiation. He used a large glass prism to disperse the sunlight onto three thermometers with carbon-blackened bulbs. Toward the red end of the spectrum, the heating effect became apparent. However, just beyond the red, where there was no visible light, the temperature appeared at its greatest.

Herschel referred to this newly discovered phenomenon as "radiant heat" and the "thermometrical spectrum." Erroneously, he considered this form of energy as being different from light. Whilst his conclusions may appear surprising to us, we must remember that there was no concept of an electromagnetic spectrum, let alone that visible light formed only a small part of it. It was left to Ampere, in 1835, employing the newly invented thermocouple, to demonstrate that NIR had the same optical characteristics as visible light and conclude that they were the same phenomenon. Ampere's contribution, often overlooked, is important because it introduces, for the first time, the concept of the *extended spectrum*.

However, Herschel [2] clearly attached great importance to the analysis of light. In a letter to Professor Patrick Wilson, he concludes:

...And we cannot too minutely enter into an analysis of light, which is the most subtle of all active principles that are concerned with the mechanism of the operation of nature.

By the beginning of the twentieth century, the nature of the electromagnetic spectrum was much better understood. James Clerk Maxwell had formulated his four equations determining the

propagation of light, and the work of Kirchoff, Stefan, and Wien were neatly capped by Max Planck's radiation law in 1900.

Observationally, little progress had been made. Fraunhofer used a newly produced diffraction grating to resolve the sodium "D" lines in a Bunsen-burner flame as early as 1823 and Kirchoff had visually recorded the atomic spectra of many elements by the 1860s. Sadly, lack of suitable detection equipment impeded real progress outside the visible part of the spectrum.

1.2 THE FIRST INFRARED SPECTRA

An important step was taken in the early 1880s. It was noted that the photographic plate, invented in 1829 by Niepce and Daguerre, had some NIR sensitivity. This enabled Abney and Festing [3] to record the spectra of organic liquids in the range 1 to 1.2 μm in 1881. This work was of great significance; not only did it represent the first serious NIR measurements but also the first interpretations, because Abney and Festing recognized both atomic grouping and the importance of the hydrogen bond in the NIR spectrum.

Stimulated by the work of Abney and Festing, W. W. Coblentz [4] constructed a spectrometer using a rock-salt prism and a sensitive thermopile connected to a mirror galvanometer. This instrument was highly susceptible to both vibration and thermal disturbances. After each step in the rotation of the prism, corresponding to each spectral element to be measured, Coblentz had to retire to another room in order to allow the instrument to settle. Each pair of readings (with and without the sample in the beam) was made with the aid of a telescope to observe the galvanometer deflection. It took Coblentz a whole day to obtain a single spectrum. Around 1905 he produced a series of papers and ultimately recorded the spectra of several hundred compounds in the 1- to 15- μm wavelength region.

Coblentz discovered that no two compounds had the same spectrum, even when they had the same complement of elements (e.g., the isomers propan-1-ol and propan-2-ol). Each compound had a unique "fingerprint." However, Coblentz noticed certain patterns in the spectra; for example, all compounds with OH groups, be they alcohols or phenols, absorb in the 2.7 μm region of the spectrum. In this way, many molecular groups were characterized. He also speculated the existence of harmonically related series. Essentially, Coblentz gave chemists a new tool, spectroscopy, where they could obtain some structural information about compounds.

It is interesting to note that contemporaries of Coblentz were working on exciting, new, instrumental designs, which, years later, were to become the mainstay of present-day spectrometry. Rowland developed large, ruled diffraction gratings and concave gratings, in particular, in the 1880s. In 1891, A. A. Michelson [5] published a paper describing the two-beam interferometer.

1.3 A STEADY EVOLUTION

During the first half of the twentieth century many workers extended the spectral database of organic compounds and assigned spectral features to functional groups. While infrared spectroscopy had moved away from being a scientific curiosity it was used very little; suitable spectrometers did not exist and few chemists had access to what instruments there were. Over half a century was to pass between Coblentz's original work and the routine use of spectroscopy as a tool; indeed, two-thirds of a century would pass before routine NIR measurement made its debut.

Possibly, the first quantitative NIR measurement was the determination of atmospheric moisture at the Mount Wilson observatory by F. E. Fowle in 1912 [6] followed, in 1938, by Ellis and Bath [7] who determined amount of water in gelatin. In the early 1940s, Barchewitz [8] analyzed fuels and Barr and Harp [9] published the spectra of some vegetable oils. In the late 1940s Harry Willis, working at ICI, used a prewar spectrometer to characterize polymers and later employed NIR for the measurement of the thickness of polymer films.

The state of the art by the mid-1950s is summarized by Wilbur Kaye [10,11], in 1960 by R. E. Goddu [12] and in 1968 by K. Whetsel [13]. It is interesting to note that up to 1970, only about 50 papers had been written on work concerning NIR.

In the 1930s, lead sulphide (PbS) was being studied as a compound semiconductor, and the advent of the World War II stimulated its development as an infrared detector for heat-sensing purposes. In the 1950s, PbS became available for commercial applications as a very sensitive detector for the 1- to 2.5- μm wavelength region. The NIR region, at last, had a good detector.

Research into NIR spectra (1 to 2.5 μm) as opposed to the mid-infrared (mid-IR) (roughly 2 to 15 μm) had a slow start. Many spectroscopists considered the region too confusing with many weak and overlapping peaks of numerous overtone and combination bands (making assignments difficult). Compared with the mid-IR absorption features were very weak (by two or three orders of magnitude) and, because of the overall complexity, baselines were hard to define. However, two aspects of NIR technology were initially overlooked. First, the PbS detector was very sensitive and because tungsten filament lamps (particularly quartz halogen) were a good source of NIR radiation, diffuse reflection measurements were possible. Second, relatively low-cost instruments could be manufactured because detectors, light sources, and, importantly, optics made from glass were inexpensive.

1.4 THE DIGITAL REVOLUTION

Modern NIR technology relies heavily on the computer (and the microprocessor in particular), not only for its ability to control and acquire data from the instrument, but to facilitate calibration and data analysis. The foundations of data analysis were laid down in the 1930s. Work on the diffuse scattering of light in both transmission and reflection, by Kubelka and Munk [14] in 1931, opened the door to NIR measurements on solids. In 1933, Hotelling [15] wrote a classic paper on principal components analysis (PCA), and Mahalanobis formulated a mathematical approach for representing data clustering and separation in multidimensional space.

In 1938, Alan Turing created the first programmable computer, employing vacuum tubes and relays. By the 1950s, the first commercial computer, UNIVAC, was available. By the mid-1950s, FORTRAN, the first structured, scientific language had been developed by Backus at IBM. The first personal computer (PC) was probably the Altair in 1975, followed in 1977 by the Commodore PET, the same year that saw Bill Gates and Paul Allen found Microsoft. IBM joined the fray with their first PC in 1981 and their designs set the format for compatibility. PC sales of around 300,000 in 1981 rocketed to 3 million in the next year. The PC soon became the driving force behind NIR instrumentation.

Starting in the 1950s there was a growing demand for fast, quantitative determinations of moisture, protein, and oil. Kari Norris, already working for the USDA, was charged with solving the problem for wheat. He then took the bold step of choosing NIR, working with primitive means by today's standards. In 1968, Ben-Gera and Norris published their initial work on applying multiple linear regression (MLR) to the problem of calibration relating to agricultural products. The early 1970s saw the birth of what was to become the laboratory instrument sector of NIR with the emergence of names like Dickey-John, Technicon, and Neotec all in the United States.

At the same time, and quite separately, online process instruments emerged. In Germany, Pier Instrument produced a two-filter sensor with tube-based electronics. In 1970, Infrared Engineering (in the United Kingdom) and Anacon (United States), both employing integrated circuit (IC)-based electronics, entered the marketplace. A few years later Moisture Systems Corporation (United States) entered the field. Online instrumentation is now used for both continuous measurement and process control over a wide range of applications including chemicals, pharmaceuticals, tobacco, food, drinks, and web-based products [16,17].

During the 1980s, the microprocessor was integrated into the designs of most instruments. Much more sophisticated data acquisition and manipulation was now possible. The scope of data treatment display and interpretation was enhanced to include MLR, partial least squares, PCA, and cluster

analysis. Third-party software suppliers have emerged offering a wide choice of data treatments, freeing the user from the constraints of instrument suppliers. Subsequent chapters of this book are devoted in detail to these issues.

NIR technology has evolved rapidly since 1970 and has now gained wide acceptance. In many sectors, it is now the measurement of choice. Its history is far richer than can be presented within the scope of this chapter and so some references for further reading have been included [18–33].

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2 Basic Principles of Near-Infrared Spectroscopy

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2.1 INTRODUCTION

The increasing demand for product quality improvement and production rationalization in the chemical, petrochemical, polymer, pharmaceutical, cosmetic, food, and agricultural industries has led to the gradual substitution of time-consuming conservative analytical techniques (GC, HPLC, NMR, MS) and nonspecific control procedures (temperature, pressure, pH, dosing weight) by more specific and environmentally compatible analytical tools. In this respect, of the different methods of vibrational (mid-infrared [MIR], near-infrared [NIR] and Raman) spectroscopy, primarily the NIR technique has emerged over the last decade — in combination with light-fiber optics, new in- and on-line probe accessories, and chemometric evaluation procedures — as an extremely powerful tool for industrial quality control and process monitoring.

With this development the wavelength gap between the visible and the MIR region that has over a long period been lying idle is eventually also filled with life and exploited according to its real

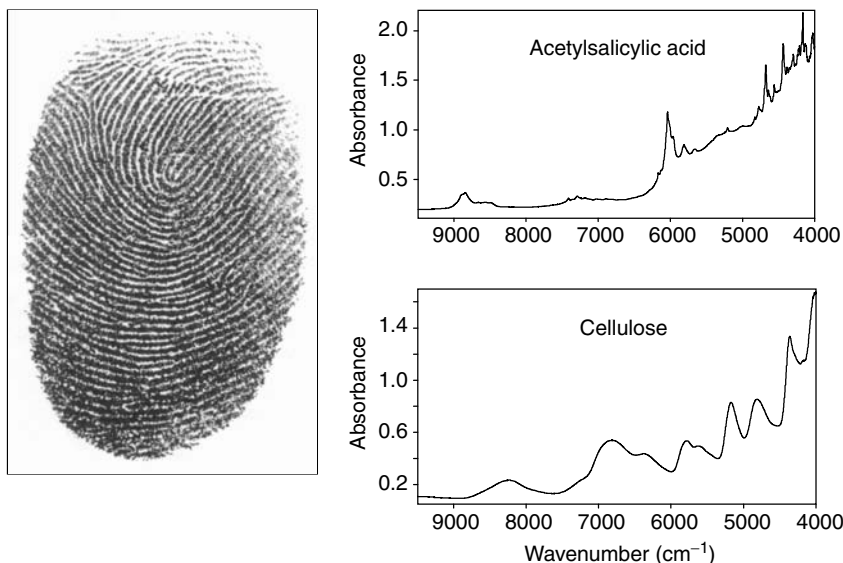


FIGURE 2.1 The NIR spectra of acetylsalicylic acid and cellulose: fingerprints of the chemical composition and the physical state of order.

potential. The period of idling can be mainly contributed to two facts:

- On the one hand, conservative spectroscopists did not accept the frequently broad and overlapped overtone and combination bands of the NIR region as a complementary and useful counterpart to the signals of the fundamental vibrations observed in the Raman and MIR spectra. Figure 2.1 shows the NIR spectra of a crystalline, pharmaceutical active ingredient (acetylsalicylic acid) and an amorphous excipient (cellulose). The characteristic absorption bands with significantly different half-bandwidth clearly demonstrate that this prejudice is not justified and that the NIR spectrum is not only a fingerprint of the chemical composition but also a signature of the physical state of order of the material under investigation.
- Most of the early users of NIR spectroscopy were, with few exceptions, working in the field of agriculture, taking advantage of this new nondestructive analytical tool and having low or no interest to further exploit the spectroscopy behind the data in scientific depth.

Although the situation has not yet changed to the point of equivalent recognition of NIR compared to MIR and Raman spectroscopy, today NIR spectroscopy is at least an accepted technique for industrial applications. It should be emphasized, however, that NIR spectroscopy is not only a routine tool but has also a tremendous research potential, which can provide unique information not accessible by any other technique. Several chapters of this book will certainly prove this statement.

Historically, the discovery of NIR energy is ascribed to W. Herschel in 1800 [1,2]. As far as the development of instrumentation and its breakthrough for industrial applications in the second half of the twentieth century was concerned, it proceeded in technology jumps [3]. In this respect, large credit has to be given to researchers in the field of agricultural science, foremost K. H. Norris [4,5], who have recognized the potential of this technique already in the early fifties. At the same period, with few exceptions [6–8], comparatively low priority had been given to NIR spectroscopy in the chemical industry. This situation is also reflected by the fact that the NIR spectral range was for a long time only offered as a low- or high-wave number add-on to ultraviolet-visible (UV-VIS) or MIR spectrometers, respectively.

This situation has dramatically changed since about the mid-eighties when stand-alone NIR instrumentation became widely available. Since the early nineties, the availability of efficient chemometric evaluation routines, light-fiber optics coupled with specific probes for a multitude of purposes, and the subsequent fast progress in miniaturization, based on new monochromator/detector designs, has launched NIR spectroscopy into a new era for industrial quality and process control.

2.2 BASIC PRINCIPLES OF VIBRATIONAL SPECTROSCOPY

In order to provide a minimum basis to put the different vibrational spectroscopies (Raman, MIR, and NIR) into perspective as far as their theoretical and instrumental fundamentals and their individual advantages are concerned, a short comparative overview is given here. For more detailed information the interested reader is referred to the pertinent literature [9–21].

Although the three techniques are very different in several aspects, their basic physical origin is the same: signals in the MIR, NIR, and Raman spectra of chemical compounds can be observed as a consequence of molecular vibrations. However, while Raman spectroscopy is a scattering technique, MIR and NIR spectroscopy are based on the absorption of radiation (Figure 2.2).

2.2.1 THE ABSORPTION TECHNIQUES OF MIR AND NIR SPECTROSCOPY

2.2.1.1 The Harmonic Oscillator

We will first treat the methods based on the phenomenon of absorption and consider a harmonic diatomic oscillator model where the vibrating masses m_1 and m_2 (Figure 2.2) lead to changes of the internuclear distance $<10\%$. In this case, Hooke's law applies and the potential energy, V , can be

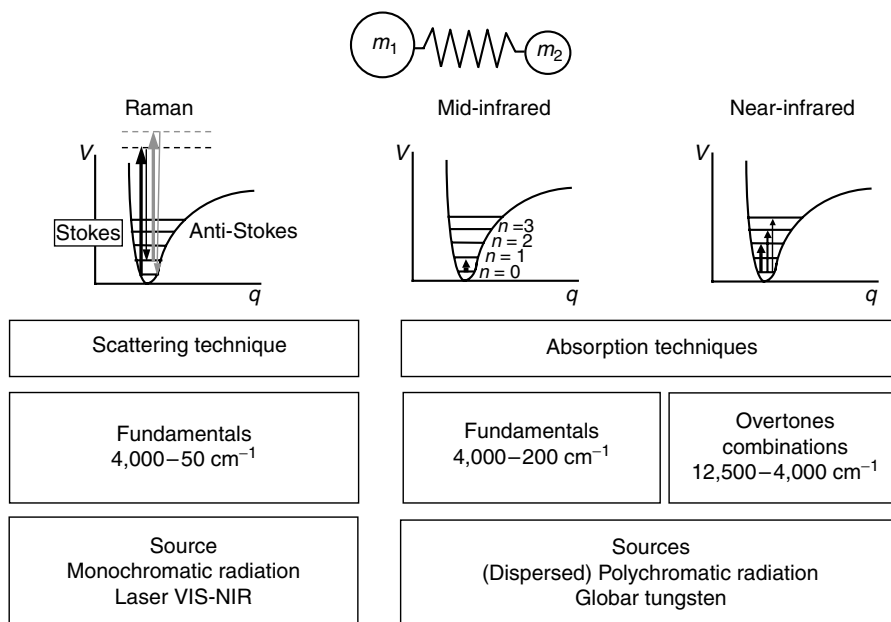


FIGURE 2.2 The principles of Raman, MIR, and NIR spectroscopy (see text).

represented by [22]

$$V = \frac{1}{2}k(r - r_e)^2 = \frac{1}{2}kq^2 \quad (2.1)$$

where k is the force constant of the bond, r is the internuclear distance during the vibration, r_e is the equilibrium internuclear distance, and $q = (r - r_e)$ is the displacement coordinate. The potential energy curve of such an oscillator is parabolic in shape and symmetrical about the equilibrium bond length r_e . This model leads to the vibrational frequency ν_0 :

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (2.2)$$

where the reduced mass m is given by:

$$m = \frac{m_1 m_2}{m_1 + m_2} \quad (2.3)$$

From Equation (2.2) and Equation (2.3), it becomes obvious that the vibrational frequencies are very sensitive to the structure of the investigated compound, and this is the basis for the widespread application of infrared spectroscopy for structure elucidation.

A quantum mechanical treatment by the Schrödinger equation shows that the vibrational energy has only certain discrete values that are given by [22]:

$$E_n = h\nu_0 \left(n + \frac{1}{2} \right) \quad (2.4)$$

where h is Planck's constant, ν_0 is the vibrational frequency defined above and n is the vibrational quantum number that can only have integer values 0, 1, 2, 3, ... and so on. If the energy levels are expressed in wave number units (cm^{-1}), they are given by [3]:

$$G_n = \frac{E_n}{hc} = \bar{\nu}_0 \left(n + \frac{1}{2} \right) \quad (2.5)$$

where c is the speed of light and $\bar{\nu}_0$ is the wave number corresponding to the frequency ν_0

$$\bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad (2.6)$$

Interaction of infrared radiation with a vibrating molecule, however, is only possible if the electric vector of the radiation oscillates with the same frequency as the molecular dipole moment, μ . Thus, a vibration is infrared active only if the molecular dipole moment is modulated by the vibration [9] and

$$\frac{\partial \mu}{\partial q} \neq 0 \quad (2.7)$$

where q is the vibrational coordinate. The requirement of a dipole moment change during the vibration makes MIR spectroscopy specifically sensitive to polar functionalities (see below and Figure 2.3).

For the harmonic oscillator the energy levels expressed in Equation (2.4) and Equation (2.5) are equidistant and transitions are only allowed between neighboring energy levels with

$$\Delta n = \pm 1 \quad (2.8)$$

Raman	MIR	NIR
$\frac{\partial \alpha}{\partial q} \neq 0$	$\frac{\partial \mu}{\partial q} \neq 0$	$\frac{\partial \mu}{\partial q} \neq 0$ / Anharmonicity $m_2 \ll m_1$
Polarizability	Dipole moment	Anharmonicity
Homonuclear e.g., C=C	Functionalities Polar e.g., C=O	CH/OH/NH Functionalities
High structural selectivity		Low structural selectivity
$I_{\text{Raman}} \propto c$	$\log \frac{I_0}{I} = A = a \cdot b \cdot c$ (Beer's law)	

FIGURE 2.3 Specific characteristics of Raman, MIR, and NIR spectroscopy (I_0 , incident radiation; I , transmitted radiation; A , absorbance; a , absorptivity; b , sample thickness; c , sample concentration) (see text).

According to the Boltzmann distribution, most molecules at room temperature populate the ground level $n = 0$, and consequently the allowed, so-called fundamental, transitions between $n = 0$ and $n = 1$ dominate the vibrational absorption spectrum (Figure 2.2). The potential of MIR spectroscopy as a structure elucidation tool is based on the fact that the majority of absorption bands of chemical compounds corresponding to fundamental vibrations occur in this wave number region (4000 to 200 cm^{-1}).

2.2.1.2 The Anharmonic Oscillator

However, the picture of the harmonic oscillator cannot be retained at larger amplitudes of vibration owing to:

- Repulsive forces between the vibrating atoms.
- The possibility of dissociation when the vibrating bond is strongly extended.

Accordingly, the allowed energy levels for an anharmonic oscillator have to be modified [3,22,23]:

$$G_n = \frac{E_n}{hc} = \bar{\nu}_0 \left(n + \frac{1}{2} \right) - \chi \bar{\nu}_0 \left(n + \frac{1}{2} \right)^2 \quad (2.9)$$

where χ is the anharmonicity constant.

Unlike the harmonic oscillator, energy levels are no longer equidistant and the strict selection rule of Equation (2.8) is expanded to transitions over more than one energy level (see Equation (2.10)). Furthermore, the potential energy curve is represented by an asymmetric Morse function [3,9,22] as shown in Figure 2.2. Generally, a nonlinear molecule containing N atoms will have $3N - 6$ vibrational degrees of freedom, while a linear molecule has only $3N - 5$ [3,24]. The number of vibrational degrees of freedom represents the number of fundamental vibrational frequencies of the molecule or the number of different “normal modes” of vibration. For a given molecule, a normal mode of vibration corresponds to internal atomic motions in which all atoms move in phase with the same frequency, but with different amplitudes. Additionally to these normal vibrations transitions corresponding to

$$\Delta n = \pm 2, \pm 3, \dots \quad (2.10)$$

are now also allowed and are called first, second, and so on, overtones.

Apart from overtones, combinations of different vibrational transitions (sum and difference “tones”) may also be observed. However, the probability of these transitions decreases significantly with their order, and generally the absorption bands corresponding to overtone or combination vibrations have much lower intensity than their fundamental analogs. Contrary to the MIR, the NIR region contains almost exclusively absorption bands that can be assigned to overtone and combination vibrations. Unfortunately, the overlap of these overtone and combination bands strongly decreases the specificity of NIR spectroscopy (especially for interpretation purposes) and was one of the main reasons why this technique has been neglected by conservative spectroscopists for such a long time.

