

Overview

Historical Perspectives

Chemistry is a science which has a middle position as both the server and the one served with respect to other disciplines. In addition, one can understand the special field of analytical chemistry as an important focal point of technology, from which many types of services to other sciences are delivered, and into which many of the developments in other fields are incorporated. The point of making this observation is to emphasize that Chemistry (and particularly Analytical Chemistry) acts as both the donor and recipient from the collective technical knowledge of man, which means that the field is subject to continuous change and rapid growth. The obvious consequence of this situation is that it is useful to make periodic assessments and reassessments of the so called "state of the art" in particular areas. This volume developed out of the awareness of the need to develop an accurate account of the current status of quantitative infrared methods of analysis, and to provide a clear presentation of the power of this technique in the context of modern computerized infrared spectroscopic instrumentation.

Much of the sense of need for this work was generated during discussions centered around revision of the ASTM Recommended Practices for General Techniques of Infrared Quantitative Analysis (E 168). It became apparent during the work on revision of E 168 that so much had occurred and was still occurring to change the nature of quantitative work in infrared spectroscopy that the revised E 168 could not include a comprehensive discussion of all areas of the topic. Consequently the E 168 work group narrowed its focus to generate a document which would deal with general guidelines and the most major of issues in quantitative infrared. To expand on the more complicated issues in greater detail, a symposium was planned, from which articles could be generated to form a separate, more lengthy publication. The symposium was organized and held at the 1984 annual meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) in September in Philadelphia, Pennsylvania. The symposium was cosponsored by FACSS and ASTM. Additional financial assistance was provided by Digilab (subsidiary of BIO-RAD Corp.) and is gratefully acknowledged.

It is somewhat ironic that infrared spectroscopy started its industrial scientific life as a quantitative tool. One of the first commercially produced infrared spectrometers was codeveloped by scientists working during the early 1940s at American Cyanamid and Perkin-Elmer, to handle the problem of characterizing styrene-butadiene polymers in the defense related issue of synthetic rubber production. In the following decade gas chromatography replaced infrared in many quantitative industrial applications, and infrared was generally relegated to the task of molecular identification. The loss of favor by infrared with respect to quantitative applications could be easily understood in terms of the relative difficulty in carrying out the analysis with the instruments of the era. Not only was there a question concerning ordinate and abscissa reproducibility in the spectral data, but the result of instrument operation was just an ink trace on a piece of paper. This left the analyst with the task of measuring transmittance values with a ruler and calculating absorbances and concentrations with a slide rule or desk calculator, or even just a piece of graph paper.

The introduction of the double beam infrared spectrometer provided a simpler and more aesthetically pleasing spectrum from which to work, but it did not alleviate the basic difficulties involved in obtaining a reliable quantitative result without excessive effort or tedium. Moreover, the optical null double beam instruments introduced an additional source of error in terms of the uncertainty of the location of the zero transmittance point, and this caused some concern among analysts.

Major changes occurred in the seventies. Some of the important factors were incorporation of microprocessor technology into infrared instruments, development of desk-top microcomputers, and the evolution of Fourier transform infrared (FT-IR) spectrometers into reliable, powerful and affordable instruments for measuring spectra at high signal to noise ratios, even with relatively low transmittance samples. There were two subtle factors which shaped the progress of infrared quantitative analysis during this era. The first was that FT-IR instruments required their own integral computing system to produce spectra from interferograms by Fourier transformation. This meant that spectroscopists and analytical chemists obtained, often for the first time, a powerful computing device of their own which was not dominated and controlled by outside personnel from industrial computing centers. Coupled with this was the fact that vendors of FT-IR instruments provided some additional software besides the Fourier transformation algorithm, which allowed easy transmittance-absorbance interconversion, spectral subtraction, and even computerized quantitative routines.

During the same period dispersive instruments experienced substantial improvements, major among which was the development of the microprocessor controlled ratio recording infrared spectrometer. Among the advantages of the ratio recording systems was that an accurate measure of the zero percent transmittance point could be obtained. In the late seventies microcomputers

began their rapid incursion into scientific laboratory instrumentation. Often these systems were called anything but computers, in an effort to enhance their chances of being retained under the auspices of the laboratory personnel rather than those of the company's computing center. However, before the end of the 1970s, it appeared that no serious instrument vendor would consider designing a product for the future without providing for internal or external computing facilities. This set the stage for the arrival of the age of computerized quantitative infrared. Infrared instruments had improved to the point that the data were generally accurate and reproducible, and small computing devices were attachable or built internally which could evaluate the spectra and calculate the results automatically with methods that could be designed and tailored by the laboratory chemist.

