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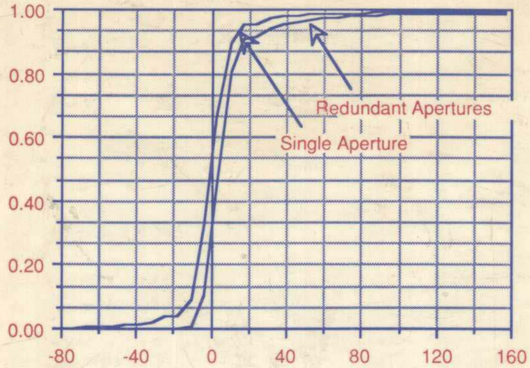
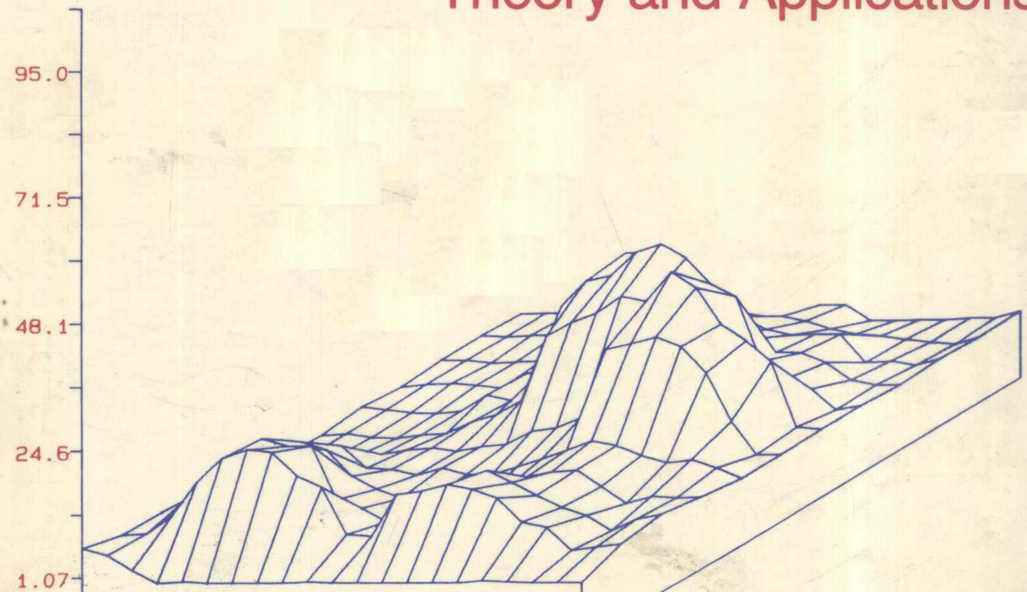


Infrared Microspectroscopy

Theory and Applications



edited by

Robert G. Messerschmidt • Matthew A. Harthcock

INFRARED MICROSPECTROSCOPY

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Preface

Infrared microspectroscopy, the coupling of optical microscopy and infrared spectroscopy, is not a new concept. In the 1940's instrumentation for recording infrared spectra on areas of a sample isolated using an optical microscope with all-reflecting optics was designed and limitedly utilized in a coupled mode with a dispersive infrared spectrophotometer. Until the early 1980's analysis of microscopic samples using infrared spectroscopy largely involved the use of what is referred to as "traditional" microsampling techniques. These "traditional" microsampling techniques involve, for example, pinhole masking or micro potassium bromide pellets.

In the 1970's a coupled Raman spectrometer and optical microscope became and continues to be a popular vibrational spectroscopic microprobe technique. Much has been written on the application of Raman microprobe techniques for obtaining vibrational spectra on microscopic particles as small as one micrometer. However, the continuous fluorescence problems associated with Raman spectroscopy have prevented broader application of the Raman microprobe.

In the early 1980's, a resurgence in the use of infrared microspectroscopy occurred for two basic reasons. First, the advantages (predominantly the multiplex and energy throughput advantages) of Fourier transform infrared (FT-IR) spectrophotometers versus dispersive instrumentation have allowed convenient and routine operation of an all-reflecting microscope with an infrared spectrophotometer. Currently, the diffraction limit of infrared radiation (10-20 micrometers) is the limiting condition for obtaining absolute spectra from a given area of a material. The second reason is trends in technology. Various fields of science are requiring different and specific answers to problems that "traditional" analytical instrumentation cannot provide, as will be demonstrated many times in this book.

The past several years have seen increasing attention to the field of infrared microspectroscopy. Various symposia have been held at meetings such as the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), the Eastern Analytical Symposium (EAS), the Pittsburgh Conference, and the Microbeam Analysis Society. The first book published on the topic appeared in August of 1987. The book, edited by Dr. Patricia B. Roush (Perkin Elmer Corporation), is based on a symposium chaired by Dr. Roush, containing nine papers on various areas of infrared microspectroscopy, and is titled *The Design, Sample Handling, and Applications of Infrared Microscopes* (ASTM Special Technical Publication 949, 1987).