However, the availability of (a) chemometric evaluation procedures for qualitative discrimination and quantitative determination [25–28] and (b) the perception that the low band intensities can be advantageously exploited in terms of larger sample thicknesses and therefore much easier sample handling has eventually led to the breakthrough of the NIR technique.

2.2.1.3 The Calculation of Overtones and Anharmonicities

With Equation (2.9) the wave number position of the fundamental vibration $\bar{\nu}_1$ or an overtone $\bar{\nu}_n$ ($n = 2, 3, \dots$) of the anharmonic oscillator can be given by [23]

$$\bar{\nu}_n = G_n - G_0 = \bar{\nu}_0 n - \chi \bar{\nu}_0 n(n+1) \quad (2.11)$$

$\bar{\nu}_0$ is not directly accessible and from the absorption spectra only the wave numbers $\bar{\nu}_1, \bar{\nu}_2, \dots$ may be obtained. Therefore, we substitute $\bar{\nu}_0$ in Equation (2.9) by

$$\bar{\nu}_0 = \frac{\bar{\nu}_1}{1 - 2\chi} \quad (2.12)$$

and can derive

$$\bar{\nu}_n = \frac{\bar{\nu}_1 n - \bar{\nu}_1 \chi n(n+1)}{1 - 2\chi} \quad (2.13)$$

for $n = 2, 3, 4, \dots$

Thus, if the wave number position $\bar{\nu}_1$ of the fundamental vibration and the anharmonicity constant χ are known, the wave number positions of the overtones can be calculated by Equation (2.13). Alternatively, χ can be calculated if, for example, $\bar{\nu}_1$ and $\bar{\nu}_2$ are known.

The intensities of overtone absorption bands depend on the anharmonicity, and it has been shown [23] that vibrations with low anharmonicity constants also have low overtone intensities. X–H stretching vibrations, for example, have the largest anharmonicity constants and therefore dominate the spectra in the NIR region. Table 2.1 summarizes the anharmonicity constants of the vibrations of some characteristic functionalities.

TABLE 2.1
Anharmonicity Constants χ
for Selected Vibrations [23]

$\chi \nu(\text{CH})$	$\sim 1.9 \times 10^{-2}$
$\chi \nu(\text{CD})$	$\sim 1.5 \times 10^{-2}$
$\chi \nu(\text{CF})$	$\sim 4 \times 10^{-3}$
$\chi \nu(\text{CCl})$	$\sim 6 \times 10^{-3}$
$\chi \nu(\text{C=O})$	$\sim 6.5 \times 10^{-3}$

2.2.1.4 Fermi Resonance, Darling–Dennison Resonance, and the Local Mode Concept

Apart from overtone and combination vibrations, some other characteristic effects may contribute to the appearance of signals in a vibrational spectrum [3].

A resonance that leads to a perturbation of the energy levels can occur if two vibrational levels belong to the same symmetry species and have similar energy. Such an accidental degeneracy of, for example, an overtone or a combination band that has the same symmetry and nearly the same frequency as that of a fundamental vibration is called Fermi resonance [29,30], and this leads to two relatively strong absorption bands that are observed at somewhat higher and lower frequencies than the expected unperturbed frequency positions. When this perturbation takes place, the weaker absorption in the spectrum “steals” intensity from the stronger one. Typical examples of Fermi resonance have been analyzed for the Raman [14] as well as for the NIR spectra of CO₂ [3,31], but this phenomenon has also been reported for numerous other compounds [3,9,14].

A resonance that is of importance in the NIR spectra of water has been discussed by Darling and Dennison [32] but can also occur in other molecules containing symmetrically equivalent X–H bonds. Thus, of the three normal modes of water — ν_2 bending vibration (1595 cm⁻¹), ν_3 anti-symmetric stretching (3756 cm⁻¹), and ν_1 symmetric stretching (3657 cm⁻¹) — the two stretching vibrations absorb at similar wave number positions but belong to different symmetry species and therefore cannot interact directly. However, energy levels of these vibrations associated with specific vibrational quantum numbers n_1 , n_2 , and n_3 [3,32] can interact if they belong to identical symmetry species and have similar energies. These interactions then lead to several pairs of NIR absorption bands with appreciable intensities.

Finally, a few comments shall be made on the concept of local modes as compared to normal modes [3,33–35]. The main idea of the local mode model is to treat a molecule as if it were made up of a set of equivalent diatomic oscillators, and the reason for the local mode behavior at high energy (>8000 cm⁻¹) may be understood qualitatively as follows. As the stretching vibrations are excited to high energy levels, the anharmonicity term $\chi \bar{\nu}_0$ (Equation (2.9)) tends, in certain cases, to overrule the effect of interbond coupling and the vibrations become uncoupled vibrations and occur as “local modes.”

The absorption bands in the spectrum can thus be interpreted as if they originated from an anharmonic diatomic molecule. This is the reason why NIR spectra are often said to become simpler at higher energy. Experimentally, it is found that the inversion from normal to local mode character occurs for high energy transitions corresponding to $\Delta n \geq 3$.

2.2.2 THE SCATTERING TECHNIQUE OF RAMAN SPECTROSCOPY

Whereas scanning MIR and NIR spectrometers operate with a polychromatic source for the individual frequency range (Figure 2.2) from which the sample absorbs specific frequencies corresponding to its molecular vibrational transitions (mostly fundamental vibrations for the MIR and overtone or combination vibrations for the NIR), in Raman spectroscopy the sample is irradiated with monochromatic laser light whose frequency may vary from the VIS to the NIR region. This radiation excites the molecule to a virtual energy state that is far above the vibrational energy levels of this anharmonic oscillator for a VIS-laser and in the range of high overtones for an NIR-laser excitation (Figure 2.2 and Figure 2.4).

From the excited energy level, the molecule may return to the ground state by elastic scattering, thereby emitting the Rayleigh line that has the same frequency as the excitation line and does not contain information in terms of the molecular vibration (this case is not shown in Figure 2.2 and Figure 2.4). If it returns to the first excited vibrational level by inelastic scattering, the emitted Raman line (so-called Stokes line) (Figure 2.2) has a lower frequency (wave number), and the difference to the excitation line corresponds to the energy of the fundamental transition that can also be observed as

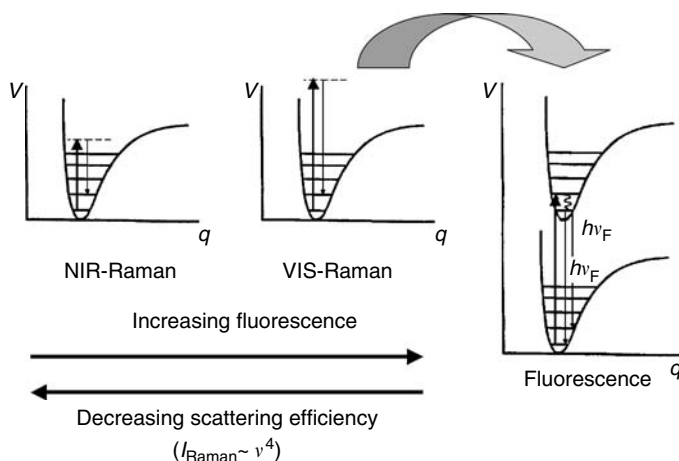


FIGURE 2.4 Fluorescence and scattering efficiency in NIR- and VIS-Raman spectroscopy.

an MIR absorption band. In the case of the anti-Stokes line, where the starting level is the first excited vibrational state and the molecule returns to the ground state by inelastic scattering (Figure 2.2), the emitted Raman line is of higher frequency (here too, the frequency difference to the excitation line corresponds to the fundamental transition) but of lower intensity compared to the Stokes line, due to the lower population of the excited state (law of Boltzmann). Commonly, the Stokes lines are used for practical Raman spectroscopy.

One of the limiting factors for the application of the Raman technique, however, becomes evident by comparing the intensity of the laser source and the scattered radiation [9,15,19–21]

$$I_{\text{Raman}} \approx 10^{-4} I_{\text{Rayleigh}} \approx 10^{-8} I_{\text{source}} \quad (2.14)$$

From these figures it can readily be derived that a sensitive detection of the Raman line alongside an efficient elimination of the Rayleigh line are experimental prerequisites for the successful application of Raman spectroscopy. As shown in Figure 2.2, Raman and MIR spectroscopy cover approximately the same wave number region with the Raman technique extending further into the far-infrared (FIR) region (down to about 50 cm^{-1}) owing to instrumental limitations of the MIR (primarily because of the MIR detector cut-off). In some cases, this additional frequency range is valuable, since it often contains absorptions of lattice modes of molecular crystals that may be very characteristic for a specific polymorph (e.g., of a pharmaceutical active ingredient).

An important relation for the comparison of VIS- vs. NIR-Raman spectroscopy, is the dependence of the scattered Raman intensity I_{Raman} on the fourth power of the excitation frequency ν_{exc}

$$I_{\text{Raman}} \approx \nu_{\text{exc}}^4 \quad (2.15)$$

The impact of this relationship with reference to the application of either VIS- or NIR-Raman spectroscopy for an individual problem will be outlined below.

A similar condition as for MIR spectroscopy holds for the Raman effect and a molecular vibration can only be observed in the Raman spectrum if there is a modulation of the molecular polarizability α [9,15,19–21]:

$$\frac{\partial \alpha}{\partial q} \neq 0 \quad (2.16)$$

Hence, Raman spectroscopy is primarily sensitive to vibrations of homonuclear bonds (Figure 2.3). From the selection rules (Equation (2.7) and Equation (2.16)), it becomes obvious that MIR and

Raman spectroscopy are complementary techniques and the application of both methods can be very helpful for the efficient elucidation of a molecular structure.

2.2.3 A COMPARISON OF THE QUALITATIVE AND QUANTITATIVE ASPECTS OF RAMAN, MIR, AND NIR SPECTROSCOPY

The different excitation conditions of Raman, MIR, and NIR spectroscopy (Figure 2.3) lead to extremely different signal intensities of these techniques for the same vibration of a specific molecular functionality.

NIR spectroscopy covers the wave number range adjacent to the MIR and extends up to the VIS region ($4,000$ to $12,500\text{ cm}^{-1}$) (Figure 2.2). NIR absorptions are based on overtone and combination vibrations of the investigated molecule, and owing to their lower transition probabilities, the intensities usually decrease by a factor of 10 to 100 for each step from the fundamental to the next overtone [3,11,23]. Thus, the intensities of absorption bands successively decrease in the direction from the MIR to the visible region, thereby allowing an adjustment of the sample thickness (from millimeters up to centimeters), depending on the rank of the overtone.

This is a characteristic difference to MIR and Raman spectra, where the signal intensities of the fundamental vibrations vary irregularly over the whole frequency range and depend exclusively on the excitation conditions of the individual molecular vibrations (Equation (2.7) and Equation (2.16)). As pointed out above, these different excitation conditions lead to the complementarity of the Raman and MIR technique as structural elucidation tools, because Raman spectroscopy predominantly focuses on vibrations of homonuclear functionalities (e.g., $\text{C}=\text{C}$, $\text{C}-\text{C}$, $\text{S}-\text{S}$), whereas the most intense MIR absorptions can be traced back to polar groups (e.g., $\text{C}-\text{F}$, $\text{Si}-\text{O}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}-\text{C}$).

NIR spectroscopy, on the other hand, requires — in addition to the dipole moment change — a large mechanical anharmonicity of the vibrating atoms (see Figure 2.3) [3,23]. This becomes evident from the analysis of the NIR spectra of a large variety of compounds, where the overtone and combination bands of CH , OH , and NH functionalities dominate the spectrum, whereas the corresponding overtones of the most intense MIR fundamental absorptions are rarely represented. One reason for this phenomenon is certainly the fact that most of the $\text{X}-\text{H}$ fundamentals absorb at wave numbers $>2000\text{ cm}^{-1}$ so that their first overtones already appear in the NIR frequency range.

The polar groups leading to the most intense fundamental absorptions in the MIR (e.g., $\nu(\text{C}-\text{F})$, $\nu(\text{C}=\text{O})$, $\nu(\text{Si}-\text{O})$) on the other hand absorb at wave numbers $<2000\text{ cm}^{-1}$, so that their first (and sometimes higher) overtones still occur in the MIR region. Owing to the intensity loss for each step from the fundamental to the next overtone, the absorption intensities of these vibrations have become negligible by the time they should occur in the NIR range. The best example in this respect is the $\nu(\text{C}-\text{F})$ absorption band at about 1200 cm^{-1} (e.g., of poly[tetrafluoroethylene]), which is one of the most intense absorption bands in the MIR owing to the large dipole moment of the $\text{C}-\text{F}$ bond.

However, because of the small anharmonicity constant (see Table 2.1), the first and the second overtones that are expected at about 2400 and 3600 cm^{-1} , respectively, have already strongly reduced intensity, and no further overtone vibrations of this functionality can be observed in the NIR region. In fact, poly(tetrafluoroethylene) is used as a nonabsorbing standard material (Spectralon®) for the NIR region.

Anharmonicity plays also an important role in the evaluation of the fundamental and overtone vibration intensities of functionalities with a high hydrogen-bonding tendency such as $\nu(\text{O}-\text{H})$ and $\nu(\text{N}-\text{H})$. Figure 2.5a shows the MIR spectrum of the $\nu(\text{N}-\text{H})$ region of a polyamide 11 (PA 11) film of about $30\text{ }\mu\text{m}$ thickness at room temperature. Under these conditions, the majority of the $\text{N}-\text{H}$ -groups ($\sim 99\%$) occur in the associated, hydrogen-bonded form. This is directly reflected in the very low intensity of the $\nu(\text{N}-\text{H})_{\text{free}}$ absorption at 3450 cm^{-1} relative to the dominating $\nu(\text{N}-\text{H})_{\text{assoc}}$ absorption at 3300 cm^{-1} .

If the same polymer is investigated at room temperature with a film thickness of about $750\text{ }\mu\text{m}$ in the NIR region, the spectrum shown in Figure 2.5b is obtained. Here, the intensity ratio of the

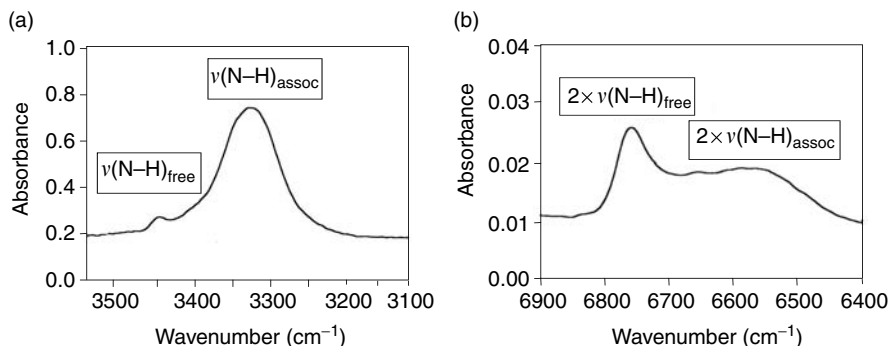


FIGURE 2.5 (a) MIR spectrum of polyamide 11 film in $\nu(\text{N-H})$ fundamental absorption region and (b) NIR spectrum in $2 \times \nu(\text{N-H})$ overtone absorption region.

$2 \times \nu(\text{N-H})_{\text{free}}$ (6760 cm^{-1}) relative to the broad $2 \times \nu(\text{N-H})_{\text{assoc}}$ absorption at about 6510 cm^{-1} is reversed, although the state of order of the polymeric material has not been changed [36]. The explanation for this effect is that, owing to its larger anharmonicity, the intensity of the $\nu(\text{N-H})_{\text{free}}$ overtone absorption is strongly enhanced relative to the corresponding overtone vibration of the associated N-H-groups [37,38]. Hydrogen bonding is equivalent to increasing the mass of the vibrating H-atom, thereby leading to a reduction of mechanical anharmonicity of the $\nu(\text{N-H})_{\text{assoc}}$ vibration and a decrease of its absorption intensity. The uncontrolled use of absorption intensities without proper care for their absorptivities (a) in Beer's law (Figure 2.3) would therefore lead to dramatic errors in the estimation of the extent of hydrogen bonding.

The superposition of many different overtone and combination bands in the NIR region causes a very low structural selectivity for NIR spectra compared to the Raman and MIR analogs where many fundamentals can usually be observed in isolated positions. Nevertheless, NIR spectra should also be assigned in as much detail as possible with reference to their molecular origin [3,36,39]; this allows a more effective application for research purposes and combination with chemometric evaluation procedures. For the assignment of overtones and combination bands in the NIR to their corresponding fundamentals in the MIR, it is recommended that the wave number notation be used instead of the widespread wavelength (nm or μm) scale. It should be mentioned, however, that the wave-number positions of the overtones deviate with increasing multiplicity from the exact multiples of their fundamentals owing to the anharmonicity of the vibrations [3,11,23].

As far as the quantitative evaluation of vibrational spectra is concerned, MIR and NIR spectroscopy follow Beer's law, whereas the Raman intensity I_{Raman} is directly proportional to the concentration of the compound to be determined (Figure 2.3). To avoid compensation problems, in most cases, quantitative Raman spectroscopy is performed with an internal reference signal in the vicinity of the analytical absorption band being analyzed.

An important issue for the implementation of a technique as an industrial routine tool is the sample preparation required for this technique. In this respect, it can be seen from Figure 2.6 that Raman and NIR spectroscopy have considerable advantages over MIR spectroscopy, which usually requires individual sample preparation steps before data acquisition. Only the technique of attenuated total reflection (ATR) [16,40] circumvents time-consuming sampling procedures for MIR spectroscopy.

2.2.4 A COMPARISON OF THE BASIC INSTRUMENTATION OF RAMAN, MIR, AND NIR SPECTROSCOPY

Figure 2.7 summarizes the present state of the most frequently used monochromator/detection principles for the different scanning spectroscopies. As mentioned above, in Raman spectroscopy two

Raman	MIR/ATR	NIR
No sample preparation	Sample preparation required (except ATR)	No sample preparation
Small sample volume (μL) or sample thickness (μm)		Large sample thickness (Up to cm)
Quartz light-fiber optics ($>100\text{ m}$)	Chalcogenide or AgCl light-fiber optics ($<10\text{ m}$)	Quartz light-fiber optics ($>100\text{ m}$)
AT-line/In-line probes	ATR-probes	Transmission transfection diffuse-reflection probes

FIGURE 2.6 Process-control aspects of Raman, MIR, and NIR spectroscopy.

Raman	MIR/ATR	NIR
NIR-Raman (FD) VIS-Raman (CCD)	FT-IR	Grating FT-NIR AOTF Diode-array

FIGURE 2.7 The current monochromator/detection principles of scanning Raman, MIR, and NIR spectrometers.

techniques are presently in current use:

1. Excitation by a VIS-laser (in the range from 400 to 800 nm) combined with monochromatization of the scattered radiation by a holographic grating and simultaneous detection of the dispersed, narrow frequency ranges by a charge-coupled device (CCD) detector.
2. NIR-laser excitation (1064 nm) and measurement in a Fourier-Transform (FT) spectrometer.

In Figure 2.4 the trends of the main limiting factors — fluorescence and low scattering efficiency — have been outlined with reference to the two excitation mechanisms. Thus, both alternatives establish only compromises and the choice of the applied technique depends on the individual problem.

If a molecule is irradiated with visible radiation, it may be excited to an energy level of the next higher electronic state. Return to the ground state or an excited vibrational level of the original electronic state can easily proceed via fluorescence as shown in Figure 2.4. Thus, for a large proportion of samples, irradiation with visible light causes strong fluorescence by additives or impurities (or by the sample itself), which will superimpose and in many cases inundate the Raman spectrum of the sample. The use of NIR-laser excitation confers a number of advantages on a Raman system. Both fluorescence and self-absorption are very much reduced in the Raman signal, and, owing to the lower energy of the excitation radiation, thermal degradation is also less of a problem. However, these advantages are partly neutralized by the disadvantages of using a low-frequency laser as the source.

The NIR-Raman technique is obviously less sensitive due to the ν^4 -dependence of the scattering efficiency (Figure 2.4). Thus, a shift of the excitation line from the VIS region (e.g., Ar⁺-ion laser, 488 nm/20,492 cm⁻¹) to the NIR region (1064 nm/9398 cm⁻¹) reduces the scattering intensity. At 0 cm⁻¹, the sensitivity of a Nd-YAG laser is 23 times lower than that of an Ar laser, and at

$4,000\text{ cm}^{-1}$ this factor has increased to 87 [3,41,42]. As shown in Figure 2.7, however, NIR-Raman spectroscopy is performed on FT-spectrometers, and the sensitivity loss can be compensated by accumulation of multiple scans. As a valuable compromise to suppress fluorescence and at the same time retain an acceptable scattering efficiency, excitation with a diode laser at 785 nm (12739 cm^{-1}) is increasingly used [10,19–21].

As far as MIR spectroscopy is concerned, today almost exclusively FT-based instruments with different interferometer designs are in routine use (Figure 2.7). Contrary to Raman and MIR spectroscopy, scanning NIR spectroscopy offers the largest multiplicity of monochromator/detection principles. Thus, apart from different designs with moving parts, such as grating instruments and FT-spectrometers with Michelson or polarization interferometers (with NIR-transparent quartz wedges) two fast-scanning approaches with no moving parts are available: diode-array systems and acousto-optic tunable filters (AOTF) [10]. Recently, a micro-electro-mechanical-system (MEMS) FT-NIR spectrometer based on a Fabry–Perot interferometer that combines a high spectral resolution and rapid-scanning capability has been brought to the market [43]. Although miniaturization has already progressed significantly with AOTF and diode-array spectrometers, the last mentioned system has launched NIR spectroscopy in a new era of miniaturization and microfabrication technology.

