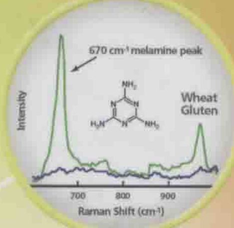
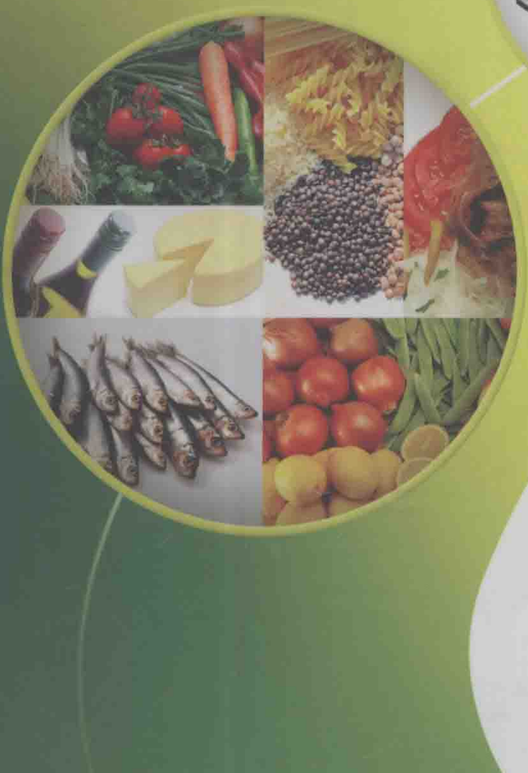
Editors
Eunice C. Y. Li-Chan, Peter R. Griffiths and John M. Chalmers





Applications of Vibrational Spectroscopy in Food Science

Volume I
Instrumentation and Fundamental Applications

WILEY

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Vibrational Spectroscopy

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Volume I: Instrumentation and Fundamental Applications

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Preface

The quality, authenticity and safety of the foods and beverages that we consume on a daily basis are of critical importance to society. Food scientists and technologists working in industry, government, or academia all over the world therefore are actively engaged in analysis of foods and beverages in order to both ensure their safety and maximize their quality, as well as to address the longer term goal of discovering new information that will enhance their product development and process optimization.

To meet these analytical needs, the approach most commonly adopted by food scientists has typically involved steps for isolation and separation, such as solvent extraction, high-performance liquid chromatography, or gas chromatography, followed by detection using ultraviolet-visible spectroscopy, fluorescence, mass spectrometry, and so on, but traditionally, relatively rarely using vibrational spectroscopy. In practice, students in many food science programs are given very little exposure to vibrational spectroscopy, except perhaps for the isolated organic chemistry laboratory experiment in which the purified product of a chemical reaction might be subjected to mid-infrared (mid-IR) spectroscopy for identification. It is therefore not surprising that for most of the last century, vibrational spectroscopy was not commonly a part of the "analytical toolbox" of most food scientists and technologists, and there were only a few reported applications of vibrational spectroscopy in food science.

This situation changed beginning in the 1970s and 1980s with the pioneering work of Karl Norris (at the Instrumentation Research Laboratory of the United States Department of Agriculture in Beltsville, Maryland) and Phil Williams (at the Canadian Grain Commission in Winnipeg, Manitoba) and their colleagues in establishing near-infrared (NIR) spectroscopy for the expedient analysis of cereals and soy beans. Since this early work, there have been dramatic advances in the technologies for measuring NIR spectra, as well as in the development of algorithms for preprocessing and multivariate statistical analysis (chemometrics) of NIR spectral data in order to obtain accurate and reproducible quantitative information on the components of foodstuffs. Even more significant advances have been made in the instrumentation for mid-IR and Raman spectroscopy. These techniques are highly complementary to NIR spectroscopy, in that their spectra are more amenable to interpretation without the need for chemometrics—although chemometric algorithms are also being used commonly now to process mid-IR and Raman spectra—but are less suitable for very fast on-line measurements. The advantages of minimal sample preparation, rapid analysis, and a "green" methodology have led to a surge of intense interest in exploring vibrational spectroscopy for the analysis of food composition, detection of adulteration and contamination, and prediction of sensory, nutritional, or physical properties. At the same time, the growing recognition of the usefulness of vibrational spectroscopy for food quality assessment and process monitoring has generated interest in developing commercially available instruments dedicated to "user-friendly", routine analysis of specific food commodities.

As with many other analytical techniques, vibrational spectroscopy has both advantages and tremendous potential, but also limitations and challenges. The purpose of this book is to provide information on the fundamental theoretical basis underlying vibrational spectroscopic techniques as well as on practical tips and pointers to generate meaningful spectral data. We hope that the information in this book will enable both the novice as well as the experienced user to adopt these techniques and furthermore to consider innovative ways in which vibrational spectroscopy may be applied to address specific analytical and research needs in food science.