This book of eighteen chapters is an outgrowth of symposia organized and held at FACSS XIII and EAS by the editors (FACSS-Harthcock, EAS-Messerschmidt) during the fall of 1986 and contains the theory behind the development of a high performance infrared microscope. Also included are the considerations necessary for using infrared microspectroscopy, for example, for imaging a sample and for coupling it with high performance liquid chromatography (HPLC). Finally, a variety of applications of the use of infrared microspectroscopy are contained in this volume.

The chapters in this book often address both specifics about a technique (e.g., sampling handling and new methods of using infrared microspectroscopy) and applications of the technique to various scientific fields (e.g., polymer characterization and semiconductor technology). The editors have chosen to classify the chapters in this book into the following categories:

- Instrumentation Considerations and Technique Advances in Infrared Microspectroscopy
- Analysis of Polymers by Infrared Microspectroscopy
- Applications of Polarized Infrared Microspectroscopy
- Application of Infrared Microspectroscopy to the Semiconductor Industry
- Application of Infrared Microspectroscopy to Biological and Pharmaceutical Research
- Miscellaneous Applications of Infrared Microspectroscopy

It will be apparent that several of the chapters overlap several of the general catagories above.

From the categories, one can see the impact the field of infrared microspectroscopy is having. The opening chapter by Messerschmidt explains the theory of operation and design of an FT-IR microscope. Topics such as Redundant Aperturing™ versus single aperturing, the numerical aperture, signal-to-noise ratio, coherence, etc. are discussed as they relate to the performance of an FT-IR microscope. Harthcock and Atkin reveal methodology using infrared microspectroscopy for obtaining images of a material based on functional group maps. Presented as a new imaging technique, examples of the application of this technique to polymer characterization are included.

Lang et al. in their chapter present considerations in keeping a clean working environment for doing infrared microspectroscopy. This chapter is more for the benefit of the new infrared or vibrational microspectroscopist who should be aware of contamination potential than for the optical microscopist who has been aware of contamination potential for years.

Polymer characterization is obviously an area that infrared microspectroscopy is influencing extensively. Humecki discusses sample preparation and analysis of polymers and contaminants in or from various matrices. Gerson and Chess describe the use of reflectance infrared microspectroscopy for delineating the failure of a polymer composite. Mirabella describes the simultaneous measurement of infrared and differential scanning calorimetry data to study changes in polymer structure which occur at various temperatures. The future of this technique for polymer characterization is also addressed by Mirabella.

The use of polarized infrared microspectroscopy is also addressed, in large part as it applies to polymeric materials. Chase discusses the details in obtaining accurate dichroic spectra from single polymer fibers. The advantage of using Redundant Aperturing in the measurement of dichroic spectra of single fibers is also described. Brasch and Lustiger describe the use of polarized infrared microspectroscopy to investigate the amount of tie molecules present in polyethylene. Hill and Krishnan provide examples of dichroic measurements on single crystals and polymers using infrared microspectroscopy.

The use of infrared microspectroscopy has been prescribed in the semiconductor industry for about the last seven years. Madden et al. describe how the technique is used to address contamination problems in the semiconductor industry. Krishnan shows the use of infrared spectra for determining the epitaxial layer thickness of a semiconductor and for determining contaminants in the wafers (e.g., oxygen, carbon).

In the chapter by Fuller and Rosenthal the potential of infrared microspectroscopy for studying biological specimens is shown. For example, the authors show how spectra can be obtained on a few red blood cells. The full potential of infrared microspectroscopy in the biological and medical sciences has definitely not been realized to date and it will certainly expand in these fields. Reffner shows in his chapter how polymorphic behavior, of pharmaceutical importance, can be investigated using infrared microspectroscopy. Reffner also includes an introduction which defines several terms used throughout this book.

Fraser et al. demonstrate the coupling of infrared microspectroscopy for problem solving in the industrial environment. They also identify the complementary nature of Raman microprobe spectroscopy and infrared microspectroscopy.

Schiering also provides various examples of the technique's use in an industrial or quality control environment. An example of the use of a diamond cell for flattening materials for analysis by infrared microspectroscopy is included and a nice brief history of infrared microspectroscopy is given. Sommer et al. describe the use of infrared microspectroscopy for studying paper chemistry.

The final chapter, by Wooton and Hughes, discusses the application of grazing angle reflectance infrared microspectroscopy to characterize the surface of metals which had been treated with various lubrication oils.

This book is intended to provide an overview of the theory and applications of infrared microspectroscopy. As observed from the contents and noted repeatedly by the authors, the influence of this technology has spanned many fields of science. The impact of infrared microspectroscopy is only starting to be realized. The material presented within the covers of this book provides a sampling of the data which can be obtained from this analytical technique.

The editors wish to thank each of the contributing authors for their chapters and their prompt response to issues related to getting this book to press. Also, the editors wish to thank the governing boards of the Federation of Analytical Chemistry and Spectroscopy Societies and the Eastern Analytical Symposium for their permission to publish this book, which is based on papers first given at their meetings. One of the editors (MAH) would like to express his appreciation to The Dow Chemical Company for allowing him the opportunity to serve as a co-editor of this book, his family for their understanding during the time it took to put this book together, and particularly his wife, Patricia, for assisting in some of the secretarial duties necessary to complete this book.