2.2.5 IMPORTANT ASPECTS FOR THE IMPLEMENTATION OF RAMAN, MIR, AND NIR SPECTROSCOPY IN PROCESS CONTROL

In Figure 2.6, the most important aspects for the implementation of the individual spectroscopies as process-monitoring tools are addressed. The very small, representative sample volume or thickness in Raman and MIR/ATR spectroscopy may certainly lead to problems if special care is not taken to avoid the formation of a stationary layer on the reactor window or on the ATR crystal. In this respect, NIR spectroscopy is the method of choice in view of the comparatively large sample volume/thickness involved in these measurements. The ability to separate the spectrometer from the point of sampling is certainly a great advantage for Raman and NIR spectroscopy.

Although light fibers based on chalcogenides, ZrF_4 , and AgCl are also available for MIR spectroscopy, it should be mentioned that their cost, attenuation properties, and mechanical stability are still inferior compared with the well-established quartz fibers. Specific probes are available for all three techniques. NIR spectroscopy offers an especially wide range of in-line, on-line, and at-line transmission and diffuse-reflection probes designed for the measurement of liquids and solids. Large differences can also be identified with respect to the ability of measuring aqueous solutions. Water is an extremely strong absorber in the MIR and also a strong NIR absorber, thereby limiting the available wave number regions in both techniques.

In contrast, it is a weak Raman scatterer and it is recommended to consider Raman spectroscopy as an analytical alternative for aqueous solutions. Care has to be taken, however, with the NIR-Raman FT-technique ($1064\text{ nm}/9398\text{ cm}^{-1}$), because, owing to the absorption of the water-overtone vibration at about 7000 cm^{-1} , the Raman spectrum may be modified relative to the VIS-laser excited Raman spectrum [44].

2.3 CONCLUSION

Over the past years MIR, NIR, and Raman spectroscopy have been further developed to a point where each technique can be considered a potential candidate for industrial quality-control and process-monitoring applications. However, adding up the specific advantages and disadvantages of the individual techniques, NIR spectroscopy is certainly the most flexible and advanced alternative.

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3 Continuum and Discontinuum Theories of Diffuse Reflection

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3.1 INTRODUCTION

The use of near-infrared (NIR) diffuse reflection for the quantitative analysis of products and commodities is now widely accepted. For many of the algorithms developed to achieve multi-component determinations from the diffuse reflection spectra of powdered samples, a linear dependence of band intensity on analyte concentration is not absolutely mandatory for an analytical result to be obtained. Nonetheless it is probably true to say that all of these algorithms yield the most accurate estimates of concentration when the intensity of each spectral feature is linearly proportional to the analyte concentration. In an analogous manner to transmission spectrometry, reflectance is input to most of these algorithms as $\log(1/R')$, where R' is the reflectance of the sample relative to that of a nonabsorbing standard, such as a ceramic disk. The use of $\log(1/R')$ as the preferred ordinate is contrary to what most physical scientists would consider appropriate for a diffuse reflection measurement on an optically thick sample. Thus an understanding of the theories of diffuse reflection and the validity of the assumptions for each theory should be helpful in understanding the strengths and limitations of NIR diffuse reflection. Perhaps, it will even help to explain why accurate analyses may be made when band intensities are expressed as $\log(1/R')$.

The *continuum* theories of Schuster and of Kubelka and Munk are presented in some detail in this chapter along with a summary of the discrete ordinate approximation of the radiation transfer equation and the diffusion approximation. Together with some of the earlier work on light scattering, an understanding of the importance of the assumptions in arriving at the final solutions that are experimentally valid can be achieved. To a greater or lesser extent, all continuum theories describe model systems and require certain assumptions, such as negligibly small particle size, that are not valid in practice. Several of the drawbacks of these models may be overcome by the use of *discontinuum* models in which the assumptions of a homogenous sample composed of infinitesimally small particles are not invoked. These models are discussed in some detail in the final part of this chapter.

3.2 DIFFUSE VS. DIRECTED RADIATION

The descriptions of diffuse reflection assume that there is a unique direction of light incident upon the sample, and that a plane perpendicular to this direction passes through the sample. A beam of light is called *directed* or *collimated* if all the light is going in a direction perpendicular to the plane of the sample. We then say that the sample is *directly illuminated*. Most commercial spectrometers, to a reasonable approximation, produce a directed incident beam. Light that is scattered from the sample toward a detector on the opposite side of the sample is said to be detected *in transmission*. Light that is scattered from the sample toward a detector on the same side of the sample is said to be detected *in reflection*. If the angle of reflection is equal to the angle of incidence, the reflection is said to be *specular*. Radiation reflected at all other angles is *diffuse*. The sum of the specularly and diffusely reflected radiation is the *remitted* radiation. For samples with a matte finish, especially powdered samples, the specularly reflected radiation is generally of low intensity. Hence measurement of the radiation from this type of sample is frequently known as *diffuse reflection spectrometry*.

3.2.1 LAMBERT COSINE LAW

The phenomenon of diffuse reflection is easily observed in everyday life. Consider for example the intensity of radiation reflected from a completely matte surface such as a sheet of white paper. The remitted radiation is everywhere of the same intensity no matter what the angle of observation or angle of incidence is. It was the same observation that led Lambert [1] to be the first to attempt a mathematical description of diffuse reflection. He proposed that the remitted radiation flux I_r in an area f cm² and solid angle ω steradians (sr) is proportional to the cosine of the angle of incidence α

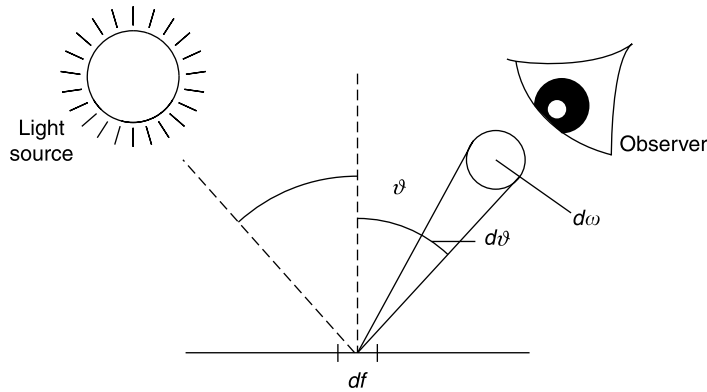


FIGURE 3.1 Schematic representation showing variables used in the Lambert cosine law.

and the angle of observation ϑ (see Figure 3.1), that is,

$$\frac{dI_r/df}{d\omega} = \frac{CS_0}{\pi} \cos \alpha \cos \vartheta = B \cos \vartheta \quad (3.1)$$

where S_0 is the irradiation intensity in W/cm^2 for normal incidence, B is the radiation density or surface brightness in $\text{W}/\text{cm}^2/\text{sr}$, and the constant C is the fraction of the incident radiation flux that is remitted. C is generally less than 1 since some radiation is always absorbed.

Equation (3.1) is known as the Lambert cosine law and, according to Kortüm [2], can be derived from the second law of thermodynamics, although Wendlandt and Hecht [3] disagree. According to Kortüm, it is rigorously valid only for a black-body radiator acting as an ideal diffuse reflector (i.e., the angular distribution of the reflected or remitted radiation is independent of the angle of incidence). It is, however, contradictory to call a black-body radiator an ideal diffuse reflector since all incident radiation is absorbed by a black-body and none is absorbed by an ideal diffuse reflector. An ideal diffuse reflector has never been found in practice and therefore deviations (large and small) always occur from the Lambert cosine law. Various workers, including Wright [4] and Pokrowski [5–8], have reported the results of experimental investigations that were designed to prove or disprove the Lambert cosine law. They found that in general the law holds true only when both the angle of incidence α and the angle of observation ϑ are small.

3.3 ABSORPTION AND SCATTER BY A SINGLE PARTICLE

The terminology used to describe the interaction of light and matter is rather dependent on the size and shape of the particle(s). This is because in limiting situations, some of which we encounter every day, what is observed depends on the nature of the reflecting medium. For example, we see our image in a mirror and call it a *reflection*. In this case, the “particle” has a large flat smooth surface. We look at a glass of milk and say that the white color is a result of the scattering of light by particles or oily droplets in the milk.

When one is describing the interaction of light in situations other than these limiting cases, the result can be somewhat confusing. Terms used by those who study this interaction are described below. The thing that is in common for all the situations is that some of the light may be lost to *absorption*.

When a beam of light is incident on a particle with large flat, smooth surfaces, the word *reflection* describes the process by which light is remitted from the (front) surface. We refer to the passage of light through the particle as *transmission*. If the light entering the particle hits the surface at an

angle, we call the bend in the light path at the surface as *refraction*. A treatment that uses these terms is called *geometric optics*.

When light encounters a very small particle, light is said to be *scattered* by the particle. It might be *back-scattered*, somewhat like reflection, or *scattered in the forward direction*, somewhat like transmission, but here the term *diffuse transmission* refers to the intensity of a *directed* beam of light after it has encountered a collection of particles compared to what it was at the macroscopic surface of the particles. Some of the light is lost to absorption by the particles and some to scatter by the particles, and the rest of the beam is transmitted. The sum of the effects of absorption and scatter is called *extinction*.

What for the case of small particles is called *backward* and *forward scatter* is, for the case of particles with large, flat surfaces, the sum of *reflection* and *transmission*. For infinitesimally small particles, *continuum theories* of diffuse reflection may be applied. As particles get larger, it becomes more likely that the terms for geometrical optics will be applied and *discontinuum theories* are more relevant.

A theory developed by Stokes in the 1860 is generally accepted as describing absorption, remission and transmission by plane parallel layers (sheets). Discussion of this theory is contained in the section on discontinuum theories, along with the discussion of an assembly of sheets. There is no generally accepted theory that describes the absorption and scatter by a collection of spheres as an assembly, although a brief discussion of Melamed's theory is also contained in the discontinuum section. There is, however, a good theoretical description of absorption and scatter by a single, isolated sphere, the cornerstone of which is Mie theory.

3.3.1 MIE SCATTERING

One of the more generally accepted theories of the scattering of light was developed around 1900 by Mie [9]. Mie scattering relates primarily to the scattering of radiation by isolated particles. Only a very brief introduction will be given here, although Kortüm [2] has presented a less abbreviated description. (The reader is referred to References 10–12 for a comprehensive survey, not only of Mie theory but also the theories of Rayleigh, Gans, Born, and others.) Mie obtained solutions to the Maxwell equations [3] that describe the angular distribution of both the intensity and the polarization of scattered radiation for a plane wave scattered once (single scattering) by a particle that can be both dielectric and absorbing. In Mie's description, the particle was spherical, with no limitation on its size. He showed that the angular distribution of scattered radiation for single scattering is not isotropic. The basic equation that was developed by Mie is

$$\frac{I_{\theta s}}{I_0} = \frac{\lambda^2}{8\pi^2 R^2} (i_1 + i_2) \equiv q(\theta_s) \quad (3.2)$$

where $I_{\theta s}$ is the scattered intensity at angle θ at a distance R from the center of the sphere; I_0 is the intensity of the incident radiation, and λ is the wavelength of the incident radiation. The symbols i_1 and i_2 represent complicated functions of the angle of the scattered radiation, the spherical harmonics or their derivatives with respect to the cosine of the angle of scattered radiation, the refractive index of both the sphere and its surrounding medium, and the ratio of the particle circumference to wavelength. Equation (3.2) applies only to the case of a dielectric nonabsorbing particle and unpolarized incident radiation. If the particle is absorbing, the complex refractive index must be used in the determination of i_1 and i_2 .

Mie theory, although general for spherical particles of any size, is valid only for single scattering and therefore directly applicable only to chemical systems in which particles are well separated. For example, scattering by the gases of the atmosphere (the molecules of which are well separated) is a special case of Mie theory, that is, the case where the particle is much smaller than the wavelength of incident radiation. The theory of scattering by particles of this type was developed and explored

by Rayleigh [13,14]. In fact, Kortüm stated that “Rayleigh scattering constitutes a limiting case of the Mie theory for very small particles if only dipole radiation is taken into account” [2].

Mie theory describes the fraction of light that is scattered by a spherical particle in terms of its linear absorption coefficient and the difference between the refractive index of the particle and that of the medium in which it is suspended. It does so uniquely for scatter in every direction. There are some generalizations about the results:

1. For very small particles, the total scatter in the forward direction is equal to the total scatter in the backward direction. (The scatter is mirrored in the forward and backward directions, though not equally at all angles.)
2. For large particles, the scatter in the forward direction is much larger than the scatter in the backward direction.
3. For particles having a size that is a small multiple of the wavelength, there are diffraction ripples in the scattered intensity that can be significant enough to be observed.

There are additional characteristics of radiation that has been scattered from spheres that also have to do with the wave character of light. Let us assume that we have a particle that is large compared to the wavelength of the light. It is then meaningful to talk about reflection from the surface of the sphere, and refraction of the light that enters the sphere. If the absorption of the material of which the particle is composed is large enough, all of the light that enters the sphere is absorbed. The sphere is then *opaque*, and will cast a shadow. However some of the light scattered by the edges of the particle will be diffracted to the center of the shadow of the particle forming diffraction rings. When the incident radiation is a plane wave, this is called a Fraunhofer diffraction pattern, shown in Figure 3.2.

Using the terms of geometric optics, we say that the light that is incident upon the particle is all accounted for by reflection from the external surface of the sphere, the absorption by the sphere and light transmitted through the sphere. The diffraction pattern arises because there is additional light, not directly incident on the sphere, that is scattered by the sphere. In cross section, this light is within a circle around the sphere. The circle has twice the area as the cross section of the sphere, and has a radius of 1.4 times that of the sphere [15]. The area between the cross section of the sphere and the circle is equal to the cross-sectional area of the sphere. The light incident on this area gives rise to the diffraction pattern.

Most applications of NIR reflection analysis involve samples for which it is expected that multiple scattering will take place within the sample. After multiple scattering events, the special effects of scattering from individual spheres tend to be lost. The investigations of Theissing [16] assumed multiple scattering from particles that were sufficiently well separated that interference and phase

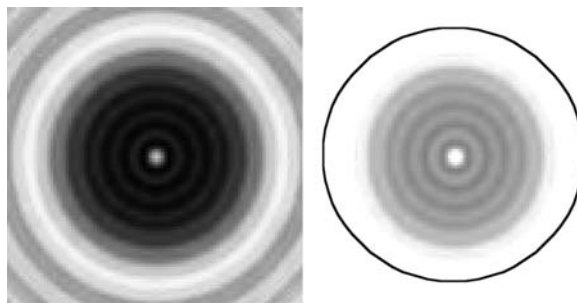


FIGURE 3.2 A Fraunhofer diffraction pattern under two different contrast levels. The circle drawn around the right hand pattern has a radius 1.5 times that of the geometrical shadow of the object. The area between the shadow and the circle represents the area from which the light to form the pattern is obtained. (The patterns were calculated using the Fresnel Diffraction Explorer, which may be obtained from Dager Research: <http://daugerresearch.com/>)

differences between the scattered radiation from the various particles are negligible. *Scattering order* was defined as the number of times a photon is scattered. Theissing found that with an increase in the order of scatter, the forward scattering predicted by Mie theory decreases and the angular distribution of scattered radiation tends to be isotropic. He also found that the larger the ratio of particle circumference to wavelength (designated p), the greater must be the order of scatter to produce an isotropic distribution. For example, if p is 0.6 and the ratio of the refractive index of the sphere to its surrounding medium (designated m) is 1.25, twofold scattering is required for an isotropic distribution of the reflected radiation. But if $p = 5$ and $m = 1.25$, a scattering order of 8 is required for isotropic reflection of radiation. (As a qualitative result, the above is not surprising, given that if a sample is thick enough, almost all the scatter from a collection of spheres is in the backward direction.)

The diameters of particles that are examined by NIR diffuse reflection spectrometry are typically fairly large, on the order of 100 μm , and so p will be large. It is expected that for a sufficiently large number of particles and a sufficiently thick sample (the bounds necessary to define what is sufficient being unknown), multiple scattering does occur for most samples of the type used for NIR reflection analysis. This means that for both already established applications of NIR reflection analysis and potential applications being considered, a theory for multiple scattering within a densely packed medium is required to describe quantitatively the change in reflectance with a change in concentration.

For most samples of the type for which NIR reflection analysis may be possible, the scattering density is large, the ratio of particle circumference to wavelength is much greater than 1, and the particles are so densely packed that the phase relations and interference between scattered beams cannot readily be described. Thus for samples of this type, no general quantitative solution to the problem of multiple scattering has been found. In this case, the scientist must resort to the use of phenomenological theories. (Once the reader has reached the section on discontinuum theories, it will be seen that these theories often have more in common with the theory described for sheets than for spherical particles.) Several of the continuum theories have been rather consistently represented as being a two-flux approximation to the equation of radiative transfer (ERT) (which they are). In the following section, we will occasionally make reference to what they have in common with the theory of sheets.

3.4 CONTINUUM THEORIES OF DIFFUSE REFLECTION

3.4.1 TWO-FLUX TREATMENTS

Much work that has been done on two-flux treatment of the diffuse reflection of radiation has evolved from a general radiation transfer equation. In simple terms, a radiation transfer equation can be written as

$$-dI = \kappa \rho I ds \quad (3.3)$$

An equation such as this describes the change in intensity, dI , of a beam of radiation of a given wavelength in a sample, the density of which is ρ and for which the pathlength is ds . κ corresponds to the attenuation coefficient for the total radiation loss whether that loss is due to scattering or absorption. The general form of the radiation transfer equation that is used in the derivation of most phenomenological theories considers only plane-parallel layers of particles within the sample and can be written as

$$\mu \frac{dI(\tau, \mu)}{d\tau} = -I(\tau, \mu) + \frac{1}{2} \omega_0 \int_{-1}^{+1} p_0(\mu, \mu') I(\tau, \mu') d\mu' \quad (3.4)$$

where μ is the cosine of the angle ϑ with respect to the inward surface normal; μ' is the cosine of the angle ϑ with respect to the outward surface normal; $d\tau$ is the optical thickness and is equal to

$\kappa\rho dx$ where dx is the distance between the boundaries of one plane-parallel layer; I is the intensity of the beam of radiation striking the layer; $\omega_0 = \sigma/(\sigma + \alpha)$ is the albedo* for single scattering, with the scattering and absorption coefficients σ and α , respectively. The scattering phase function $p_0(\mu, \mu')$ denotes the probability for scattering from direction μ' into μ . If every element scatters isotropically, $p_0(\mu, \mu') = 1$ and is independent of the angle between the incident radiation and the scattered radiation. Chandrasekhar has published extensively on radiation transfer and his work is summarized in Reference 17. Other authors who have contributed to the literature on this topic more recently are Truelove [18] and Incropera et al. [19].

3.4.2 SCHUSTER'S THEORY

Schuster was interested in the astrophysical problem of radiation passing through interstellar space. He envisioned a dilute suspension of particles, in which the particles were luminescent, in addition to being absorbing and scattering. The derivation below follows Kortüm [2] in that the luminescence terms are not included. Kortüm calls α (the fraction of light incident upon a particle that is absorbed) the true absorption coefficient of single scattering and σ (the fraction of light incident upon a particle that is scattered) the scattering coefficient for single scattering. It is important to note that this is not what spectroscopists usually mean by a coefficient. In spectroscopy, the coefficient is that quantity, which when multiplied by a pathlength, is used in the calculation of the fraction of incident light that is absorbed or scattered. When the fractions themselves are used as the coefficient (as was done by Kortüm), the unit of thickness of the coefficient is implied to be the particle diameter. Thus coefficients of single scattering are really probabilities.

The classic paper *Radiation Through a Foggy Atmosphere* published in 1905 by Schuster [20] described a particle theory designed to solve a particular problem. However, it was described by Kortüm as an attempt to find a solution of the radiation transfer equation by using the simplified assumption of two oppositely directed radiation fluxes. Radiation traveling in a forward direction through a sample (forward with respect to the direction of the incident radiation) is designated as I . Radiation traveling in the opposite direction is labeled as J . With this simplification, Schuster derived the following two differential equations:

$$\frac{-dI}{d\tau} = (k + s)I - sJ \quad (3.5)$$

$$\frac{dJ}{d\tau} = (k + s)J - sI \quad (3.6)$$

where

$$k = \frac{2\alpha}{\alpha + \sigma} \quad (3.7)$$

and

$$s = \frac{\sigma}{\alpha + \sigma} \quad (3.8)$$

The symbol s used by Schuster is identical to the albedo ω_0 for single scattering. It is relevant to discuss a coefficient of single scattering for a continuum model in that these coefficients relate to the reflectance measured as if the particles in the model were “exploded” apart so that only single scattering could occur.

* In other disciplines, the *albedo* of an object refers to its optical reflectivity, that is, the extent to which it reflects light.

If the boundary conditions are set as

$$I = I_0 \quad \text{at } \tau = 0$$

$$I = I_{(\tau)} \rightarrow 0; \quad J = 0 \quad \text{at } \tau = \tau \quad \text{for } \tau \rightarrow \infty$$

Equations (3.5) and (3.6) are strictly valid only for an *ideally diffusing medium* where there is no change in the degree of dispersion of the light within the sample. The differential equations for the radiant flux in an ideally diffusing medium can be readily integrated. Solutions displayed immediately below may be obtained subject to the boundary conditions that:

1. the intensity of flux I is equal to the incident intensity at a penetration depth of zero, and
2. the intensity of both I and J is zero at “infinite depth,” that is, the sample thickness at which there is no further change in the measured diffuse reflection.

$$R_{\infty} = \frac{J_{(\tau=0)}}{I_0} = \frac{1 - (k/(k + 2s))^{1/2}}{1 + (k/(k + 2s))^{1/2}} \quad (3.9)$$

This equation can be rewritten as

$$\frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} = \frac{2\alpha}{\sigma} \quad (3.10)$$

Equation (3.10) gives the reflectance behavior for isotropic scattering when two oppositely directed radiation fluxes are assumed in the direction of the surface normal. The function $((1 - R_{\infty})^2/2R_{\infty})$ is commonly known as the Kubelka–Munk (K–M) function and is usually given the symbol $f(R_{\infty})$, although it is interesting to note that in their original paper [21], Kubelka and Munk did not derive this expression. Kubelka actually published the derivation of this equation [22] 17 years later.

