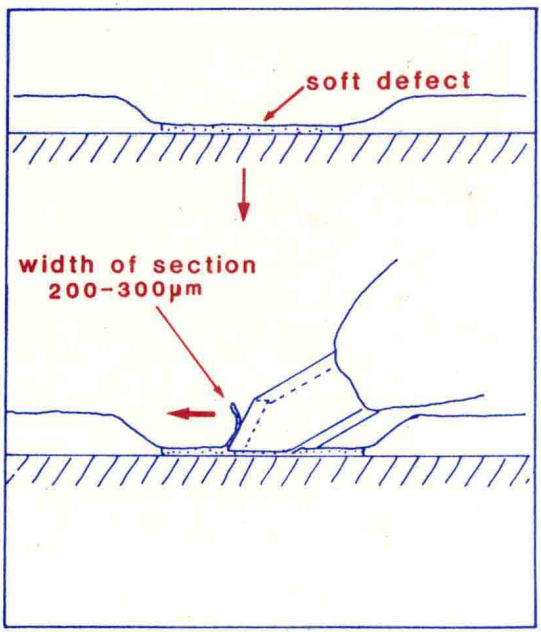
PRACTICAL SPECTROSCOPY SERIES VOLUME 19



Practical Guide to Infrared Microspectroscopy

edited by
Howard J. Humecki

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Marcel Dekker, Inc. New York • Basel • Hong Kong

Library of Congress Cataloging-in-Publication Data

Practical guide to infrared microspectroscopy / edited by Howard J. Humecki.
p. cm. -- (Practical spectroscopy ; v. 19)
Includes bibliographical references and index.
ISBN 0-8247-9449-4 (alk. paper)
1. Infrared spectroscopy. 2. Fourier transform spectroscopy.
I. Humecki, Howard J. II. Series.
QD96.I5P733 1995 94-42808
543'.08583--dc20 CIP

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This book is printed on acid-free paper.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

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Preface

Many new analytical techniques, when they first appear on the scene, fill a need of their inventors or developers. Those who share that need quickly adopt the new techniques and expand upon them. Sometimes these developers diffuse into a network that freely exchanges information regardless of their applications. This has not been the case with infrared microspectroscopy (IMS) to any significant degree. Of course, IMS is not a new technique; it is, in fact, an old one that has enjoyed a rebirth of sorts. But, because the lines of information within a specialty have been established for so long a time, there seems to have been little effort to communicate with others in diverse fields who may be exploring along similar avenues. For example, those in the packaging industry using IMS to examine multilayer thin films have little opportunity to discuss methodology with forensic scientists examining multilayered paint chips, and neither talks to art conservators even though there are considerable areas of overlap where each might profit from the others' experience.

To satisfy this need, resulting from a rapidly developing technology and expanding interest in this technique, required input from individuals having extensive experience in IMS and expertise in a wide range of specialties. I have attempted to bring together experts from various fields to discuss where and how they apply IMS in the solution of problems peculiar to their particular field or industry. Some have felt that it is important to preface their presentations with a discussion of theoretical considerations that show the limitations of IMS in regard to the problems under consideration. Rather than ask that these discussions be limited, I welcomed them as needed reminders that IMS has limitations that we must keep in mind when planning our approach to a difficult problem.

Likewise, an obvious extension of such limitation are techniques that complement or support evidence obtained by IMS. No method should be forced to stand alone if additional information can be obtained by other means. As my colleague Joe Barabe reminds me, "If you have a hammer, the only problem you can solve is a nail." Today, we have many tools at our disposal and, although this book is devoted to IMS, we must not fail to consider other means if they help us with needed information.

Robert Messerschmidt has been involved in the design and development of several microscopes for use with IMS. In Chapter 1, Bob describes theoretical considerations in instrument design that apply to the design of microscopes, and he discusses how they might affect performance. Some design features that have little importance in the design of standard instruments have enormous impact on the performance and the quality of the spectra generated for very small specimens.

Much to the chagrin of some spectroscopists, the transition from "standard" spectroscopy to microspectroscopy has not been an easy one. No one is better qualified to demonstrate the link between light microscopy and IMS than John Reffner, who with Pamela Martoglio demonstrates that light microscopy goes hand in hand with IMS.

K. Krishnan, Jay Powell, and Steve Hill discuss the principles of FT-IR microimaging, starting with a description of the essential components and their function and interaction. They describe applications of this technique on polymer, mineral, biological and semiconductor specimens.

The semiconductor industry has taken full advantage of IMS, not only to solve contamination problems but also to study materials and manufacturing processes. In Chapter 4, Kate Chess explores the use of reflectance techniques including ATR and grazing angle objectives in the study of surfaces, surface treatments, and processing problems in the electronics industry.

A study of thin films and laminates, and especially the problems associated with their manufacture, can be particularly difficult to solve. Richard Duerst and his associates describe how they have dealt with the variety of problems relating to surface defects, embedded particles, and diffusion of additives across an interface. They have included an example of analyzing a multilayer packaging film and of contour mapping of an interpenetrating network.