We would like to stress, however, that despite the enormous success of NIR spectroscopy for the rapid analysis of cereals and other raw materials, this book is not just about NIR spectroscopy; it is about the three prime techniques of vibrational spectroscopy. Our goal was to show how each of these—NIR, mid-IR, and Raman spectroscopy—plays a role in food science. For example, a fundamental investigation into the changes that occur on treating foods, whether by cooking, freezing, or irradiation, would be difficult to carry out by NIR spectroscopy as the spectra are far less amenable to visual interpretation than mid-IR and Raman spectra. We hope that our choice of subject matter will allow the reader to obtain an appreciation of when a given type or combination of vibrational spectroscopy approaches is the most appropriate.

The book is organized as five parts in two volumes, with Volume 1 (Parts 1 to 3) on instrumentation, techniques and fundamental research applications, and Volume 2 (Parts 4 to 5) illustrating the applications to food, drink and related materials. In Part 1, after a general introduction to the application of vibrational spectroscopy in food science, the theory, instrumentation, sampling techniques, and data processing algorithms that are used for mid-IR, NIR, and Raman spectroscopy are described in some detail. Several of the more recent instrumental developments, such as mid-IR and Raman imaging, confocal Raman microspectroscopy, and surface-enhanced Raman spectroscopy, are then introduced in Part 2, along with examples of their application to the analysis of foods.

Part 3 describes the ways in which vibrational spectroscopy is used for the study of chemical changes to components such as oils and lipids, carbohydrates and proteins in various foods including meat and fish, and also to food packaging, that occur as a consequence of storage or process treatments, such as thermal processing, exposure to air, heat, cold and irradiation. Most of these studies require the interpretation of often quite subtle spectral changes and thus involve the use of mid-IR and Raman spectroscopy in view of the relative ease with which these spectra can be interpreted as compared with NIR spectra.

The chapters in Part 4 cover the analysis of bulk materials such as cereals, rice and oilseeds, fruit and vegetables, fish, meat, milk, cheese and other fermented dairy products, wine and alcoholic beverages, as well as ingredients and additives such as edible fats and oils, sweeteners, polysaccharides, and proteins. Here, both because many products can be analyzed with either no or minimal sample preparation and because chemometric techniques obviate the need for spectral interpretation, NIR spectroscopy plays a major role. However, the other vibrational spectroscopies also give key information on or insights into these commodities. For example, following the chapter on the analysis of wheat by NIR spectroscopy, the information that can be obtained by mid-IR microspectroscopy is described.

The final chapters in Part 5 cover aspects related to the application of vibrational spectroscopy techniques for compositional analysis in the context of regulatory compliance, adulteration, authenticity, and traceability, as well as for the detection of spoilage or pathogenic microorganisms and chemical contaminants germane to food safety.

During the time that we were preparing this book, it became very clear that many papers that have been published on the application of vibrational spectroscopy in food science contain errors that have been propagated over many years to the point that they have become lore. Some of these simply refer to the nomenclature. An example is labeling the abscissa of mid-IR and Raman spectra as "Wavenumbers (cm^{-1})" rather than the correct "Wavenumber (cm^{-1})". This is like labeling an axis as "Distances (km)" or "Times (s)"! Unfortunately, several instrument manufacturers label their spectra in this manner, which makes it difficult to persuade authors that it is incorrect. Another very common error involves calling reflection spectra "reflectance spectra", even though the same author will usually refer to a transmission spectrum correctly. Again, this error is frequently propagated in manufacturers' literature. We have tried to apply all terms used in this book in the correct manner. To this end, we have drawn on the nomenclature that is recommended in the journal *Applied Spectroscopy*, which can be found at the following URL:

http://www.s-a-s.org/media/pdf/2010/03/17/apls-64-01-136.pdf.

We also noted that some bands in the mid-IR and Raman spectra of the components of foods were frequently assigned incorrectly, and that once these assignments had been published in the food science literature, those assignments were usually taken as "gospel" in subsequent papers. We have made a strong effort to check that all bands that have been assigned in the various chapters of this book are in agreement and consistent with the assignments published in authoritative books on the interpretation of IR and Raman spectra.

When one of us (PRG) told colleagues that he is coediting a book on the applications of vibrational spectroscopy in food science, the usual reaction was "Oh, not another book on NIR spectroscopy." In fact, many food scientists who routinely apply NIR spectroscopy in their work are surprised to learn how much information is contained in mid-IR and Raman spectra. We hope that the material in this book proves that mid-IR and Raman spectroscopy have their place alongside NIR in the study of foods and beverages and that all three techniques need to be considered before settling on the optimum approach.

Eunice C. Y. Li-Chan
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May 2010

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Part One

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