We may imagine that the “foggy atmosphere” above is divided into layers, each containing a number of particles. In the limit of infinite dilution, there will be one particle in such a layer. For such a condition, there can be no multiple scatter between particles in the same layer. The above formulation carries with it an implicit assumption that the fraction $(\alpha + \sigma)$ is insignificant compared to 1. This limitation is somewhat relieved by the discontinuous solution

$$f(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} = \frac{\alpha(2 - \alpha - \sigma)}{\sigma} \quad (3.11)$$

This is the discontinuous equivalent of the Schuster equation for isotropic scatter.

3.4.3 KUBELKA–MUNK THEORY

Kubelka and Munk [21] obtained a solution to the radiation transfer problem similar to Schuster’s. While Schuster was considering a “foggy atmosphere,” Kubelka and Munk were considering the “optics of paint layers.” There are significant differences in the way the problem was set up, the most notable being that that Kubelka and Munk solved their differential equations for the case of remission, not isotropic scatter. Their solution resulted in an equation for remission from an infinitely thick coating expressed in terms of the probability of events in an infinitesimal layer of the coating that absorbs (a) and remits (r) a certain constant portion $a \, dx + r \, dx$ of all the light passing through it, where a , the absorption constant and r , the scattering constant, are specific constants of the coating under consideration. You will notice similarity of this approach to that of Dahm and Dahm as shown in Equation (3.83).

In later work, Kubelka [22] published a treatment that is applicable to spectroscopy, which is generally referred to as the K–M theory. It is this later work that we will describe here, following the

treatment of Kortüm [2]. The solution shown here will be obtained through an exponential derivation. A detailed description of a hyperbolic solution can be found in Reference 2.

Unlike Schuster, Kubelka envisioned using the solution for dense systems. While Schuster defined the two constants k and s in terms of the absorption and scattering coefficients for single scattering, Kubelka simply defines K and S in the equations as absorption and scattering coefficients for the densely packed sample as a whole. A tabulation of the variables that are used in their derivation is found in Table 3.1. Figure 3.3 shows a schematic representation of the type of system for which Kubelka and Munk derived their solution.

We will first describe how Kubelka and Munk arrived at the two fundamental differential equations that, once solved, give the simplified solution similar to the one in Equation (3.10). Their stated

TABLE 3.1
Variables Used in the Development of Kubelka's Simplified Solution to the Radiation Transfer Equation

d	Sample layer thickness
$+x$	Downward direction through the sample
$-x$	Upward direction through the sample
$x = 0$	Illuminated surface
$x = d$	Unilluminated surface
I	Radiant flux in $+x$ direction
J	Radiant flux in $-x$ direction
I_0	Incident flux
ϑ	Angle at which a particular ray traverses through dx
dx	An infinitesimal layer
$dx / \cos \vartheta$	Pathlength of a particular ray traversing dx
$d\xi_I$	Average pathlength of radiation passing through dx in the $+x$ direction
$\partial x / \partial \cos \vartheta$	Angular distribution of I 's intensity in the $+x$ direction
$d\xi_J$	Average pathlength of radiation passing through dx in the $-x$ direction
E	Fraction of radiation absorbed per unit pathlength in the sample
σ	Fraction of radiation scattered per unit pathlength in the sample

Note: Neither ε or σ are exactly the same as the corresponding parameters defined by Schuster.

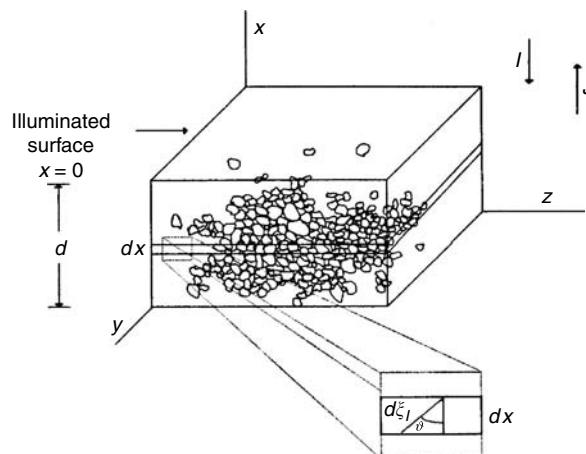


FIGURE 3.3 Schematic representation of a sample for which the K–M equation was derived. Consider the cube as a sample throughout which the particles (only shown in a portion of the sample) are randomly distributed.

assumptions are on page 33. Since they were modeling a dense, particulate system, they needed to take two factors into account. First, because the system was particulate, scattering would diffuse directed radiation. Consequently, in order to avoid the untenable situation that radiation would start out directed and become diffuse during the course of a measurement, they considered systems for which the irradiation began as diffuse. Second, they modeled the particulate system as a sheet, though the word layer is used in Table 3.1. The thickness of the layer is dx , and the continuous mathematics requires that thickness of the layer be infinitesimal. Since the angle through dx , ϑ , that the path of the radiation might follow can be between 0 and 90°, the average pathlength for radiation passing through dx in the $+x$ direction can be found by the following integral:

$$d\xi_I = dx \int_0^{\pi/2} (\partial I / I \partial \vartheta) (d\vartheta / \cos \vartheta) \equiv u dx \quad (3.12)$$

The above formulation holds for a sheet with no voids and for which there are no scattering points within the layer. Kortüm has shown that if the layer were comprised of scattering and absorbing points (i.e., particles of infinitesimal size), the average pathlength through the layer would be twice the geometrical thickness of the layer. Now, if the layer were composed of spherical particles (and an assumption of single scatter within the layer were made) the pathlength through the particles would be unchanged by the angle of incidence on the layer. For real particles we would expect the effect of diffuse radiation to be somewhere between no change and the factor of two increase.

If no absorption or scattering has occurred, the illumination of the layer dx could be described by

$$I d\xi_I = Iu dx \quad (3.13)$$

Since, however, absorption and scattering do occur, the decrease in intensity of the illumination of dx can be shown by including a combination of absorption and scattering coefficients:

$$\begin{aligned} (\varepsilon + \sigma) I d\xi_I &= (\varepsilon + \sigma) Iu dx \\ &= \varepsilon Iu dx + \sigma Iu dx \end{aligned} \quad (3.14)$$

The term $\varepsilon Iu dx$ represents that component of the radiation that is absorbed while the term $\sigma Iu dx$ represents that component of the radiation that is scattered. Radiation traveling in the $-x$ direction (the J flux) also has a corresponding average pathlength through dx

$$d\xi_J = dx \int_0^{\pi/2} (\partial J / J \partial \vartheta) (d\vartheta / \cos \vartheta) \equiv v dx \quad (3.15)$$

Again, if no absorption or scattering were to take place for radiation traveling in this direction, then the illumination of the layer dx in the $-x$ direction would be described by

$$J d\xi_J = Jv dx \quad (3.16)$$

The corresponding equation can be written for the absorption and scattering that occurs for the J radiation flux:

$$(\varepsilon + \sigma) J d\xi_J = (\varepsilon + \sigma) Jv dx = \varepsilon Jv dx + \sigma Jv dx \quad (3.17)$$

Similarly to Equation (3.14), the term $\varepsilon Jv dx$ corresponds to that part of the radiation which is absorbed while the term $\sigma Jv dx$ corresponds to that part of the radiation which is scattered. It is necessary to know, however, the actual change dI or dJ in the radiation fluxes, I and J , which were incident on the layer dx , respectively, after traversing dx . Not only does the absorption and

scattering of the forward radiation flux affect I , but the component of the scattered J radiation flux will also affect I and therefore dI . The same correlation can be made for J and therefore for dJ . It must therefore be true that

$$-dI = \varepsilon u I dx - \sigma v I dx + \sigma u J dx \quad (3.18)$$

$$-dJ = \varepsilon u J dx - \sigma v J dx + \sigma u I dx \quad (3.19)$$

The signs in the above equations are indicative of the fact that as x increases I must decrease and J must increase.

If the sample is an ideal diffuser, then the angular distribution of the radiation flux through a plane layer dx in a given direction is

$$-\frac{\partial I}{\partial \theta} = I \sin 2\theta = 2I \sin \theta \cos \theta \quad (3.20)$$

$$\frac{\partial J}{\partial \theta} = J \sin 2\theta = 2J \sin \theta \cos \theta \quad (3.21)$$

These expressions can then be substituted into Equation (3.11) and Equation (3.14) describing the average pathlength of radiation through dx to solve for this quantity. Doing so we find that $d\xi_I = u = 2$. Likewise, $d\xi_J = v = 2$. If we now substitute for u and v in the differential Equation (3.18) and Equation (3.19) we obtain:

$$-dI = 2\varepsilon I dx - 2\sigma I dx + 2\sigma J dx \quad (3.22)$$

$$dJ = 2\varepsilon J dx - 2\sigma J dx + 2\sigma I dx \quad (3.23)$$

Using Kortüm's notation [2], the absorption coefficient of the material k is equal to ε and the scattering coefficient of the material s is equal to σ . We can then designate $K = 2k$ and $S = 2s$ to obtain the two fundamental simultaneous differential equations from which a simplified solution to the general radiation transfer equation can be found:

$$-dI = K dx - SI dx + SJ dx \quad (3.24)$$

$$dJ = KJ dx - SJ dx + SI dx \quad (3.25)$$

It should be noted here that Kubelka and Munk define scattering differently than does Mie (or Schuster). Mie defines scattering as radiation traveling in any direction after interaction with a particle. Kubelka and Munk defined scattered radiation as only that component of the radiation that is backward reflected into the hemisphere bounded by the plane of the sample's surface. In effect, the defining of S as equal to $2s$ makes S an isotropic scattering coefficient, with scatter equal in both the forward and backward directions.

It may also be noted that, subject to the conditions of infinitesimal particle size, the above differential equations will still hold true even if collimated radiation at an angle of 60° to the surface normal is used instead of diffuse irradiation since for an incident angle of 60° :

$$d\xi_{IJ} = \frac{dx}{\cos 60^\circ} = \frac{1}{0.5} = 2 = u = v \quad (3.26)$$

The differential equations can be simplified by setting

$$\frac{S + K}{S} = 1 + \frac{K}{S} \equiv a \quad (3.27)$$

and $J/I \equiv r$. The simplified form of Equation (3.22) and Equation (3.23) then becomes

$$-dI/S dx = -aI + J \quad (3.28)$$

$$dJ/S dx = -aJ + I \quad (3.29)$$

Dividing the first equation by I and the second equation by J , and then adding the two equations, it is found that

$$dr/S dx = r^2 - 2ar + I \quad (3.30)$$

Using the principle of separation of variables to solve differential equations we obtain

$$I(r^2 - 2ar + 1)^{-1} dr = S dx \quad (3.31)$$

Since the integration must be done over the entire thickness of the sample, the boundaries are

$$x = d: (J/I)_{x=d} = R_g = \text{reflectance of the background} \quad (3.32)$$

$$x = 0: (J/I)_{x=0} = R = \text{reflectance of the sample} \quad (3.33)$$

Equation (3.31) can be integrated using partial fractions where the first step in the fractionation is

$$\frac{dr}{(r^2 - 2ar + 1)} = \frac{1}{(r + (2ar - 1)^{1/2})(r - (2ar - 1)^{1/2})} dr \quad (3.34)$$

The solution of Equation (3.31) can then be found to be

$$\ln \frac{(R' - a - (a^2 - 1)^{1/2})(R_g - a + (a^2 - 1)^{1/2})}{(R_g - a - (a^2 - 1)^{1/2})(R - a + (a^2 - 1)^{1/2})} = 2Sd(a^2 - 1)^{1/2} \quad (3.35)$$

Since it is assumed that the layer is of infinite depth, that is, $d = \infty$ and $R_g = 0$, Equation (3.35) is reduced to

$$(-a - (a^2 - 1)^{1/2})(R_\infty - a(a^2 - 1)^{1/2}) = 0 \quad (3.36)$$

which can be solved for the reflectance R_∞ :

$$R_\infty = \frac{1}{a + (a^2 - 1)^{1/2}} = \frac{1}{1 + K/S + ((K/S)^2 + 2K/S)^{1/2}} \quad (3.37)$$

Rearranging Equations (3.37) in terms of the ratio K/S we obtain an equation similar to the one derived from the work of Schuster:

$$\frac{(1 - 2R_\infty + R_\infty^2)}{2R_\infty} = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \quad (3.38)$$

The above derivation is mathematical and is valid subject to the limitations of the mathematics used. Several assumptions were made, either explicitly or implicitly, in Kubelka's derivation. Most of these should not be viewed as assumptions upon which his solution depended, but rather as a description of the kind of experimental arrangement and samples to which the equations they derived would be

most applicable. The assumptions are listed below:

1. The radiation flux (I and J) travels in two opposite directions.
2. The sample is illuminated with monochromatic radiation of intensity I_0 .
3. The distribution of scattered radiation is isotropic so that all regular (specular) reflection is ignored.
4. The particles in the sample layer (defined as the region between $x = 0$ and $x = d$ are randomly distributed.
5. The particles are very much smaller than the thickness of the sample layer d .
6. The sample layer is subjected only to diffuse irradiation.
7. Particles are much larger than the wavelength of irradiation (so that the scattering coefficient will be independent of wavelength), although if only one wavelength is to be used then this assumption is not relevant.
8. The breadth of the macroscopic sample surface (in the yz plane) is great compared to the depth (d) of the sample and the diameter of the beam of incident radiation (to discriminate against edge effects).
9. The scattering particles are distributed uniformly throughout the entire sample.
10. The absorption by any one particle is small (which is, of course, the case if the particles are infinitesimally small).

A few points might be made about the assumption of isotropic scatter. If there is specular reflection in the scatter, there may be preferential directions of travel through the sample, and the assumption of diffuse radiation will be violated. Assumption 3 points out that the effect of front-surface reflection is ignored in their treatment. This assumption has often been interpreted as meaning that forward and backward scatter from a particle are assumed to be equal. As stated above, related to Equation (3.24) and Equation (3.25), the assumption of isotropic scatter of this kind is also built into their treatment.

Subject to the assumption of infinitesimal particle size, the diffuse reflectance is a function only of the ratio of two constants, K and S , and not of their absolute values. For small particles (i.e., good approximations to infinitesimal particle size), Equation (3.38) can be used to quantitatively determine the concentration. If K is assumed to be proportional to the absorption coefficient obtained in transmission, the equation can be rewritten as shown in Equation (3.39), where a is the absorptivity of the analyte.

$$\frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \propto \frac{ac}{S} \quad (3.39)$$

While this is not an exact relationship, as many of the above assumptions are not accurately adhered to in practice, it is very useful for two reasons. First, other treatments of diffuse reflection do not allow R_∞ to be converted into a simple parameter that varies approximately linearly with the concentration of a component of a powdered sample (similarly to absorbance $[\log(1/T)]$ for transmission spectroscopy). If S can be assumed to be constant among a group of samples and the baseline of the spectrum is at a constant value (vide infra), this relationship can be used to quantitatively determine the concentration, c , of an absorbing analyte by preparing a “Beer’s law” plot of the K–M function vs. concentration.

Second, the relationship allows the effect of scattering on diffuse reflection spectra to be understood and forecast. Simply put, the greater the scattering, the weaker the absorption metric. This was demonstrated by Chaffin and Griffiths [23] who measured extended NIR diffuse reflection spectra of three types of polyethylene, a loosely packed powder (high S), an opaque high-density polyethylene (HDPE) bottle (intermediate S) and a translucent milk jug (low S). These spectra are shown in Figure 3.4. The intensity of the first harmonic of the C–H stretching mode at approximately

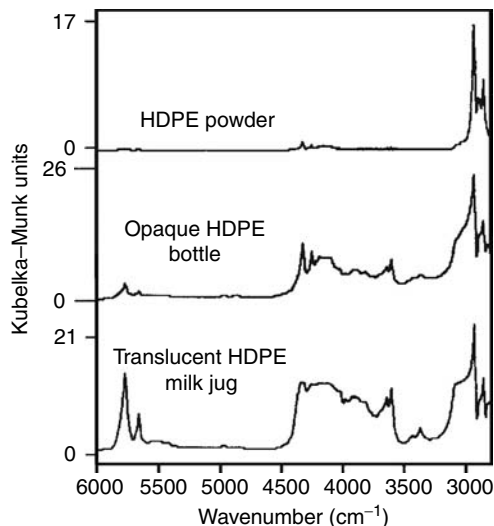


FIGURE 3.4 Extended NIR diffuse reflection spectra of various polyethylene samples. (Reproduced from N. C. Chaffin and P. R. Griffiths, *Appl. Spectrosc.*, 52: 218–221 (1998) by permission of the Society for Applied Spectroscopy Copyright 1998.)

5800 cm^{-1} is greatest for the spectrum of the sample with the lowest scattering coefficient and least for the sample with the highest scattering coefficient.

This result can be explained by a simple consideration of the path of the photons that are back-scattered (remitted) back to the detector. When the scattering coefficient is high, the scattered photons follow a short path in the sample before re-emerging from the face of the sample at which they entered. Thus the pathlength through the absorbing particles is short and the absorption bands are weak. Conversely, when the scattering coefficient is low, the remitted photons that reach the detector pass through many more absorbing molecules in the sample and the absorption bands are relatively strong.

Other scientists in the field [24–28] derived expressions similar to those of Schuster [20] and Kubelka and Munk [21]. Earlier theories developed by Gurevic [29] and Judd [30,31] were shown by Kubelka [22] to be special cases of the K–M theory, while Ingle [32] showed that the formulas derived by Smith [33], Amy [34], and Bruce [35] can be derived from the equations of Kubelka and Munk.

Because the simplified solution obtained by Kubelka is a two-constant equation and therefore experimentally testable, and because so many other workers' derivations are derivable from Kubelka and Munk's work, their solution is the most widely accepted, tested and used. Other workers have derived solutions to the radiation transfer equation that are more complicated than these two-constant formulas. For example, a third constant has been added to account for different fractions of forward and back scattering [36]. Ryde [37,38] included four constants since a difference in the scattering between incident light and internally diffused light is assumed, while Duntley [39] developed a model with eight constants, as a difference between both the absorption and scattering coefficients due to incident and internally diffused radiation was assumed. However, none of these theories is readily applicable in practice, and therefore the treatment of Kubelka is most often applied.

3.4.4 DISCRETE ORDINATE APPROXIMATION

Another two-constant approach, based on a discrete ordinate approximation of the radiation transfer equation [17,40] was recently applied to describe the diffuse reflectance in the NIR [41,42]. In this

approach, the integral in Equation (3.4) is approximated by a weighted sum over discrete directions (i.e., representing the diffuse radiation field inside the sample by radiation fluxes in distinct directions)

$$\int_{-1}^{+1} p_0(\mu, \mu') I(\tau, \mu') d\mu' = \sum_{j=-N}^N a_j p_0(\mu_i, \mu_j) I(\tau, \mu_j) \quad (3.40)$$

where the directions μ_j are chosen to be zeros of Jacobi polynomials

$$P_n^{(0,1)}(2\mu_j - 1) = 0 \quad (3.41)$$

with the corresponding coefficients a_j given by [40]:

$$a_j = \frac{1}{\mu_j^2 (1 - \mu_j) [P_n^{(0,1)'}(2\mu_j - 1)]^2} \quad (3.42)$$

Introducing Equation (3.40) into Equation (3.4) leads to system of differential equations:

$$\mu_i \frac{dI(\tau, \mu_i)}{d\tau} = -I(\tau, \mu_i) + \frac{\omega_0}{2} \sum_{j=-N}^{j=+N} a_j p_0(\mu_i, \mu_j) I(\tau, \mu_j) \quad (3.43)$$

For the case of three radiation fluxes ($j = -1, 0, +1$) the directions and coefficients are given by

$$\mu_{-1} = -\frac{2}{3}, \quad \mu_0 = 0, \quad \mu_{+1} = +\frac{2}{3}, \quad a_{-1} = \frac{3}{4}, \quad a_0 = \frac{1}{2}, \quad a_{+1} = \frac{3}{4} \quad (3.44)$$

and the system of three differential equations can be solved analytically to obtain the diffuse reflectance and transmittance as a function of the optical thickness τ and the albedo ω_0 [43]. With a given sample thickness d and the relations $[\tau = (\alpha + \sigma)d]$ and $[\omega_0 = \sigma/(\alpha + \sigma)]$, the diffuse reflectance and transmittance can also be described as a function of the scattering coefficient σ and the absorption coefficient α (here, the coefficients are defined according to the Mie theory).

In the case of a diffusely illuminated, isotropically scattering and optically thick sample (Kubelka and Munk's assumptions), the three-flux approximation yields the following relation between the ratio α/σ and the diffuse reflectance R_∞ [39]:

$$\frac{\alpha}{\sigma} = \frac{3}{8} \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{3}{8} \frac{K}{S} \quad (3.45)$$

The factor $\frac{3}{8}$ in Equation (3.45) is identical to the result of Mudgett and Richards [44], who related the ratio of the K–M absorption to scattering coefficient to the corresponding ratio of the Mie coefficients. This relationship may be obtained by simple geometrical considerations. The K–M K is an absorption coefficient for the two-flux case. You will recall that the K–M absorption coefficient is equal to twice the absorption coefficient for single scatter or $[K = 2\alpha]$. Then, as similarly written in Equation (3.10):

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{2\alpha}{\sigma} \quad (3.46)$$

Mie theory is for spheres of finite size, and the coefficients are for a point of infinitesimal size. For a finite object, the total absorption is related to the volume around this infinitesimal point, and the

scatter is proportional to the cross-sectional area of the object. Including these factors in the above equation, we obtain the two-flux description of absorption and scatter by a finite sphere:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{2\alpha(4/3\pi r^3)}{\sigma(\pi r^2)} = \frac{8\alpha r}{3\sigma} \quad (3.47)$$

Notice that the K–M function for a finite sphere is proportional to the radius of the sphere, and that the coefficients will change with particle size.