Probably no industry has exploited IMS more than law enforcement, where trace evidence plays a vital role in determining the success or failure of an investigation. Many of the techniques used by forensic scientists are also practiced by scientists in other fields. Scott Ryland describes in detail the steps involved in analyzing forensic paint evidence. Scott not only deals with the preparation of specimens, but also presents a detailed scheme for classifying and identifying the types of binders in single and multilayer applications.

Light microscopy and infrared spectroscopy are seen as the most useful techniques for identifying synthetic fibers. Edward Bartick, Mary Tungol, and Akbar Montaser compare sample preparation techniques, debating the pros and cons of

flattened versus "as is." They consider in great detail the effects of pressure, sheer force, and contamination on matching a questioned fiber to a suspected source. They present results of studies on the variations of peak area ratios for various copolymers and discuss results of studies of dichroism in single fibers.

Some of the problems encountered in art conservation bear certain similarities to those in forensics. Identification of protective coatings and fibers is a problem common to both, although sample preparation and the compositions may differ considerably as does the provenance of the articles and objectives of the analysis. Michele Derrick illustrates applications of IMS for the identification of coatings as well as some unique applications of IMS for the study of degradation of cultural artifacts, ancient and relatively modern.

The pharmaceutical industry has accepted IMS enthusiastically. In Chapter 9, Scott Aldrich and Mark Smith describe in detail the application of microscopical methods to problem solving in the pharmaceutical industry. They show in their examples not only the application and solution of problems, but in addition the need for detailed information concerning the history of the sample. The provider of the sample often has information that is vital in designing the analytical scheme.

The infrared microspectroscopy of mineral specimens presents unique problems, not the least of which is sample preparation. Very thin mineral specimens are difficult to polish, and often the thickness required to study one region of absorption is inappropriate for another. Anne Hofmeister discusses these problems and describes some techniques for preparing and carrying out both qualitative and quantitative analyses on small mineral specimens.

The previous chapters deal with applications and pertinent theory of IMS. It should be apparent that sample preparation is the single most important factor in determing the quality of information generated. Anna Teetsov, in Chapter 11, has carried sample preparation to a fine art describing techniques that some might find daunting. Methods for collecting a scattering of fine particles and droplets from surfaces and depositing them on a single spot on a salt plate are described, as are other simple but elegant techniques.

The last chapter deals with the identification of polymers in highly filled and pigmented systems through identification of their pyrolsis products. Nylons and polyesters can be subjected to controlled hydrolysis and their hydrolysis products may be recovered and identified by IMS.

I hope the reader will find these pages a handy guide to the basic theory of IMS and a ready source of information on techniques and applications. I would like to thank each of the authors for the thoughtfulness they have given to their topics, and the detail and professionalism in their presentation. My special thanks go to Bob Muggli, a friend, colleague, and early innovator in IMS, for his advice and editorial help.

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Minimizing Optical Nonlinearities in Infrared Microspectroscopy

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1. INTRODUCTION

There are several fundamental concepts that should be understood to perform FT-IR microspectroscopy successfully which are unimportant in macrospectroscopy. 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 that 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 or infrared region of the spectrum, at low magnification. However, to deal with the behavior of light when the eye is aided, for instance in a microscope system, 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 affected is the spatial resolution of the measurement. That is, the energy reaching the detector contains spectral information from a larger physical area than is expected or desired. This has its 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.

1.1. Rationale for an FT-IR Microscope

Infrared microscopes for dispersive spectrometers were developed in several academic laboratories in the late 1940s and early 1950s [1–3] but were used by only a handful a researchers. Even when Perkin-Elmer introduced a commercial unit in 1953 [4], not many people jumped on the bandwagon. A fairly in-depth search of the literature reveals few references to the infrared microscope in the 1960s and 1970s.

In the late 1970s, FT-IR spectrometers were starting to make their presence felt. A well-respected group of champions was at that time extolling the virtues of this type of instrument, such as higher resolution, lower noise, and better frequency accuracy than the ubiquitous dispersive instruments. Interestingly, an infrared microscope attached to an FT-IR spectrometer tends to restrict one of the inherent FT advantages: the throughput (Jacquinot) advantage. The optical throughput of an optical system is described by the equation

$$\Theta_x \Theta_s = A\,\Omega_s \qquad \text{cm}^2 \cdot \text{sr} \tag{1}$$

where A is the area and Ω_s is the solid angle subtended by the limiting aperture of the system (in the FT-IR microscope, this would be the area-defining aperture). Because a microscope is by definition used for small samples, the sample area contribution to the throughput calculation is reduced. On the other hand, one would like to increase the other factor, solid angle, as much as possible to