The efforts of those who have contributed in an editorial capacity should not go unmentioned. Most importantly, the editors wish to thank Ms. Jennifer Sting and Ms. Andrea Mikolowsky, who have completely produced this book (except for some of the figures) using Apple Macintosh® computers. Chapters received from the authors either were already in a machine-readable format or were brought into the Macintosh via an optical character reader. The chapters were then formatted into a standard Marcel Dekker page format using Aldus Pagemaker® software. Appropriate spaces were left for later insertion of figures, except in cases where the figure was Macintosh generated as is the case in the chapter by Messerschmidt. Equations were entered using A. Bonadio

Associates' Expressionist™ software. Indexing was done using Microsoft Excel® software. Camera-ready copy was output using an Apple Laserwriter® printer. Ms. Sting and Ms. Mikolowsky are to be congratulated for their hard work and perseverance through the production of a book such as this using state-of-the-art production techniques. Additional editorial assistance and proofreading were contributed by Mr. Donald Sting, Dr. John Reffner, Mr. Seth Lefferts, Mr. Robert Sebes, Mr. Thomas Mattone, and Ms. Joan Kwiatkoski. Mr. Lefferts also served as computer problem-solver. We extend our thanks to all mentioned.

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We would also like to thank the staff of Marcel Dekker, Inc., for their cooperation, most notably Ms. Rosemarie Krist and Ms. Vickie Kearn.

The editors would like to note that all chapters were received from the authors by no later than May 1987. All papers were accepted for publication no later than November 1987.

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Instrumentation Considerations and Technique Advances in Infrared Microspectroscopy

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Application of Infrared Microspectroscopy to Biological and Pharmaceutical Research

Miscellaneous Applications of Infrared Microspectroscopy

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Minimizing Optical Nonlinearities in Infrared Microspectrometry

ROBERT G. MESSERSCHMIDT *Spectra-Tech, Inc., Stamford, Connecticut*

1.1 INTRODUCTION

There are several fundamental concepts that should be understood in order to successfully perform FT-IR microspectroscopy which are unimportant in macro-spectroscopy. Many of these concepts are a result of optical principles which, to other than an optical physicist, may seem to contradict one's understanding of optics. In fact, some of the concepts necessary to describe the behavior of imaging in the infrared microscope *do* contradict classical geometric optics!

Most readers will be familiar with the concepts of the laws of reflection and refraction, and the concept of magnification. These are the basis of geometric optics, and can be summarized by one simple equation, Snell's Law of Refraction. This formula describes the bending of light as it passes through materials of differing refractive indices and past surfaces of various curvatures. A special case of this law for mirror surfaces states that upon the encounter of a "ray" of light with a reflective surface, the angle of incidence of that light ray with respect to the surface will equal the angle of reflection.

Many readers will also know about the common optical aberrations which can be predicted and proved through the application of geometric optical ray tracing. These, such as spherical aberration, chromatic aberration and coma (offense against the sine condition), are controllable. It is the optical designer's responsibility to keep these aberrations small enough so that they are unobjectionable in a given application.

This is as far as one routinely needs to go in the design of instruments to be used in the visible region of the spectrum, at low magification. However, in order to deal with the behavior of light when the eye is aided, for instance in a microscope system, then the diffraction of light energy must be considered. Diffraction occurs everywhere, not only in microscopes. Insofar as the eye is an optical instrument, the image of everything one looks at is altered by diffraction. Fortunately, given the acceptance angle of light into the eye and the wavelengths involved, the diffraction effect is below the resolution limit. Therefore, one does not notice the effect.

The diffraction effect in infrared microspectroscopy manifests itself as a blurring of the image information which one obtains in order to measure the spectrum of a given sample. Primarily, the spatial resolution of the measurement is affected. That is, the energy reaching the detector contains spectral information from a larger physical area than is expected or desired. This has it's obvious consequences. Spurious energy and/or spectral peaks can be present in the resultant spectrum, inviting quantitative and qualitative misinterpretation. Unfortunately, diffraction is a physical phenomenon, and it is therefore not possible to eliminate the problem. But there are design considerations that can minimize the effect.

1.2 GENERAL CONSIDERATIONS

The general layout of an infrared microscope is shown in Figure 1. It consists of transfer optics to bring the infrared radiation from the interferometer, imaging both the source image and the pupil image (the beamsplitter image) through the microscope. The visible optical train is parfocal and colinear with the infrared radiation. This is achieved in setting up the microscope by viewing through a series of small pinholes, and then aligning for infrared energy through the same pinholes. In actual use, the area of interest is brought to the center of the field of the microscope under visible (transmitted or reflected) light. Then the area to be analyzed is delineated with high contrast apertures in the remote image planes of the sample. Preferably these apertures are variable in size so that the area of interest may be "zeroed in on". Since the optical geometry is the same for the visible evaluation and the infrared detection, the diffraction