Unlike the Mie theory, the discrete ordinate approximation assumes that the sample is continuous matrix of points that absorb and scatter. The values for the coefficients obtained from the discrete ordinate approximation will also change and deviate substantially from the Mie coefficients as the particle size becomes large. This has been called the *hidden mass effect* [42].

To obtain solutions that are relevant for most common spectrometers, for which sample illumination is usually (almost) directional, the intensity $I(\tau, \mu)$ in Equation (3.4) is separated into the reduced incident intensity $I_{\text{dir}}(\tau, \mu)$ and a diffuse intensity $I_{\text{diff}}(\tau, \mu)$

$$I(\tau, \mu) = I_{\text{dir}}(\tau, \mu) + I_{\text{diff}}(\tau, \mu) \quad (3.48)$$

where $I_{\text{dir}}(\tau, \mu)$ is given by

$$I_{\text{dir}}(\tau, \mu) = \frac{F_0}{2\pi} e^{-\tau} \delta(\mu - 1) \quad (3.49)$$

with the directional impinging flux F_0 . Substituting Equation (3.47) and Equation (3.48) into the radiation transfer Equation (3.4) and taking advantage of the δ -function in the presentation of I_{dir} leads to the radiation transfer equation as a function of only the diffuse intensity I_{diff} plus a source function

$$\frac{\omega_0}{4\pi} p(\mu, 1) F_0 e^{-\tau} \quad (3.50)$$

which accounts for the attenuated incident radiation. A more detailed discussion and analytical expressions of the diffuse reflectance and transmittance as a function of τ and ω_0 can be found in the publication by Kuhn et al. [43]. In the case of a directly illuminated, isotropically scattering and optically thick sample, the three-flux approximation yields

$$\frac{\alpha}{\sigma} = \frac{(1 - R_\infty)^2}{2R_\infty} \frac{6}{5(R_\infty + 4)} \quad (3.51)$$

or its inverse

$$R_\infty = \frac{-(4(\alpha/\sigma) + (6/5)) + 2(4(\alpha^2/\sigma^2) + 3(\alpha/\sigma))^{1/2}}{2(\alpha/\sigma) - (6/5)} \quad (3.52)$$

3.4.5 DIFFUSION THEORY

A totally different approach to investigate the radiation transfer is the diffusion approximation, which is often used in biomedical applications [45,46]. The propagation of the photons in a sufficiently thick sample, with a scattering coefficient that is much larger than the absorption coefficient, can be described by a diffusion process (analogous to Fick's law of mass diffusion). Similar to

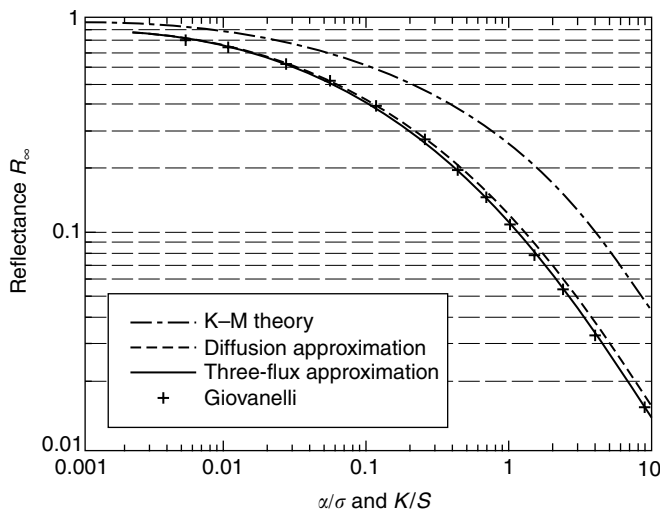


FIGURE 3.5 Diffuse reflectance R_∞ of an isotropic, optically thick sample according to the three-flux approximation, the diffusion approximation, Giovanelli and the K–M theory.

Equation (3.37) and Equation (3.52), the diffuse reflectance of an optically thick sample R_∞ can be expressed as a function of the ratio α/σ , which for directional sample illumination yields [47].

$$R_\infty = \frac{1}{1 + 3(\alpha/\sigma) + (5/3)(3(\alpha^2/\sigma^2) + 3(\alpha/\sigma))^{1/2}} \quad (3.53)$$

The result of applying the different radiative transfer models that describe the diffuse reflectance of an optically thick sample are compared with each other in Figure 3.5. The diffusion approximation (Equation (3.52)), the three-flux approximation (Equation (3.51)) and the data according to a numerical solution of the radiative transfer equation by Giovanelli [48] were calculated for directional sample illumination. The data according to the K–M theory (Equation (3.38)) were obtained for diffuse sample illumination. Thus, the differences between the K–M theory and the other models are due to the different illumination conditions as well as due to differences in the definition of K/S and α/σ . In practice, the three-flux approximation is in very good agreement to the calculations of Giovanelli, whereas the diffusion approximation exhibits increasing deviations for larger α/σ -ratios (corresponding to smaller albedos). For $\alpha/\sigma = 1$ or $\omega = 0.5$, the relative deviations are in the order of 7%.

It should be mentioned that in all the models presented above, specular reflection at the air-sample boundary is neglected; thus these models are only valid for loose powders and have to be used with care for other samples.

3.4.6 DEVIATIONS FROM THE KUBELKA–MUNK EQUATION AND THE EFFECT OF ANISOTROPIC SCATTER

Although the K–M treatment is most often applied to diffuse reflection spectra of dilute dispersions of absorbing materials in a nonabsorbing powdered matrix, it is usually found that, for measurements taken in the mid-infrared or ultraviolet-visible region of the spectrum where the absorptivities of absorption bands may be quite high, plots of $f(R_\infty)$ vs. c , the concentration of the absorbing component, deviate from linearity even at quite low concentrations ($c > \sim 1\%$). For NIR spectra, band absorptivities are usually significantly weaker, so that linear plots of $f(R_\infty)$ vs. c may often be obtained even at fairly high concentrations when the absorptivity of the matrix is zero. On the other

hand, if the analyte has strong absorption bands, NIR diffuse reflection spectra of binary mixtures are no longer adequately described by K–M theory. This was originally thought to be caused by the simple two-flux model (shown in Figure 3.3) breaking down.

The effect of front-surface reflection can be readily seen from the spectra of the two polyethylene bottles in Figure 3.4 [22]. In each case, the K–M function reaches a maximum value of about 18, corresponding to a reflectance, R_∞ , of about 0.05. Since the Fresnel (specular) reflectance at normal incidence for these samples (which have a refractive index of about 1.5) is about 0.04, a reflectance of 0.05 is not unreasonable, especially when the collection optics used for these measurements are taken into account. For NIR spectra, where absorption is so weak that it has little effect of the refractive index, there will always be some maximum value of $f(R_\infty)$ that can be measured in practice (typically about 20). This value will be dependent on the optics used to collect the remitted radiation. One result of reflection from the front surface of the sample is to lead to nonlinear plots of $f(R_\infty)$ against the concentration of an absorbing component in a nonabsorbing matrix, with $f(R_\infty)$ approaching its maximum value asymptotically in a similar way to the effect of stray light in any measurement made with a grating monochromator [49]. Correction for reflection from the front surface of the sample significantly increases the range of linearity.

In a way, because reflection from the first layer of the sample is considered in a different way to the behavior of later layers, this correction can be considered to be an intermediate step between continuous and discontinuous approaches to diffuse reflection. Prior to the development of the discontinuous equations, the nonlinearity was very troublesome to experimenters, and the reason for the departure from linearity was much debated. Besides specular reflection, other proposed culprits were the effect of absorption by the matrix [50,51], and the subject of this section, anisotropic scatter.

One of the assumptions listed at the start of the earlier discussion of K–M theory is that the medium scatters isotropically. Chandrasekhar [17] gave an exact solution of the radiation transfer equation for an isotropically scattering medium, that is, a medium for which the albedo for single scattering, ω_0 , is equal to the scattering phase function, $p(\cos \theta)$, where θ is the angle of scattering from a direction given by $\mu' = \cos \vartheta'$ and ϕ' into a direction given by μ and ϕ . ω_0 is identical to Schuster's scattering coefficient for single scattering, s , given earlier as

$$\omega_0 = \frac{\sigma}{\alpha + \sigma} \quad (3.54)$$

For isotropic scattering, $p(\cos \theta)$ is equal to unity. For anisotropic scattering, the isotropic phase function $p(\cos \theta)$, or ω_0 , is modified by multiplying ω_0 by a factor of $(1 + x \cos \theta)$ so that

$$p(\cos \theta) = \omega_0(1 + x \cos \theta) \quad (3.55)$$

where x is the *anisotropy factor*. Chandrasekhar has also described exact solutions to the radiation transfer equation in this case, but the solution is far too complex to be applicable to the quantitative analysis of powdered mixtures.

The solution has been put into a more tractable form by several workers, including Pitts [52] who developed an approximate solution and Giovanelli [48] who put Pitts's solution into a more useful form (now most commonly known as the Pitts–Giovanelli formula) which gives the reflectance as a function of the direction cosine of the angle of incidence μ_0 as

$$R(\mu_0) = \frac{\omega_0}{2(\chi)^{1/2} + 3 - \omega_0\chi} \left[-x + \frac{3 + (1 - \mu_0)x}{1 + \mu_0(\chi)^{1/2}} \right] \quad (3.56)$$

where

$$\chi = (3 - \omega_0x)(1 - \omega_0) \quad (3.57)$$

If the components of a binary mixture are designated 1 and 2, and the relative weight of those components $W = W_2/W_1$ so that the concentration of component 2 is $W/(W + 1)$, the albedo of single scatter may be expressed as

$$\omega_0 = \frac{1 + P_1 W}{P_2 + P_3 W} \quad (3.58)$$

where $P_1 = \sigma_2/\sigma_1$, $P_2 = (\alpha_1 + \sigma_1)/\sigma_1$, and $P_3 = (\alpha_2 + \sigma_2)/\sigma_1$. Equation (??) may be expressed in terms of the weights, absorption coefficients, and scattering coefficients of the individual components as

$$\omega_0 = \frac{\sigma_1 W_1 + \sigma_2 W_2}{(\alpha_1 + \sigma_1)W_1 + (\alpha_2 + \sigma_2)W_2} \quad (3.59)$$

Thus the Pitts–Giovanelli equation requires four empirical parameters, P_1 , P_2 , P_3 , and x , for a complete characterization of the diffuse reflectance of a binary mixture. Although spectra can be *fit* over a wide concentration range to Equation (3.56) by a suitable selection of the values of these parameters, obtaining good estimates of these parameters a priori is difficult or impossible. Thus the Pitts–Giovanelli treatment is never used in practice to obtain linear plots of a function of the measured reflectance at a wavelength corresponding to an absorption band of the analyte against concentration, even for a binary mixture of an absorbing analyte in a nonabsorbing matrix. This treatment has been shown by Hecht to describe the diffuse reflectance of visible radiation by a model system consisting of soluble absorbers in a liquid medium containing nonabsorbing scattering particles [53,54]. In a related study (again in the visible region of the spectrum), Hecht [55] showed that the Pitts–Giovanelli formula is a good approximation to the equation for radiation transfer even for large values of the anisotropy factor x . He suggested that this result indicates that the breakdown of the K–M theory is not so much due to the failure of the two-flux approximation as to the neglect of anisotropy of scatter.

There is a bit of a paradox in these results. On the one hand, the concept of anisotropy is irrelevant to the two-flux case. The forward scatter is no different than the transmitted beam and so can be neglected. For this reason, the discontinuous methods described in the next section use a concept of remission instead of scatter (as did Kubelka and Munk in their original work). On the other hand, the scatter from a finite particle is undeniably anisotropic. Further, voids may be thought of as producing an extreme case of anisotropic scatter, with all radiation scattered forward, and none back. So while we do not agree that neglect of anisotropy causes breakdown of the two-flux theories, the model of a continuum of anisotropically scattering points is, in principle at least, a better model for real samples than a continuum of isotropically scattering points.

An alternative treatment was developed by Rozenberg [56] and is based on the work of Kuznetsov [57]. Here reflectance is treated as the sum of several components, with each successive term representing increased multiplicity of scatter. The principal independent variable in the Rozenberg treatment is the ratio of the absorption and scattering coefficients β , that is, $\beta = \alpha/\sigma$. If β is sufficiently large, the reflectance R may be described by the equation

$$\frac{1}{R} = \frac{1}{R_0} \frac{(1 + \beta)^2}{1 + \beta/Q} \quad (3.60)$$

where R_0 is the reflectance of the diffusely reflecting matrix in the absence of an absorbing component ($\beta = \beta_0$) and Q is a quantity that defines the relative contribution of higher multiplicities of scatter when $\beta = \beta_0$. β and Q can also be expressed in terms of the reflection r , forward scatter t , and

absorption a of a single layer, where $a + r + t = 1$, as

$$\beta = \frac{a}{r + 1} \quad (3.61)$$

and

$$Q = 1 + \frac{t}{r + t} \quad (3.62)$$

Defining R' as R/R_0 , it can be seen that

$$R' = \frac{1 + \beta/Q}{(1 + \beta)^2} \quad (3.63)$$

In terms of the relative weight W defined above, an expression for β has been derived [58] which is formally analogous to the expression for W_0 in the Pitts–Giovanelli treatment (Equation (3.58)), that is,

$$\beta = \frac{p_1 + p_2 W}{1 + p_3 W} \quad (3.64)$$

where $p_1 = \alpha_1/\sigma_1$, $p_2 = \alpha_2/\sigma_1$ and $p_3 = \sigma_2/\sigma_1$. Again, the visible reflectance of model systems has been fit quite accurately by adjusting the parameters of the Rozenberg equation [58]. In practice, however, neither the Pitts–Giovanelli treatment nor the Rozenberg treatment is particularly relevant for “real-world” samples which often have more than two components and may have a wide range of particle shapes and diameters. Thus a more practical basis for obtaining quantitative data from diffuse reflection spectra must be found.

An alternative way of looking at the nonlinearity of plots of $f(R_\infty)$ vs. c is through discontinuum treatment, which is discussed in more detail later in this chapter. If α is the probability of a photon being absorbed by a layer of the sample, and σ is the probability that it is scattered, the discontinuous equivalent of the K–M equation can be written as

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} = \frac{\alpha(2 - \alpha - \sigma)}{\sigma} \quad (3.65)$$

If we consider infinitesimal layers, the fractions α and σ are very small compared to 2 and can be neglected. In this case, Equation [3.39] will yield a linear plot. However, when finite layers are considered, the function is nonlinear. This will be discussed at length in the second half of this chapter.

Before leaving this topic, one important practical question should be addressed. Since no theory of diffuse reflection, whether continuous as discussed above, or discontinuous, as discussed below, suggests that plots of $\log(1/R_\infty)$ vs. c should be linear, why do almost all practitioners of NIR spectroscopy convert reflectance to $\log(1/R_\infty)$ rather than using $f(R_\infty)$ or any other function that theory suggests should be more relevant? When samples are very carefully prepared, so that the scattering coefficient is constant in all cases, the baseline of the spectrum always has a constant value. In practice, achieving a constant scattering coefficient is exceptionally difficult (In the language of discontinuous mathematics, the distance between the layers can vary significantly depending on the way in which the sample is loaded into the cup). Measurements in the mid-infrared have shown that, provided that the sample is loaded under a constant pressure that is applied for a given amount of time, diffuse reflection spectra can be very reproducible [59,60] and plots of $f(R_\infty)$ vs. c can be linear up to the point at which front surface reflection becomes significant. For NIR diffuse reflection spectrometry, samples are usually simply loaded into a cup pressed against a quartz window. While experimentally simple, this method of presenting the sample to the spectrometer can lead to wide variations in the baseline. Because of the nature of the K–M function,

such baseline variations can significantly affect the value of $f(R_\infty)$ due to an absorption band of the sample [61].

To exemplify this argument, the baseline corrected values of $f(R_\infty)$ and $\log(1/R_\infty)$ for bands absorbing 50% of the baseline energy are listed in the table below for different baseline energies:

Baseline (at A nm) (%)	Maximum absorption (at B nm) (%)	$f(R_\infty)$			$\log(1/R_\infty)$		
		$f(R_\infty)_A$	$f(R_\infty)_B$	$f(R_\infty)_B - f(R_\infty)_A$	$\log(1/R_\infty)_B$	$\log(1/R_\infty)_A$	$\log(1/R_\infty)_A - \log(1/R_\infty)_B$
100	50	0.000	0.250	0.250	0.000	0.301	0.301
80	40	0.025	0.450	0.425	0.097	0.398	0.301
60	30	0.133	0.817	0.684	0.222	0.523	0.301
40	20	0.450	1.600	1.150	0.398	0.699	0.301
20	10	1.6000	4.050	2.450	0.699	1.000	0.301

It can be seen that the baseline-corrected values $[f(R_\infty)_B - f(R_\infty)_A]$ are strongly dependent on the baseline shift, whereas the baseline-corrected values for $[\log(1/R_\infty)_A - \log(1/R_\infty)_B]$ are identical. Even though plots of $\log(1/R_\infty)$ vs. c are nonlinear over wide ranges of concentration, the range of the analyte concentration for many samples that are studied by NIR diffuse reflection is quite small. In this case, the effect of nonlinearity of $\log(1/R_\infty)$ vs. c on the quantitative result is far less than the effect of baseline changes from one sample to the next. In practice, therefore, most practitioners convert their data to $\log(1/R_\infty)$ rather than $f(R_\infty)$.

3.5 DISCONTINUUM THEORIES OF DIFFUSE REFLECTION*

A continuum theory implicitly assumes a model for the absorption by and scatter from a particle of infinitesimal size. This model is only a reasonable approximation for samples in which the fraction of light absorbed by an individual particle is a very small fraction of the light incident upon it. The advantage of this model is that it is simple, though the mathematics that describe it are not. The discontinuum method we will describe uses mathematics no more complex than the continuum theories. However, the description of the sample is more complex. This is both the power and limitation of the discontinuum theories: they can describe more complex situations, but doing so requires a more detailed description.

Currently, no continuum or discontinuum theory produces a function that is linear with concentration of absorbers over large concentration ranges. However, the discontinuum theory can provide an understanding as to why the functions behave the way they do. A discontinuum theory can make visible that which is hidden in the implicit assumptions of continuous mathematics. The largest advantage of the discontinuous theory to a spectroscopist is that models appropriate for mixtures can be used to describe a sample.

As noted above, the phenomenological two-flux theories that have been developed on the basis of the radiation transfer equation can be considered *continuum* theories. Continuum theories consider the absorption and scattering coefficients as properties of an irradiated isotropic layer of infinitesimal thickness. On the other hand, *discontinuum* theories consider layers containing a collection of particles. Consequently, the thickness of a layer is dictated by the size of the scattering and absorbing particles. Optical constants can then be determined from the scattering and absorption properties of these particles.

* Sections 3.5 and 3.6 are drawn in large part from a book: *Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Absorption Spectroscopy of Scattering Materials* by Donald J. Dahm and Kevin D. Dahm, NIR Publications (2007).

Recently, the discontinuous approach has been applied by Dahm and Dahm [62,63] to the two-flux results obtained from the radiation transfer equation. This has resulted in being able to recast the results obtained from the continuous approach in terms of a layer of particles. This has been termed the *representative layer theory*. In the discussion of deviations from the K–M equation, we gave without proof an analogous mathematical expression reached by the discontinuous treatment (Equation (3.65)). In this section we give the derivation of some of the more important formulas in the discontinuous treatment.

3.5.1 THEORY FOR AN ASSEMBLY OF SPHERES

Melamed developed an elegant mathematical description of absorption and scatter from an assembly of close packed spheres [64]. Unfortunately, it is remembered more for its failings than its elegance. The Melamed model embodied two assumptions: There would be reflection from the front external surface of a particle (that would follow Lambert’s cosine law for a sphere), and there would be isotropic scatter from inside the particle. Within the sphere, the model took into account an infinite number of internal reflections. The model predicts that reflectance would reach a maximum as the relative refractive index approached zero. Of course, if there is no refractive index difference between that of the particle and the medium, there is no reflection from the particle.

While the primary failings of the theory were “fixed” with a modification by Simmons [65], it was Simmons himself who pointed out that simple scattering models seem to be as useful as more complex ones. Recent work in discontinuous theories has been dominated by using a two-flux model and the mathematics of plane parallel layers (sheets).

3.5.2 THEORY FOR SHEETS AND AN ASSEMBLY THEREOF

Consider a sheet under directed illumination. A sheet is an object with two large, flat, smooth, parallel surfaces with two dimensions much larger than the third. This third dimension will be referred to as the thickness. The layers are illuminated with a directed beam from a direction perpendicular to the large dimensions. The diameter of the beam is small compared to the front surface area of the layer that it strikes.

At normal incidence, the reflectance from a surface, r_0 , may be calculated from the index of refraction of the material, n_1 , and n_0 , the index of refraction of the dispersing medium (in this case air) using the Fresnel equation

$$r_0 = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2} \quad (3.66)$$

This formula neglects the effects of absorption on remission. Because in NIR, the band absorptivities are very small, the refractive index, and hence the reflectance, of a surface should not vary significantly with absorption. This is not the case in the mid-infrared region. In this case, not only the effect of absorption on r_0 , but also the fact that the refractive index varies significantly across a strong absorption band, an effect known as *anomalous dispersion*, must be taken into account when applying the Fresnel equations.

Within a layer, there is a transmission loss due to absorption, which can be calculated from the Bouguer–Lambert law by $[1 - \exp(-kd)]$, where k is the linear absorption coefficient of the material making up the layer and d is the thickness of the layer.[†] Consequently, the light incident

[†] The term Bouguer–Lambert law is not familiar to many spectroscopists. The term Beer–Lambert law or merely Beer’s law is frequently used in its place. Technically, Beer’s law refers to the observation that the contribution of an absorber to the absorbance of a sample is proportional to the concentration of the absorber. The symbol k is referred to by some spectroscopists as the *Beer–Lambert absorption coefficient*. Because of the possibility of decadic or napierian absorbance and the various units by which concentration can be expressed, several different quantities are all Beer–Lambert absorption coefficients. The term absorptivity is commonly used in equations for decadic absorbance and can include concentration in any units. The term *linear absorption coefficient* is the usual name for the *linear napierian absorption coefficient* of a pure material.

on the back surface has been diminished by absorption, and the reflection from it is correspondingly diminished.