One further development that should be mentioned is the declassification of the now commonly available mercury-cadmium telluride (MCT) detector. This device was originally developed for military purposes, but eventually was declassified and found its way into use in FT-IR instruments of the chemical laboratory. The MCT detector is operated at reduced temperatures by cooling with liquid nitrogen. It can produce high signal to noise spectra at low light levels, and is most favorably operated at high signal modulation frequencies (for example, 10 to 100 kHz). In contrast, dispersive infrared spectrometers (which generally use thermocouples) and FT-IR spectrometers fitted with room temperature deuterated triglycine sulfate (DTGS) detectors operate best at lower signal modulation velocities. For example thermocouples are operated in the general range of 10 to 100 Hz while DTGS detectors on most FT-IR instruments are operated around 1 to 2 kHz. The result was that FT-IR instruments fitted with MCT detectors showed some substantial speed advantages over dispersive spectrometers. In addition, publications appeared which described the use of FT-IR spectrometers with MCT detectors to provide some spectral subtractions even at low light levels which appeared nothing short of miraculous. Manufacturers took advantage of continued developments in electronics and computing hardware to provide FT-IR instruments at prices competitive with computerized dispersive instruments. As a result of all of these factors FT-IR developed into a buzz word and a fad which infected the analytical laboratory, and generally foretold the end of the dominance of dispersive infrared instruments except for the lower cost units.

The impact of all this on quantitative infrared is that it also foretold the virtual end of infrared instruments without the availability of data handling facilities. FT-IR, a necessarily computerized form of laboratory instrumentation, had set the standards by which all infrared work would be measured. This meant that there was substantial generalized pressure that laboratory infrared instruments would be computerized even if they were dispersive systems. As a consequence, laboratory infrared instruments would be capable of carrying out quantitative applications with a maximum of

reliability and a minimum of tedium and effort. This situation gradually developed into a major revival of interest in the possible uses of quantitative infrared for industrial analytical applications. The factors mentioned contributed strongly to the development of interest by a number of people working in the field, in the updating of the ASTM standard E 168 on General Techniques of Infrared Quantitative Analysis and also ultimately to an interest in the generation of this volume on Computerized Methods of Infrared Quantitative Analysis.

Summary of Technical Papers

The papers included in this compendium were derived from or are related to the presentations made by some of the authors at the 1984 ASTM-FACSS symposium on Computerized Methods of Infrared Quantitative Analysis. One of the values of this type of publication is that each of the authors provides a somewhat different perspective on the entire field based on his own unique experience and area of particular interest. It is hoped that this volume will not only provide interesting and informative reading in the short term, but that it will also be of use in the long term, as a useful desk reference for those who are likely to be involved in development of quantitative infrared applications in the present and future.

The first paper by Osten and Kowalski provides an interesting critical review of the developments in infrared quantitative analysis through the year 1984. Many significant references are cited, and this organization of the developments in the field should facilitate the work of future reviewers of progress in this field, and also those who wish simply to appreciate the strides that have been made thus far.

The second paper by Compton, Young, Kollar, Mooney, and Grasselli describes a number of applications related to petroleum products and makes some practical recommendations concerning the development of analytical applications. The third paper by Willis, Chalmers, Mackenzie, and Barnes is also heavily applications oriented and deals with applications which illustrate the modern use of quantitative infrared in the synthetic polymers industry.

The next group of three papers are focused on the use of computerized techniques to carry out multicomponent analysis by infrared methods. These papers give useful discussions of the mathematical aspects of these applications for those who are interested. The paper by Haaland describes an approach to dealing with nonlinear absorbance/concentration relationships with multivariate techniques such as the **K**-matrix method. Crocombe, Olson, and Hill describe some important aspects of multivariate calibration and compare the **K**-matrix and **P**-matrix methods. The paper by McClure, Roush, Williams, and Lehmann deals with the application of the **Q**-matrix

method to the analysis of a multicomponent system with a high degree of spectral overlap.

The paper by Malinowski presents the essential aspects of using factor analysis in quantitative spectroscopic applications. At this point, the techniques associated with factor analysis are still in the relatively early stages of incorporation into general use in quantitative infrared software. However, it can be foreseen that factor analytical techniques in some form will play a much heavier role in quantitative infrared software developed in the future.

The final paper by Hirschfeld emphasizes the need for caution and cross-checking in the use of computers for spectroscopic determinations. The same sentiment is echoed throughout the preceding papers, but the case for caution is made most strongly by Hirschfeld with some interesting examples to illustrate the point.

It is with deepest regret that we note the passing of our highly esteemed colleague, Tomas Hirschfeld, on 24 April 1986. He was a source of inspiration as well as information to all of us. Although he clearly remains with us through his work, he will be deeply missed by all of us. I am sure all of the authors will join me in dedicating this volume to Tomas, a scientist, colleague, and friend.

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