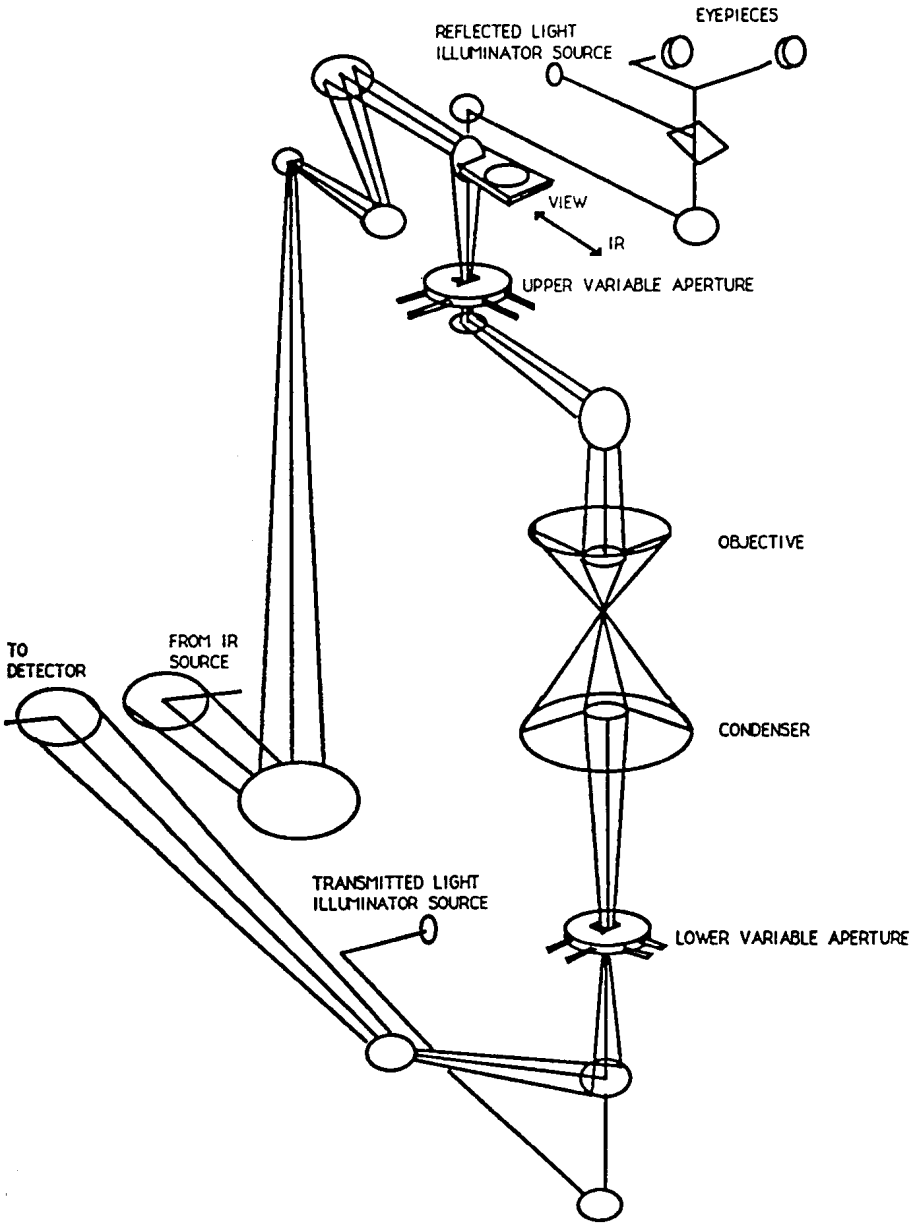

Figure 1. General layout of an FT-IR microscope.

improve signal *and* spatial resolution [5]. One normally still ends up in a region where more optical throughput than a dispersive spectrometer would allow is needed.

In addition, the other two fundamental advantages of the FT technique are still in full force: the multiplex (Felgett) and the frequency precision (Connes) advantages. The former results in a sensitivity benefit equal to the square root of the number of resolution elements. The latter relates to an improved ability to measure accurately the spectral frequency of absorption bands in a spectrum.

By 1982, the sensitivity of infrared spectroscopy had seemed to have developed to a point where low-energy and microscopic techniques were again being tried. A favorite demonstration on the floor of the Pittsburgh Conference in 1983 was obtaining the transmission spectrum of a brown paper bag: clearly, a low-energy situation. Down the aisle, another manufacturer was demonstrating the transmission spectrum of polystyrene through a 100-μm pinhole, without a beam condenser. Clearly, the stage was set for the reemergence of infrared microscopy. In the 1980s, FT-IR-based microscopes come into being, and the history of this development has been reviewed elsewhere [6]. Today, FT-IR microscopy is the chosen technique for a wide range of sampling problems, with about one-third of all FT-IR spectrometers being sold with a microscope attachment.

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, usually imaging both the source image and the pupil image (the beamsplitter image) through the microscope. The visible optical train is parfocal and collinear 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 visible evaluation and infrared detection, the diffraction effect is worse for the detection step, because the wavelength is longer. It follows that one can see the area one wants to measure more clearly than can actually be measured. For FT-IR microscopy, therefore, the spatial resolution is defined as the ability to measure the spectrum from an object delineated by the apertures without significant impurity radiation from neighboring objects. Since the infrared spectrum is quite complicated, consisting of thousands of data points, it is