The fraction of incident light remitted by a single layer, R_1 , the total transmittance through a layer, T_1 , and the fraction of light absorbed by a layer, A_1 , can be calculated from the Stokes equations [3,66]:

$$R_1 = r_0 + \frac{(1 - r_0)^2 r_0 \exp(-2kd)}{1 - r_0^2 \exp(-2kd)} \quad (3.67)$$

$$T_1 = \frac{(1 - r_0)^2 \exp(-kd)}{1 - r_0^2 \exp(-2kd)} \quad (3.68)$$

$$A_1 = 1 - R_1 - T_1 \quad (3.69)$$

The expression for R_1 above reveals an important physical insight. The expression $\exp(-2kd)$ is always between 0 and 1 and appears in a negative term of the denominator. Thus, for the case of a constant r_0 , the effect of increasing absorption will be to reduce the remission of radiation that has penetrated into a single layer. Consequently, even if the remission from a *single surface* is independent of absorption, remission from an absorbing *layer or particle*, which has both a front and rear surface, does depend on absorption. The assumption of a constant r_0 , which depends on a constant refractive index, is a good one in the NIR region. In the mid-infrared, the case is more complicated because the refractive index changes across strong absorption bands, thereby increasing r_0 . In such a case it is even more likely that the remission from an absorbing *layer or particle* depends on absorption.

Derivation of these formulas involves assuming that a fraction r_0 is reflected by the front surface and a fraction $(1 - r_0)$ is transmitted into the particle, where it is attenuated, that is, a fraction $[(1 - r_0) e^{-kd}]$ reaches the back surface. Here a fraction $[(1 - r_0)^2 e^{-kd}]$ leaves the particle in the forward direction contributing to its transmission. A fraction $[r_0(1 - r_0) e^{-kd}]$ returns back toward the front surface and is again attenuated by absorption, with $[r_0(1 - r_0) e^{-2kd}]$ reaching the front surface. Here a fraction $[r_0(1 - r_0)^2 e^{-2kd}]$ leaves the particle and contributes to the reflectance. This process continues indefinitely and is described as infinite series that converge to the above expressions.

$$R_1 = r_0 + r_0(1 - r_0)^2 e^{-2kd} + r_0^3(1 - r_0)^2 e^{-4kd} + \dots + r_0^{2n-1}(1 - r_0)^2 e^{-2nkd} \quad (3.70)$$

$$T_1 = (1 - r_0)^2 e^{-kd} + r_0^2(1 - r_0)^2 e^{-3kd} + \dots + r_0^{2n-1}(1 - r_0)^2 e^{-(2n-1)kd} \quad (3.71)$$

It is assumed that there is no divergence of the beam, and that on every pass through the layer, the light will travel exactly the distance d . This means that, with conventional spectroscopic equipment, there would be no remission detected from the sample, because it would all be reflected back directly into the incident beam.

The above derivation may be generalized for the case where r_e is the fraction of light reflected from the surface as the light *enters* the layer and r_f is the fraction of light reflected at the surface when the light *leaves* the layer. Note that the layer is still considered symmetrical in this model: the front and back surfaces both behave the same way, the distinction between r_e and r_f concerns whether light is traveling from the surrounding medium to the layer, or from the layer to the surrounding medium. For this situation, the above equations become:

$$R_1 = r_e + \frac{(1 - r_e)(1 - r_f)r_f \exp(-2kd)}{1 - r_f^2 \exp(-2kd)} \quad (3.72)$$

$$T_1 = \frac{(1 - r_e)(1 - r_f) \exp(-kd)}{1 - r_e^2 \exp(-2kd)} \quad (3.73)$$

$$A_1 = 1 - R_1 - T_1 \quad (3.74)$$

For the case of diffuse illumination, there is a difference in the distance traveled for diffuse light, as opposed to directed light. We may define a new absorption coefficient, K , which is dependent on the actual distance that the light travels through the sheet. This is different from the distance traveled by directed radiation, where the distance traveled is equal to the sample thickness. For diffuse illumination of plane parallel particles, the relationship between the two absorption coefficients is

$$\exp(-Kd) = \int_0^{\pi/2} \frac{\exp(-kd)}{\cos(\theta)} d\theta \quad (3.75)$$

The quantities $\exp(-kd)$ and $\exp(-Kd)$ are the transmittance through a sheet of thickness d for the case of direct and diffuse radiation, respectively. (This relationship is not exact because it does not account for the fact that the reflectance of a surface is dependent on angle. Furthermore, depending on the geometry of a spectrometer, integration in a second direction might be required.)

3.5.2.1 The Stokes' Formulas for an Assembly of Sheets

The equations that govern the passing of light through a sample composed of sheets are cumbersome, but they are readily solved with a computer. Let x represent the distance into the sample compared to the thickness of a single sheet. For example if x is 2, it is twice the thickness of a single sheet, and if x is $1/2$, it is half the thickness of a single sheet. From the fractions of a single layer (given by A_1 , R_1 , and T_1), we can calculate the fractions for a distance x (with $A_x + R_x + T_x = 1$) by

$$T_x = \frac{\Omega - \Omega^{-1}}{\Omega \Psi^x - (\Omega \Psi^x)^{-1}} \quad (3.76)$$

$$R_x = \frac{\Psi^x - (\Psi^x)^{-1}}{\Omega \Psi^x - (\Omega \Psi^x)^{-1}} \quad (3.77)$$

Ω and Ψ are defined by

$$\Omega = \frac{1 + R_1 + T_1^2 + \Delta}{2R_1} \quad (3.78)$$

and

$$\Psi = \frac{1 + R_1 + T_1^2 + \Delta}{2T_1} \quad (3.79)$$

where

$$\Delta = [(1 + R_1 + T_1)(1 + R_1 - T_1)(1 - R_1 + T_1)(1 - R_1 - T_1)]^{1/2} \quad (3.80)$$

Note that x can be any number, including a fraction. A real sample made up of sheets must of course have an integral number of sheets, so R_x for a fractional x does not correspond to anything physically observable, but it can be computed.

3.5.2.2 The Dahm Equation

When Dahm and Dahm [62,63] applied the discontinuous approach to the same problem as Kubelka and Munk, they made the following assumptions:

1. The sample has two large flat (but not necessarily smooth) plane parallel surfaces.
2. All radiation is directed, moving either forward or backward in a direction defined by the normal to the sample surface.

3. A sample is divided into layers. Each layer is representative of the sample as a whole and is nowhere more than one particle thick. The layer may contain voids, and there is no condition that the layer is the same thickness everywhere.
4. There is no scatter from one particle to another within the same layer.
5. The process in which radiation leaves a layer and returns into the hemisphere bounded by the plane of the sample's surface is termed remission. All remitted radiation is included in the description, whether its origin is regular reflection or backscatter.
6. Each layer will absorb a certain fraction, a , remit a certain fraction, r , and transmit a certain fraction, t .

Dahm and Dahm [62,63] have developed a discontinuum theoretical treatment based on the original work of Benford [67]. It is assumed that each layer of material is bounded by two parallel infinite planes. Of the radiation entering the i th layer, the total forward flux, that is, the fraction leaving the layer in the same direction, is t_i , and the total backward flux is r_i , and the fraction absorbed is a_i . The total forward flux includes both transmission and forward scatter and the total backward flux includes both external and internal reflection and backscatter.

Benford's equations allow the total forward and backward flux and the total absorbance to be calculated in terms of the properties of an individual layer. The overall properties for a material composed of two layers are given by

$$t_{i+j} = \frac{t_i t_j}{(1 - r_i r_j)}; \quad r_{i+1} = r_i + \frac{t_i^2 r_j}{(1 - r_i r_j)}; \quad a_{i+j} = 1 - t_{i+j} - r_{i+j} \quad (3.81)$$

If t_i , r_i , and a_i represent the known properties of a sample that contains a number i of identical layers, each of which is described by t_1 , r_1 , and a_1 , the properties of a sample containing i such layers is given by Benford as

$$t_{i+1} = \frac{t_i t_1}{(1 - r_i r_1)}; \quad r_{i+1} = r_i + \frac{t_i^2 r_1}{(1 - r_i r_1)}; \quad a_{i+1} = 1 - t_{i+1} - r_{i+1} \quad (3.82)$$

Dahm and Dahm considered what happens when the thickness of the sample is doubled or halved, and computed the total backward flux, R_∞ for an infinitely thick sample by an iterative solution of the latter set of equations. They showed that if the sample consists of an infinite number of layers, each with a forward flux of t_i , a backward flux of r_i , and absorption of a_i ,

$$f(R_\infty) = \frac{a_i}{2r_i} (2 - a_i - 2r_i) \quad (3.83)$$

The K–M equation was derived for a matrix of infinitesimally small particles. Because the numerator of the K–M function is the absorption coefficient, $f(R_\infty)$ varies linearly with the concentration of each component of the sample. However, it is known that the K–M equation is only an approximation. The Dahm Equation (3.83) may be expected to give a more exact solution for diffuse reflectance in the case of particles of finite size.

The Dahm equation is frequently expressed in terms of an Absorption–Remission function $A(R, T)$ which has as one of its characteristics that it has the same value for any thickness of a sample.

$$A(R, T) = \frac{(1 - R^2) - T^2}{R} = \frac{a}{r} (2 - a - 2r) \quad (3.84)$$

3.5.3 THE REPRESENTATIVE LAYER THEORY

3.5.3.1 Model for a Layer Representative of Particulate Solids

Use of the mathematics for plane parallel described in the last section requires that each layer in a sample has a single set of spectroscopic properties: an absorption fraction, a remission fraction, and a transmission fraction. This mathematics may be straightforwardly applied to homogeneous layers such as plastic sheets. In order to apply the mathematics to samples of particulate solids meaningfully, we need to establish a method for determining the properties of a layer of the sample from the properties of the individual particles.

In the model of the representative layer that we present here, each particle type is characterized by its composition, volume, and the average cross-sectional surface area that it presents to the incident beam. We will picture a particle as having two flat ends, each perpendicular to the incident beam. While the shape of the cross section is not important for our model, it may be pictured as a square.

Thus, a representative layer is made up of voids and of particles (shaped as boxes) of varying size. The ends of the boxes are perpendicular to the incident beam. The representative layer is of varying thickness, but is never more than a single particle thick. The layer is representative if

1. The volume fraction of each particle type is the same in the layer as in the sample as a whole.
2. For all particle types, the cross-sectional surface area in the layer is in the same proportion as the surface area of the particle type in the sample as a whole.
3. The fraction of the cross-sectional surface area that is made up of voids is the same as the void fraction of the sample as a whole.

With this model, it will be possible to calculate the properties of a representative layer from the properties of the individual particles of which it is comprised. The properties of the single particle that are of interest are the absorption, remission, and transmission of the incident beam.

3.5.3.2 Absorption and Remission of the Representative Layer

The absorption is a property of a molecule and can be well represented as a continuum, but remission is a property of an interface and may not be well represented as a continuum. In the absence of absorption, the remission is independent of the thickness of a layer. The remission fraction from a single representative layer is dependent only on the fraction of the cross-sectional surface area occupied by each type of particle and the remission power of the material of which the particle is composed. In the presence of absorption, the remission fraction diminishes (causing a reduction in the remission coefficient).

For cases where we know the thickness of the representative layer, it is possible to calculate the absorption and remission fractions for the representative layer from the remission and transmission fractions of any sample of known finite thickness, d . The absorption fraction, A_1 , of a layer is given by $[1 - \exp(-Kd)]$. (This is the value given by the plane parallel mathematics for a layer that has no remission. In the symbolism being used, the subscript refers to the number of layers. Thus A_2 would refer to the properties of two layers, not to second layer.) By implication, the absorption of a single particle, a , is given by $[1 - \exp(-Kd)]$.

A *remission coefficient* may be defined as the remission fraction of the representative layer divided by the thickness of the representative layer. For cases where the thickness of the representative layer is not known, the plane parallel mathematics can be used to obtain absorption and remission coefficients as described above. This requires an assumption that a sample can be well represented as a continuum. In this *linear* region, for a given linear absorption coefficient the absorption fraction of a particle is proportional to its thickness, and the following conditions will be observed (and will be seen in the

examples below to explain some commonly observed phenomena):

1. The contribution of a particle type to absorption is proportional to the volume fraction (including voids) of the particle type and to the absorption coefficient of the material making up the particle.
2. The contribution of a particle type to remission is proportional to the total cross-sectional surface area of the particle type in the representative layer and the remission power of the material making up the particle.
3. In a mixture of two or more particle types of similar remitting power, the Absorption–Remission function of each particle type is represented in the Absorption–Remission function of the sample weighted in proportion to surface area to volume ratio of the particle type.

In regions of higher absorption, the coefficients obtained from the plane-parallel mathematics become less reliable. Then the representative layer model is a better descriptor, though the assumptions about the shape of the particles become more important. The regions of extremely high absorption tend not to be of value for compositional analysis. Here, the contribution of a particle to the absorption of a layer is proportional to the surface area fraction of the particle type and not dependent on its thickness. The representative layer model would still be useful in applications such as image analysis.

3.5.3.3 Mathematical Expression of Model

A sample is made up of particles of various types. For each particle type, we have the following definitions of symbols:

d_i	the thickness of a particle of type i in the direction of the incident beam
ρ_i	density of a particle of type i
w_i	weight fraction of a particle of type i
v_0	void fraction of the sample
v_i	fraction of <i>occupied</i> volume in the sample composed of particles of type i
V_i	fraction of <i>total</i> volume occupied by particles of type i
s_i	fraction of particle surface area which belongs to particle type i
S_i	fraction of a cross-sectional surface comprised of particles of type i
k_i	the effective absorption coefficient of the particles of type i
b_i	the effective remission coefficient of the particles of type i
$(bd)_i$	the remitting power of the material comprising particle type i

Volume surface area and fractions, for a given particle type can be computed from weight fractions and particle density as follows:

$$v_i = \frac{w_i / \rho_i d_i}{\sum (w_i / \rho_i d_i)} \quad (3.85)$$

$$s_i = \frac{w_i / \rho_i}{\sum (w_i / \rho_i)} \quad (3.86)$$

The following formulas assume that the amount of transmitted light lost by an interaction with a single particle either to absorption or remission is small. With this assumption, for a single particle,

the fraction of light absorbed is given by the cross-sectional area and the Bouguer–Lambert law, and the remission fraction is given by the cross-sectional area and $b_i d_i$. Thus, for a representative layer

$$A = \sum S_i [1 - \exp(-k_i d_i)] \quad (3.87)$$

$$R = \sum S_i b_i d_i \quad (3.88)$$

When $k_i d_i$ is small for all particle types, the following approximation can be made:

$$A = \sum S_i k_i d_i$$

Then, since the surface area times the thickness is the volume,

$$A = \sum V_i k_i \quad (3.89)$$

This is the basis for statement 1 in the previous section.

It has been shown [3,68] experimentally that b_i is proportional to $1/d_i$. This is equivalent to saying that remission is proportional to surface area, and follows from the assumption that remission is a property of an interface. This implies that the product $b_i d_i$ is constant and a property of the composition of the material making up the particle, independent of particle size. The term $(bd)_i$ is defined as the *remitting power* of a material, and

$$R_i = \sum S_i (bd)_i \quad (3.90)$$

Note that Equation (3.90) is a special case of Equation (3.88), and is the basis for statement 2 in the previous section.

In the linear range, the approximation is reasonable that

$$A(r, t)_i = \frac{V_i a_i}{S_i r_i} \quad (3.91)$$

When all particles types are in this range, it follows that

$$A(R, T) = \frac{\sum a_i}{\sum r_i} \quad (3.92)$$

For the case where the remission fraction is the same for all particle types, $A(R, T)$ is equal to $\Sigma(V_j a_j / S_j r_j)$ which is the basis for statement 3 above.

3.6 APPLICATION OF THEORY TO MODEL SYSTEMS*

In this section, we will give several hypothetical examples, though we will compare results from the theoretical model to actual experimental data. One set of data is from a system investigated by Olinger and Griffiths [50]. Up to three components (carbazole, NaCl, and graphite) were mixed

* Section 3.6 is taken with minor modification by permission of NIR Publications Copyright 207 from: Donald J. Dahm and Kevin D. Dahm, *Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Absorption Spectroscopy of Scattering Materials* pp 133–152, NIR Publications (2007). Sections 3.6.1 and 3.6.2 resulted from a collaboration between the authors, which was based on work described in Reference 50.

during the preparation of each sample. Carbazole was intended to represent a typical organic analyte having moderate absorption. It will be referred to as the analyte. NaCl and graphite respectively represent nonabsorbing and absorbing compounds. Whether as single compounds or mixtures, they will sometimes be referred to as the matrix. In the hypothetical examples, we will use the names of these materials, even though our calculation will not necessarily use the exact properties of these materials.

If we consider a beam of light encountering a single layer of the particles, there are several possible fates for the light:

1. The light can go through a void in the layer. In these examples, we will neglect the effect of voids, which tends to be minimal in a sample of close packed particles.
2. Light can interact with the surface of any of the particles and be reflected.
3. Light can enter the NaCl particles and a portion will be scattered backward. The balance of the light will be transmitted through the particle. In modeling this system, we will assume that there is no absorption by the NaCl particles.
4. Light can enter the graphite particles and all of it will be absorbed. The absorption of graphite is very high at most wavelengths in visible and infrared regions, so this assumption well approximates an actual property.
5. Light can enter a carbazole particle and a portion of the light will be absorbed. Another portion of it will be remitted, with the balance transmitted.

In total, the layer will remit a certain fraction, which represents the sum of reflection and backscatter; absorb a certain fraction; and transmit (either directly or diffusely) the balance.

One approach to modeling the system would be to use the absorption and remission (or scattering) coefficients with the following assumptions:

- The absorption coefficient of the NaCl is zero.
- The absorption coefficient of the graphite is infinite.
- The absorption coefficient of carbazole is neither zero nor infinite.

The linear absorption coefficient of carbazole might be determined by making transmission measurements on a solution of known concentration in a nonabsorbing solvent. Such a coefficient is a material property of carbazole. Unfortunately, that is not the absorption coefficient that is referred to in the theories of diffuse reflection. The theories refer to an absorption coefficient that would be obtained by taking the absorption and remission properties of a finite sample and extrapolating them to a sample of zero thickness. For a sample of zero scatter, the two absorption coefficients would be the same. In the presence of scatter, they are different. However, at very high absorption levels, the corresponding fraction of light absorbed as defined by each coefficient becomes indistinguishable experimentally. (This should not be interpreted as meaning that the two absorption coefficients become mathematically equal at very high absorption levels. The two coefficients will both approach infinity as absorption levels becomes very large, but will always have different values at the same absorption fraction, and will change at different rates as the absorption fraction changes.)

It is the intermediate levels of absorption that are the most important for analyses. Here, the relationship between the two coefficients is rather complex. No one chose this complicated situation: nature and our mathematics thrust it on us. However, many workers either did not know about or ignored the fact that the two coefficients are not proportional. Thus we urge care when reading the literature on this issue.

The situation with the remission coefficient is equally undesirable. Two particles with the same surface reflectivity and particle size will have different remission (or scattering) coefficients if the absorption coefficient of the material within the particle is different. These differences can be

illustrated by our extremes. If there is infinite absorption by the particle, the remission from the particle will be only the reflection from the first particle surface. For the particle with no absorption (but the same surface reflectivity), there will also be remission from the back surface of the particle. When extrapolated to zero thickness, this will mean that the remission coefficient for the particle with infinite absorption will be approximately half that of the case of zero absorption. (This is an over simplification. The remission coefficient will go down with increasing absorption and then, as the absorption becomes very large, will increase [69].) Just as for the case of absorption, many workers have ignored or did not know about the change in remission coefficients. (In the older literature, what we term a remission coefficient is called a scattering coefficient. The term scattering coefficient also has other meanings. Again, care is urged when reading the literature.)

There are situations where the assumptions of proportionality of the absorption coefficients and constancy of remission coefficient are reasonable. If the fraction of light absorbed by a single particle is small, the assumptions are good. In order to describe other situations, it is desirable to use an approach that does not suffer from the complexities of coefficients referred to above. In the following examples, we will illustrate the use of the approach of discontinuum theory as embodied in the representative layer theory.

Discontinuum theories are sometimes called particle theories. We will treat a sample as an assembly of particles. For the general case, we do not know how to use our models to deduce particle properties from the spectroscopic data. We can, however, use the models to calculate the spectroscopic properties of a sample from those of the particle.

3.6.1 EXAMPLE 1: GRAPHITE IN NaCl

We will begin our series of examples by assuming that we are mixing particles that have a drastically different absorption fraction but the same remission fraction. The plot in Figure 3.6a shows how $f(R_\infty)$ (denoted there as K-M) and a/r vary as a function of the particle fraction of graphite in a mixture of graphite (infinite absorption) and NaCl (zero absorption), with each assumed to have a remission fraction of 0.04. The value of 0.04 was chosen because it is the specular reflectance at normal incidence from the surface of a planar sample with a refractive index of 1.5. The value of $f(R_\infty)$ was calculated from the Dahm Equation (3.84). Because the function $A(R, T)$ is constant for

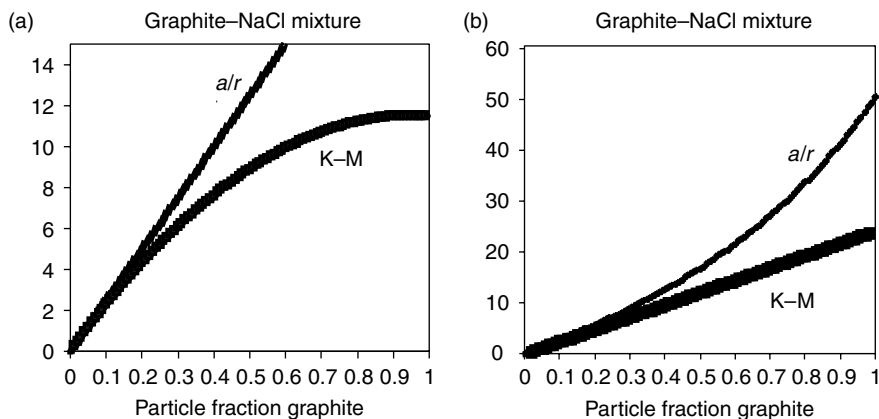


FIGURE 3.6 Variation of $f(R_\infty)$ (denoted here as K-M) and a/r as a function of the particle fraction of graphite in a mixture of graphite (infinite absorption) and NaCl (zero absorption). In chart (a), each is assumed to have a remission fraction of 0.04. In (b), the remission from the graphite is assumed to be half that from the NaCl. (Reproduced from D. J. Dahm and K. D. Dahm, *Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Adsorption Spectroscopy of Scattering Materials* (2007), by permission of NIR Publications Copyright 2007.)

any thickness of the sample, we can calculate the value for infinite thickness ($T_\infty = 0$) from the value for the single layer.

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{A(R_\infty, 0)}{2} = \frac{a}{2r}(2 - a - 2r) \quad (3.93)$$

Here the upper case letters A , R , and T are used to denote the fractions of incident light absorbed, remitted, and transmitted by a sample of any thickness. The lower case letters are used to denote the corresponding fractions for a single layer or particle. For samples of infinite thickness, the K–M function, $f(R_\infty)$, and the Absorption–Remission function, $A(R, T)$, are related by a simple factor of two. The K–M equation, as originally derived, contains a quantity related to scatter in its denominator, which with the assumption of isotropic scatter, is twice the magnitude of r .

The value for the absorption fraction of a single layer, a , varies from 0 to 1 with the fraction of the area of the sample occupied by graphite, while the value for the remission fraction, r , is constant at 0.04 (i.e., 4% of the incident radiation is reflected from either NaCl or graphite; any radiation entering a graphite particle is completely absorbed; radiation entering a particle of NaCl may be scattered within the sample in either the forward or reverse directions). Notice that the ratio a/r increases linearly with graphite concentration in this example. We may picture this situation as the sequential replacement of a clear particle (with no absorption) with an opaque particle (with infinitely high absorption). The increase in a (the absorption fraction of the layer) is proportional to the number of particles we have replaced. However, the remission from the layer is constant by our assumption. On the extreme right of the chart, the layer is completely opaque and therefore all the remission comes from reflection from the front surface of the first layer. At the left of the chart, where the particles are clear, the remission is coming from many layers. The observation of the nonlinearity in the function $f(R_\infty)$ (also true for $\log(1/R_\infty)$) is qualitatively explained as being because the effective pathlength of the light in a sample decreases with increasing absorption.

Of course, we do not literally count out particles when we make up a sample; rather we weigh them. Because graphite and NaCl have approximately the same density (2.2 g/cm^3), the particle fraction is the same as the weight fraction (assuming all particles have the same size). In later examples, we will encounter a situation where this is not true. Here we make the point that because they have the same density, particles of graphite and NaCl of the same size can be mixed to form a matrix having any desired absorption fraction. We will refer to such a matrix in Example 2.

Just above, we considered particles with vastly different absorptivities, and the same remission fraction. If we have two particles with the same refractive index but different absorptivity, the remission fraction will not be the same. The remission fraction from a highly absorbing particle (from which all the remission comes from the front surface) will be roughly half that of a lightly absorbing particle (where the remission comes from both the front and rear surfaces). It is the remission from the front surface that sets the upper limit on the K–M function.

Next, we will consider a similar system, but add that complexity. The graphite is assumed to have an absorption fraction of one and a remission fraction of 0.02, while the NaCl retains a remission fraction of 0.04 and zero absorption. The plot in Figure 3.6b shows how $f(R_\infty)$ (denoted there as K–M) and a/r vary as a function of the particle fraction of graphite in a mixture of graphite (infinite absorption, reflectance of 2%) and NaCl (zero absorption, reflectance of 4%). Notice that not only has the value of a/r changed, but it is also nonlinear, because $1/r$ is not a linear function. However, notice that the K–M plot in Figure 3.6b is linear. This is a surprising result given our contention expressed earlier that “reflection from the front surface of the sample leads to nonlinear plots of $f(R_\infty)$ against the concentration of an absorbing component in a nonabsorbing matrix, with $f(R_\infty)$ approaching its maximum value asymptotically.” If we consider the Dahm equation expressed as $f(R_\infty) = (a/2r)(2 - a - 2r)$, this behavior is explained by the nonlinearity in the ratio a/r observed in Figure 3.6b being exactly compensated by the decrease in r in the expression: $(2 - a - 2r)$. The assumptions that we made are reasonable for a system in which one particle absorbs

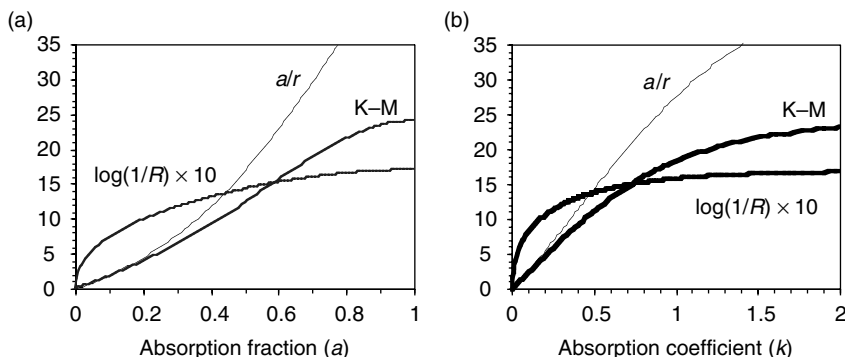


FIGURE 3.7 Functions related to a hypothetical sheet modeling particles within which the absorption fraction (a) is changing. The reflectivity (r) of the sheet surface is taken as 2%. All points plotted in chart (b) have a corresponding point in (a) with the same ordinate value, the difference between the two being the abscissa. The absorption coefficient (k) is taken as $[-\ln(1 - a)]$. (Reproduced from D. J. Dahm and K. D. Dahm, *Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Adsorption Spectroscopy of Scattering Materials* (2007), by permission of NIR Publications Copyright 2007.)

the light totally and the other not at all. However, this is not the normal situation encountered in NIR analyses.

In Figure 3.7, we consider a more normal case. We assume that all particles in a sample are identical. As the linear absorption coefficient k increases, a layer in each sample will have a progressively larger absorption fraction, which in the absence of scatter would increase linearly from 0 to 1. The collection of samples considered will have the same pattern in absorption fraction as those considered just above. The difference is that the increase is happening within a particle rather than by mixing particles with different absorption fractions. The remission fraction is calculated using the model of a Stokes sheet (described by Equation (3.67) to Equation (3.69)). The sheet surface has a reflectance of 2%, the same as that of the absorbing particles above. The remission fraction still decreases with absorption, but the decrease follows a more realistic pattern than in the earlier example. The decrease in remission again yields a nonlinear plot for a/r .

Notice that $f(R_\infty)$, labeled K-M in Figure 3.7, now varies nonlinearly with a and has a shape more typical of real samples. For the purpose of comparison, the plot of $\log(1/R_\infty)$ vs. a is also shown. The plots in Figure 3.6b and Figure 3.7 invite the conclusion that it is not only the surface reflectance in itself that causes the nonlinearity of the K-M function. It results from a rather complex interaction between the remission and absorption in a scattering sample.

The data in Figure 3.7b are the same data as in Figure 3.7a, but plotted to better mimic how the metrics vary as a function of composition. The abscissa in Figure 3.7b is the absorption coefficient (k) that would yield the absorption fraction (a) in Figure 3.7a using the formula $[k = -\ln(1 - a)]$.

3.6.2 EXAMPLE 2: CARBAZOLE IN A MATRIX OF VARYING ABSORPTION

At the time the experimental work referred to at the beginning of this series of examples [50] was undertaken, there was a belief that *matrix referencing* should remove the effect of the matrix and isolate the absorption of the analyte. The experimental data (reported in previous editions of this Handbook) showed unambiguously that, whether using $f(R_\infty)$ or $\log(1/R_\infty)$ as the metric, the matrix referencing technique would not work in the way envisioned. However, when the experimental work was done, there was not a theory available that would predict the results that were obtained.

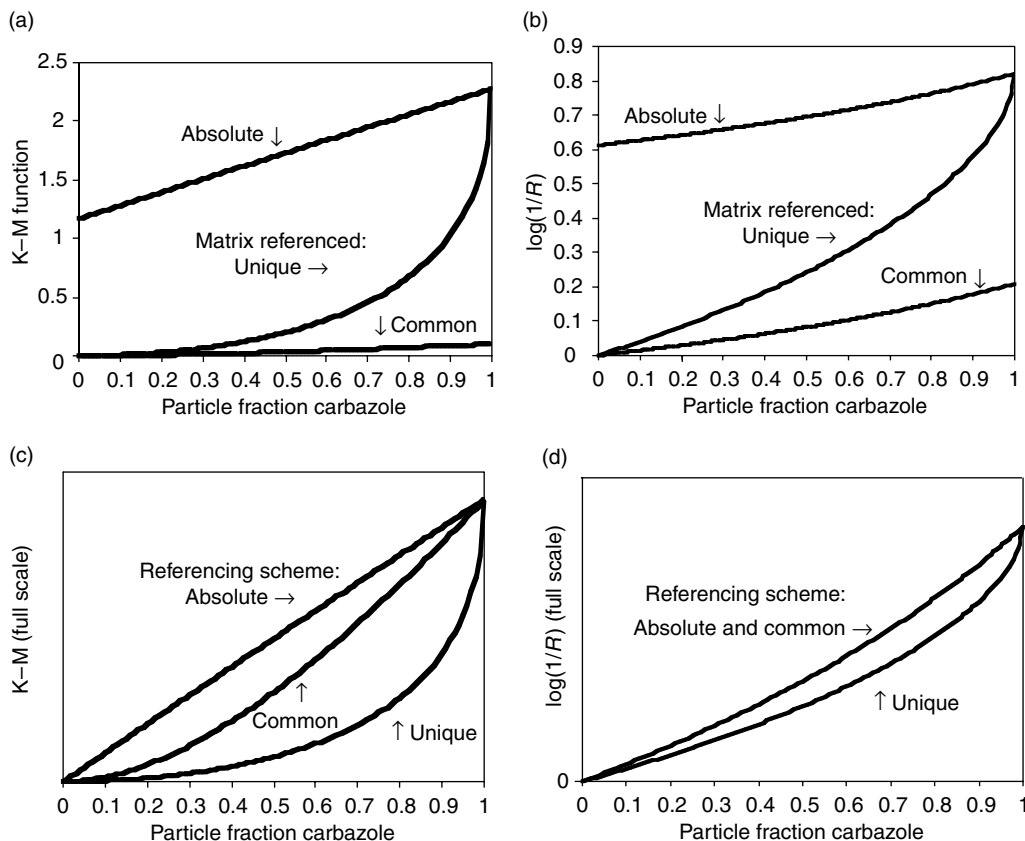


FIGURE 3.8 Variation of $f(R_\infty)$ and $\log_{10}(1/R)$ with the particle fraction of carbazole for a matrix composed of 95% NaCl and 5% carbon for three cases: (a) a referencing scheme that puts the data on an absolute scale (marked “Absolute” on figure); (b) a reference that is made up of the matrix, each particle of which has an absorption fraction of 0.05 (5%) of the light incident upon it (marked “Common” in figure); and a (c) matrix referencing scheme in which a unique reference is made for each sample (marked “Unique” in figure). Over relatively small ranges of analyte absorption, matrix absorption does not cause significant nonlinearity of K–M data collected on an absolute scale. Matrix referencing introduces nonlinearity into the data. In general, the $\log(1/R'_\infty)$ data is not linear, as can be seen in chart (d). (Reproduced from D. J. Dahm, *NIR news*, 15: 6–10 (2007), by permission of NIR Publications Copyright 2007.)

In this example, we will investigate the effects of various referencing techniques with the intent of explaining the experimental results. The four panels in Figure 3.8 each exhibit the behavior for a matrix composed of 95% NaCl and 5% carbon for all three cases. The three cases are for

1. A referencing scheme that puts the data on an absolute scale (marked “Absolute” in Figure 3.8).
2. A reference that is made up of the matrix, each particle of which has an absorption fraction of 0.05 (5%) of the light incident upon it (marked “Common” in Figure 3.8).
3. A matrix referencing scheme in which a unique reference is made for each sample (marked “Unique” in Figure 3.8). These reference materials are assumed to have the same contribution of matrix absorption in the reference (uniquely made for this sample) as in the sample. Thus if the absorption fraction for a matrix layer is 0.05 (5%), and the particle fraction of the matrix is 0.5 (50%), then the contribution of the reference material to the absorption fraction of a single layer of the sample would be $(0.05 \times 0.5 = 0.025)$ or 2.5%.

This was the referencing technique that was explored in the referenced experimental work [50].

In each case, we have assumed that the absorption fraction of the carbazole is 0.10 (10%), and that of the matrix is 0.05 (5%). The remission fraction from all particles is assumed to be 0.04 (4%).

Calculations according to the representative layer theory show that the matrix referencing techniques would not make a plot of $f(R_\infty)$ or $\log(1/R_\infty)$ more linear than data on an absolute scale. In fact, matrix referencing has the opposite effect. Notice that in Figure 3.8a, the K–M function for data on an absolute scale, for this case, varies approximately linearly with the particle fraction of carbazole. In Example 1, the corresponding function was very nonlinear. This is because here we assumed a maximum change of 5% in the absorption of a particle instead of 100%, which was the case assumed for graphite in Example 1. (This will make it clear that it is the referencing scheme that is causing the nonlinearity.) A plot of $\log(1/R_\infty)$ vs. the particle fraction of carbazole in Figure 3.8b is slightly less linear than the corresponding plot for the K–M function.

In an article by Griffiths on continuum methods of diffuse reflection in the previous edition of this *Handbook*, it was pointed out that “converting the measured reflectance of carbazole to the K–M functions yields a fairly linear plot when the carbazole analyte was dispersed in the nonabsorbing matrix (NaCl).” Consistent with this observation, the representative layer theory predicts that in this case, the unique matrix referencing would give the same plot as the line marked “Absolute” in Figure 3.8c. This is because the absorption for NaCl is very low, and thus in an infinitely thick sample, is nearly 100% reflective. Conversely, when the matrix is an absorbing one, the experimenters concluded “that $\log(1/R'_\infty)$ values provided a more linear plot over a major portion of the concentration range studied.” That conclusion seems very reasonable in light of a comparison between the lines marked “Unique” in Figure 3.8c and Figure 3.8d.

To subtract the matrix absorption successfully, two criteria must be fulfilled: (a) the reference must match the absorption of the matrix and (b) the remission from the reference must remain constant at all concentrations. In this matrix-referencing scheme, we have assured that we have matched the absorption of the matrix and kept the remission *for a single layer* constant at all concentrations. The remission of the reference will vary with concentration because the effective pathlength changes with absorption.

Figure 3.8c and Figure 3.8d show the same data as Figure 3.8a and Figure 3.8b, except that all plots are displayed full scale to show the relative linearity of each case more clearly. The K–M data which has all been referenced to a material with the same absorption (calculating the function $f(R'_\infty)$, where $[R' = R_\infty/R_{\text{ref}}]$) has a different shape than the $f(R_\infty)$ data that is on an absolute scale. The log data has the same shape, and the curves fall upon each other when expanded to full scale. This behavior is not unexpected, because taking the logarithm of a ratio is equivalent to subtracting the logs. The correct way to correct K–M data for a reference with nonzero absorption is to subtract the K–M functions, not to take their ratio. The software packages accompanying many NIR instruments do not do this. This tends to make $\log(1/R)$ a better choice for an absorption metric than K–M on those instruments for artificial reasons.

From the preceding example, it can be seen that the representative layer theory predicts that the unique matrix referencing technique would not work. In this example, we will show that the shape of the experimental curves is predicted by the representative layer theory. In this study, $\log(1/R)$ and K–M matrix referenced data were obtained from three series of infinitely thick samples:

1. Binary mixtures of carbazole and NaCl.
2. Carbazole dispersed in a matrix of NaCl and 1 wt.% graphite.
3. Carbazole dispersed in a matrix of NaCl and 5 wt.% graphite.

Using the techniques described in the preceding examples, the curves shown in Figure 3.9a and Figure 3.9b were obtained for $f(R_\infty)$ and $\log(1/R)$, respectively. Notice the only curve for which

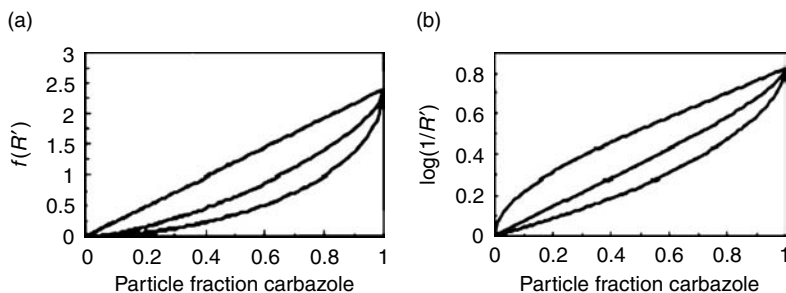


FIGURE 3.9 A unique matrix referencing scheme can yield a linear K–M plot only with a nonabsorbing matrix and when plotted against a volume based measure of concentration. The $\log(1/R_\infty)$ curves are in general not linear. From top to bottom, the lines in each chart represent 0, 1, and 5% absorption by matrix particles. The lines represent values calculated by the representative layer theory. (Reproduced from D. J. Dahm, *NIR News*, 15: 6–10 (2007), by permission of NIR Publications Copyright 2007.)

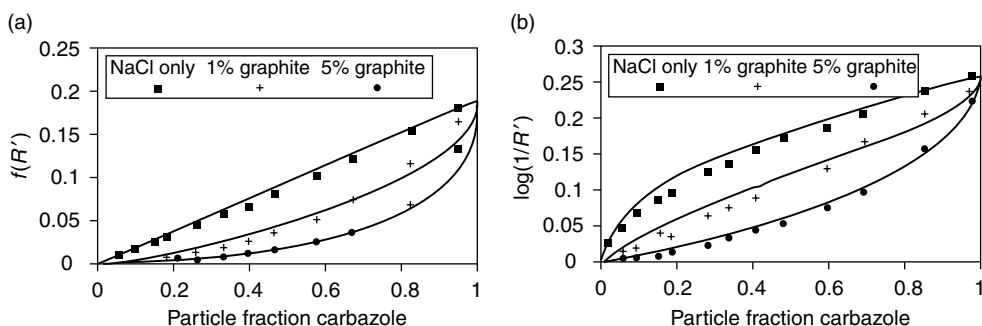


FIGURE 3.10 A unique matrix referencing scheme can yield a linear K–M plot only with a nonabsorbing matrix and when plotted against a volume based measure of concentration. From top to bottom, the lines in each chart represent 0, 1, and 5% absorption by matrix particles. The markers are experimental data. The lines are fit to the points assuming that the K–M function would be linear for all plots if an absolute reference were used. (Reproduced from D. J. Dahm, *NIR News*, 15: 6–10 (2007), by permission of NIR Publications Copyright 2007.)

a straight line is predicted is when $f(R_\infty)$ is measured under conditions where the matrix does not absorb. This line is straight because the absorption of the matrix is assumed to be zero, and thus the data for that series are on an absolute scale. If all data were on an absolute scale, the data in all three curves would form straight lines ending at the 100% carbazole absorption, although each would begin at a different point on the y-axis.

The data calculated from the representative layer theory may be compared with actual data shown in Figure 3.10. These data were originally reported by Olinger and Griffiths [50] and modified by changing the weight fraction to particle fraction, as described by Dahm and Dahm [70]. The individual points are experimental data, while the lines in these plots were calculated assuming that $f(R_\infty)$ varied linearly with the volume concentration of both the analyte and matrix. Notice the similarity between the shapes of the experimental curves and those in Figure 3.9a and Figure 3.9b, which are calculated from the representative layer theory. The absolute values of the numbers are different from the experimental data for a variety of reasons, one being that the experimental data was base line adjusted. More important, as we shall see in the next example, is that the particle properties assigned which give this fit are not necessarily those of real particles.

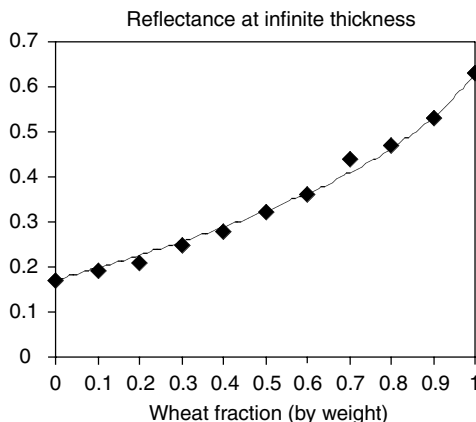


FIGURE 3.11 Reflectance measured (diamonds) by image analysis using visible light compared to reflectance calculated (line) from the Dahm equation for mixtures of wheat and rape seed meal. (Reproduced from D. J. Dahm and K. D. Dahm, *Near-Infrared Technology in the Agriculture and Food Industries*, 2nd edn. (P. Williams and K. Norris, eds.), St. Paul, MN, pp. 1–17 (2001) by permission of American Association of Cereal Chemists, Inc. Copyright 2001).

3.6.3 EXAMPLE 3: MIXTURE OF WHEAT AND RAPE SEED MEAL

Additional experimental confirmation for the usefulness of the representative layer theory comes from the work of DeVaux et al. [71,72]. This study was concerned with the fact that, in a mixture of two components with different particle sizes, the smaller particles will be *over-represented* in an absorption metric compared to the weight fractions of the components. This effect was systematically examined with a combination of image analysis and NIR spectroscopy on mixtures of “fine and coarse fractions of wheat and rape seed meal.”

In order to be able to characterize the surfaces of the mixtures by image analysis with visible radiation, mixtures were made from “raw materials of contrasting colors. A white product and a black product were chosen: wheat and rape seed meal.” Four series totaling forty samples were built from “mixtures from 0 to 100% of wheat by steps of 10%: fine wheat with fine rape seed meal, fine wheat with coarse rape seed meal, coarse wheat with fine rape seed meal, and coarse wheat with coarse rape seed meal.” Figure 3.11 shows experimental data (as diamonds) for the mixtures of fine wheat with fine rape seed meal (i.e., passed through the same size sieve). The remission of visible radiation from the mixtures increased with the concentration of “white” wheat. The reflectance values were “not placed on a straight line between the raw fractions.”

To explain the shape of an image analysis curve, it is natural to think in terms of an opaque layer, some parts of which are less reflective (darker) than others. In this example, the dark areas are assumed to reflect 0.1 (10%) of the light and absorb 0.9 (90%); while the bright areas reflect 0.9 (90%) and absorb 0.1 (10%). The reflectance is shown for this hypothetical opaque layer in Figure 3.12a. Notice that the reflectance, R , is a straight line proportional to the fraction of bright area (as it would be for any mixture composed of two components of different reflectance); as a result, the K–M and absorbance functions are both curved.

However, the reflectance from a real layer of white wheat and dark rape seed is not opaque. Light is transmitted through the white particles, interacts with interior layers of the sample, and reemerges from the sample after having undergone additional absorption. In Figure 3.12b, we see a plot of the image analysis data from mixtures of the dark rape and white wheat seed meal. Here the line representing the reflectance is curved, as is the line representing the K–M function. The $\log(1/R)$ curve, by coincidence, happens to be approximately straight in this case.

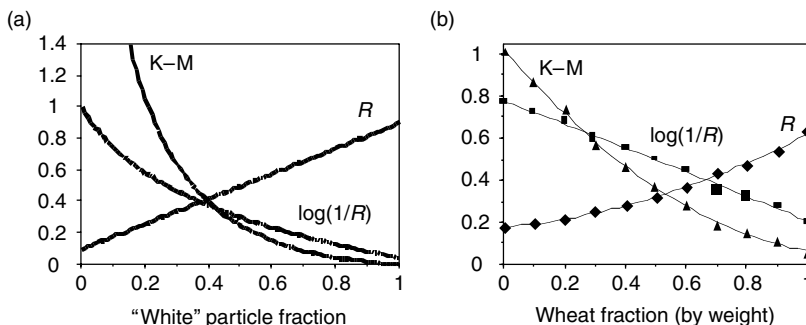


FIGURE 3.12 Variation of R , $f(R_\infty)$ and $\log_{10}(1/R)$ with particle fraction of the lighter component. (a) Calculated values when the dark areas are assumed to reflect 0.1 (10%) of the incident radiation and absorb 0.9 (90%) and the bright areas reflect 0.9 (90%) and absorb 0.1 (10%). Notice that the reflectance, R , is a straight line proportional to the fraction of bright area (as it would be for any mixture composed of two components of different reflectance); as a result, the K–M and absorbance functions are both curved. (b) The reflectance from a real layer of white wheat and dark rape seed. Light is transmitted through the white (wheat) particles, interacts with interior layers of the sample, and reemerges from the sample after having undergone additional absorption. Here the line representing the reflectance is curved, as is the line representing the K–M function. The $\log(1/R)$ curve, by coincidence, happens to be approximately straight in this case. (Reproduced from D. J. Dahm and K. D. Dahm, *Interpreting Diffuse Reflectance and Transmittance: A Theoretical Introduction to Adsorption Spectroscopy of Scattering Materials* (2007), by permission of NIR Publications Copyright 2007.)

Focusing on the line where the absorption metric is reflectance (the fraction of the incident beam that is remitted), the black rape seed particles have high absorption, while the wheat particles absorb far less. However, the line is curved because the layer is not opaque as discussed previously. Further, because the effective sample thickness is higher for wheat than for rape seed, the line is super-linear as a function of wheat fraction. As in Example 2, the representative layer theory can reasonably define the shape of these curves.

In the model used to fit these experimental data, we assumed that the remission at the left-hand side of the chart is from an opaque layer, although the opaque layer of pure rape seed is almost certainly more than one particle thick because of the effect of voids. In a sample with voids, an opaque layer must be at least two particles thick. The fractions for a hypothetical layer were calculated from the assumed characteristics of the individual components using Equation (3.84) and Equation (3.85). The R_∞ values for an infinitely thick sample making up the line in Figure 3.12 were calculated by applying an inverse form of the Dahm equation

$$R_\infty = \frac{1 + R_1^2 - T_1^2 - ((1 + R_1^2 - T_1^2)^2 - 4R_1^2)^{0.5}}{2R_1} \quad (3.94)$$

The hypothetical opaque layer that fits yields the desired R_∞ value for 100% rape seed; 0% wheat has the following parameters: $a_r = 0.83$, $r_r = 0.17$, $t_r = 0.00$. With these values for the pure rape seed layer, the following values for a pure wheat layer: $a_w = 0.089$, $r_w = 0.43$, $t_w = 0.48$ (subscript w for wheat, r for rape seed) gave the desired line.

These assigned values may be quite unreasonable for remission from a layer that contained nothing but those particles. This is a curve fitting exercise. We are manipulating four parameters to fit a line. There are many combinations of these four parameters that give the same line. Presumably, none of the sets will be the properties of a single layer of particles, because we have not included voids in the model, and a layer of particles, one particle thick, would certainly contain voids. Nonetheless, this exercise illustrates the capability of the Dahm equation and the representative layer theory to describe particulate systems, even when there is very high absorption, a place where there

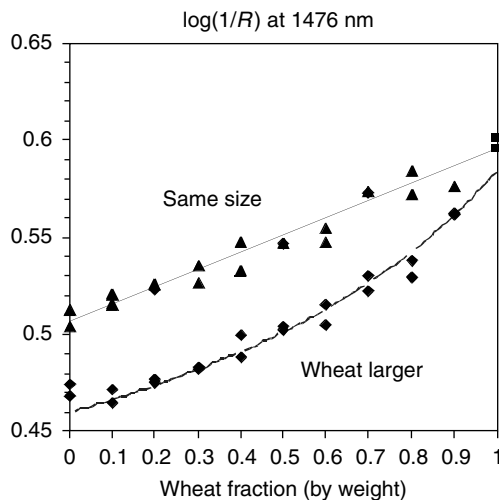


FIGURE 3.13 Variation of $\log(1/R_\infty)$ vs. the fraction of wheat in a sample composed of rape seed and wheat. The markers show the experimental values of $\log(1/R_\infty)$ vs. the fraction of wheat in the mixture while the lines show the shape predicted by the representative layer theory. The top curve is for wheat and rape seed of the same particle size. In the bottom curve, the wheat particles are twice the size of the particles of rape seed. (Reproduced from D. J. Dahm and K. D. Dahm, *Near-Infrared Technology in the Agriculture and Food Industries*, 2nd edn. (P. Williams and K. Norris, eds.), St. Paul, MN, pp. 1–17 (2001) by permission of American Association of Cereal Chemists, Inc. Copyright 2001.)

is significant departure from the K–M equation. However, this is not a method to determine straightforwardly the properties of an individual particle from the experimental data. We can not show the quantitative validity of the theory unless we know the properties of the individual particles (from other data).

In Figure 3.13, we show the effect of particle size on the spectroscopic data. We have not engaged in any curve fitting exercise. The data is taken from a region of the NIR spectrum in which absorption of both rape seed and wheat is low. This will assure that absorption levels will not cause a significant deviation from linearity of a plot of $\log(1/R)$ vs. wheat fraction. The wavelength of 1476 nm was chosen because it is the location of an absorption maximum for rape seed, even though the absorption at this wavelength range is low, as indicated by $\log(1/R)$ values of less than 0.6.

For the $\log(1/R)$ data at 1476 nm measured for two series of mixtures shown in Figure 3.13, the upper series has wheat and rape seed with the same particle size. Notice that, as expected at low absorption levels, the experimental points generally follow a straight line. The lower series has wheat particles that are twice as large as the rape seed. Here the points show a departure from linearity. The end points of the line were determined by human intervention, while the shape of the line was determined from the values for the end points weighted in proportion to the contribution of each component to the total surface area in the sample. (Surface area is inversely proportional to particle size, so the smaller particles are over-represented compared to their weight fraction.) The two series have the points at the extreme right of the chart in common. Again the data are reasonably well fit by calculations using the representative layer theory. However, this time we have not used the Dahm equation or done any curve fitting.

This data set also illustrates the problems in making reproducible measurements on mixtures of particles. The largest source of variation is probably the void fraction. The effect of void fraction on absorption is profound in close-packed mixtures, but the changes tend to occur at all wavelengths and are thus easily corrected.

Notice how the end point of the series with two particle sizes departs from the trend for the central points. Samples with only one particle size do not pack as densely as one with two sizes. In a

mixture with two sizes, the small particles ones fill in the holes between the large ones. The behavior of such samples may be understood with use of the Dahm equation (Equation (3.84)). As the void fraction decreases, both a and r increase and the factor $(2 - a - 2r)$ decreases and the value of the Absorbance/Remission function, $A(R, T)$, decreases along with it.

We believe these examples show both the usefulness of the representative layer theory in describing particulate samples. Further we have illustrated the applicability of the Dahm equation to situations where continuous theories do not work well. Finally, we have tried to make clear that, however useful the theory may be in explaining what we observe, we have not created an easy way to determine particle properties, or to correct simply absorption data so it will be linear with analyte concentration.

3.7 EXPERIMENTAL CONSIDERATIONS FOR REFLECTION MEASUREMENTS

Most analyses performed by NIR spectroscopy rely heavily on a chemometric approach. Most of these rely on some form of linear regression. The recommendations made here are guided by the assumption that the more linear the metric of reflectance as a function of analyte concentration presented to the chemometric package, the better the performance. When one is choosing an experimental arrangement, convenience generally outweighs the quest for optimal linearity. Additionally, there is no known approach that will produce linear data for the general case. However, there are some principles that we would like to extend:

1. For small particles (where “small” means that the product of linear absorption coefficient and diameter is much less than one), plots of $f(R_\infty)$ vs. c are linear for samples of infinite thickness. Achieving this linearity requires either that absorption by the matrix is very low or measurements are made using absolute reflectance.
2. For nonscattering samples placed on a specularly or diffusely reflecting substrate, $\log(1/R)$ is linear for measurements made in transfection, since this is simply a double-pass transmission measurement. For scattering samples measured in transfection, plots of $\log(1/R)$ vs. the concentration of a given component, are more linear for thinner samples than thicker ones. The most linear response is obtained when measurements are made in regions of low to moderate absorption.

The optimal experimental arrangement, of course, will depend on the purpose of the measurement, as well as the characteristics of the sample of interest. The discussions below are intended to help the analyst make better decisions in selecting an experimental arrangement.

3.7.1 DEPTH OF PENETRATION

If diffuse reflection spectrometry is to be used for quality control purposes, it is essential to know the actual investigated sample volume, which is equivalent to the radiation penetration depth or the effective sample size m_{eff} . In a publication by Berntsson et al. [73], the effective sample size of pharmaceutical powders was investigated by the three-flux approximation presented above that they called the equation of radiative transfer (ERT) method. and an empirical method they called the variable layer thickness (VLT) method. In this publication, the effective sample size m_{eff} is defined as the mass per area of the sample at which its diffuse reflectance has reached 98% of the diffuse reflectance of a corresponding optically thick sample.

To obtain m_{eff} with the use of the three-flux approximation of ERT, the scattering and absorption coefficients of the investigated powder are obtained from diffuse reflectance and transmittance measurements on optically thin samples (for a detailed discussion see [41,74]). Then, at each wavelength, the diffuse reflectance is calculated as a function of the scattering and absorption coefficients for a

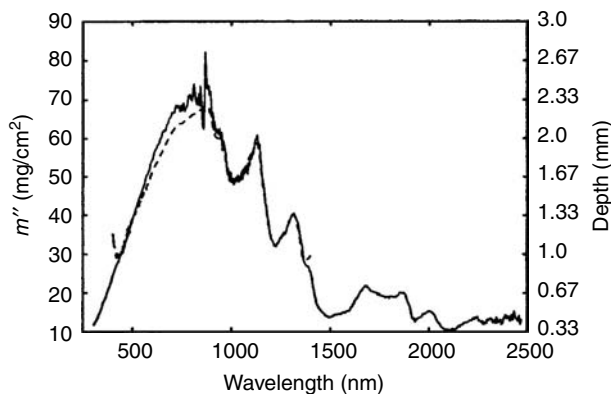


FIGURE 3.14 Effective sample size and penetration depth of microcrystalline cellulose powder according to the ERT method (solid line) and the VLT method (dashed line). (Reproduced from O. Berntsson, T. Burger, S. Folestad, L.-G. Danielsson, J. Kuhn, and J. Fricke, *Anal. Chem.*, 71: 617–623 (1999) by permission of American Chemical Society Copyright 1999.)

gradually increasing sample thickness and compared to the diffuse reflectance of an infinitely thick sample. The sample thickness for which the above 98% limit is reached corresponds to the effective sample size m_{eff} .

This method is compared to a totally independent procedure, the VLT method, where diffuse reflection spectra are collected at several controlled powder thicknesses. Assuming that the backing is either completely transparent or completely opaque, the diffuse reflectance of the powder layers increases with increasing sample thickness until the reflectance of an optically thick sample (R_{∞}) is reached. For each measured wavelength, an exponential function is fitted to the experimental data (plots of $\log(1/R)$ vs. sample thickness, where R is the measured reflectance). Using the 98% limit, the effective sample size m_{eff} can be obtained from the exponential fit (see [75] for a detailed discussion of the VLT method).

Figure 3.14 presents the effective sample size of a microcrystalline cellulose powder (MCC, particle size range: 65 to 300 μm) in the NIR region. Assuming a powder density of 0.30 g cm^{-3} , the effective mass per area is transformed into an effective penetration depth in millimeters, shown on the right axis. The wavelength dependence of the effective sample size, which is inversely correlated to the absorption coefficient, and the good correspondence of the two methods can clearly be seen. The upper limit for the VLT method was 1400 nm for the MCC sample because the curve fitting becomes unstable if the effective sample mass per area is below the smallest powder mass per area used in the measurements. However, both methods are suited to determine the actual probed sample volume of a diffuse reflection measurement.

Another approach to the determination of penetration depth in terms of “number of particles interrogated” was investigated by Olinger and Griffiths [50]. An estimate of the effective penetration depth of the beam in a diffuse reflectance measurement can be made from the measured values of $\log(1/R'_{\infty})$. If the absorptivity of a pure material in the absence of scatter is given by k , and particles of the material have an average diameter d , then the absorbance per particle is given by $a'd$, where a' is the base 10 absorptivity. By dividing the baseline corrected values of $\log(1/R'_{\infty})$ by the absorbance per particle, the effective number of particles through which the radiation reaching the detector has passed can be estimated. Olinger and Griffiths estimated the typical number of particles through which the remitted beam passes at 20. More recent work by a number of different research groups suggests that the number of particles through which the remitted beam passes may be larger than 20, but that the sample depth that is actually interrogated in a diffuse reflection measurement is no larger than about 20 particles.

3.7.2 EFFECT OF RELATIVE REFLECTANCE AND MATRIX REFERENCING

Even when we are dealing with “small” particles for which there is no significant inherent deviation from linearity of plots of $f(R_\infty)$, experimental conditions can cause a nonlinear response. Further, certain approaches that are used by experimenters, borrowed largely from transmission spectroscopy, designed to improve the linearity, actually create a nonlinear response. Such is the case with “matrix referencing.” Below we wish to make two major points:

1. Using a relative reflectance measurement will tend cause a departure from linearity when using the K–M function, but not $\log(1/R)$, as a metric for absorption.
2. Matrix referencing will cause a nonlinearity for both metrics (if the matrix has absorption).

An important point in practical NIR measurements is that a relative reflectance, R'_∞ , rather than an absolute diffuse reflectance, R_∞ , is usually measured. The relative reflectance is equal to the ratio I_S/I_R , where I_S is the intensity of radiation reflected from the sample and I_R is the intensity of radiation reflected from a reference material. (In the case of NIR reflectance spectrometry this material is usually a ceramic disk while a powdered alkali halide is usually employed for mid-infrared measurements.) Strictly speaking, the K–M equation as well as the other presented models require that an absolute reflectance, defined as the ratio I_S/I_0 , be measured, where I_S is defined as above and I_0 is the intensity of the incident radiation. Absolute intensities can, in theory, be measured by using an infinitely thick sample of a scattering, but nonabsorbing, material as the reference. (The ideal material would have the same scattering properties as the sample.) The measurement of absolute reflectance can be made directly through the use of an integrating sphere, although some care is required. An absolute reflectance can also be derived from the relative reflectance although the derivation requires several experimental measurements [2].

The determination of absolute reflectance is more important when using the K–M function as the metric for absorption than for $\log(1/R)$ data. If we define (I_S/I_R) as the relative reflectance R' , then $\log(1/R') = \log(I_R/I_S) = \log(I_R) - \log(I_S)$. The reference value $\log(I_{\text{ref}})$ is a constant offset at a particular wavelength. Furthermore, if the reference is the matrix in which the analyte is embedded, the measurement becomes a direct measure of the absorption of the analyte. However, the K–M function using relative reflectance is not linearly related to the K–M function using absolute reflectance, as shown in the examples in Section 3.6. Matrix referencing with the K–M function would require measuring the function for the matrix and the sample, each on an absolute scale and subtracting.

Kortüm [2,76] showed experimentally that the use of relative reflectance causes deviations from K–M theory if the analyte is surrounded by an absorbing matrix. This effect was shown by measuring the visible reflectance of Cr_2O_3 in an absorbing matrix relative both to the pure diluent and to a highly reflective standard (MgO). When the diluent was used as the reference, a plot of $f(R'_\infty)$ vs. concentration of Cr_2O_3 was nonlinear. When MgO was used as the reference, a similar plot yielded a straight line with a positive intercept. Kortüm states that a straight line with a zero intercept can be obtained when $f(R_{\infty,A})$ is plotted vs. c :

$$f(R_{\infty,A}) = \frac{K_A}{S} = f(R'_{\infty,A+M} \times \rho R'_{\infty,M}) - f(\rho R'_{\infty,M}) \quad (3.95)$$

where $R_{\infty,A}$ is the absolute reflectance of the analyte (A), $R'_{\infty,A+M}$ is the reflectance of the analyte + matrix relative to the reflectance of the matrix (M), ρ is the absolute reflectance of a nonabsorbing standard, and $R'_{\infty,M}$ is the reflectance of the matrix relative to the reflectance of the nonabsorbing standard. For most NIR reflectance analyses of cereal products, it is impossible to measure either the value $R'_{\infty,M}$ or $R'_{\infty,A+M}$ due to the complexity of the sample. Therefore this type of correction for the

absorption of the matrix should only be viable for samples that are relatively simple, for example, binary and ternary mixtures. Even for simple samples, use of Equation (3.95) may not be productive since treatment of this type usually does not linearize plots of $f(R'_\infty)$ vs. c for powdered mixtures measured by mid-infrared diffuse reflectance spectrometry [49], because in that case the absorption is usually very strong, and the function is inherently nonlinear even when absolute intensities are used.

It is generally accepted that the K–M equation (like Beer's law, but to an even greater extent) is a limiting equation and should only apply for weakly absorbing bands, that is, when the product of absorptivity and concentration is low. For organic materials, absorptions in the NIR are due to vibrational overtones and combination bands. The absorptivities of these bands are much weaker than the absorptivities of the corresponding fundamental vibrations. Thus most organic analytes can be considered to be weakly absorbing in the NIR even without dilution. As noted above, however, for most NIR analyses, the analyte (such as protein or lipid molecules in a cereal) is usually not isolated from other components, but is surrounded by a matrix which is not only complex but which also often absorbs the incident radiation at least as strongly as the analyte at the analytical wavelengths. In a cereal product analysis the matrix would largely consist of carbohydrate molecules. It would therefore be expected that unless a proper referencing method is used, absorption by the matrix surrounding the analyte will cause deviations from the K–M equation. Even if the intensities are properly measured, using matrix referencing (for the case of an absorbing matrix) can cause a deviation from linearity.

3.8 CONCLUSIONS

In summary, therefore, although detailed investigations of the theory of diffuse reflection spectrometry by many workers have been carried out during the last century, they have not resulted in a single metric that is proportional to analyte concentration (in the same manner as absorbance in transmission spectroscopy). Fortunately, simple conversion of reflectance values to $\log(1/R'_\infty)$ appears to be effective for many powdered samples being analyzed by NIR diffuse reflection spectrometry.

Because of the limitations inherent in representing a real sample as a continuum, the more sophisticated radiative transfer models, such as the discrete ordinate approximation or the diffusion approximation, hold little hope for obtaining for a better understanding of the effects occurring in diffuse reflection spectrometry for the general case.

Beginning with the properties of the individual particles in a mixture, the representative layer theory gives a way of calculating the properties of a layer of particles. The merging of the continuous and discontinuous approaches, as embodied in the Dahm equation, gives a way to calculate the spectroscopic properties of a sample from that of such a layer.

The inverse problem, calculating the properties of individual particles from that of a sample remains unsolved for the general case.

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Part II

Instrumentation and Calibration