NOMINATIONS REQUESTED

Nominations are open for two positions on the Board of Management to replace J. R. Durig and E. R. Nixon, whose terms expire in 1976. Prospective nominees should know about and agree to the nomination; they should also know that the position is not just an honorary one but also involves attending some meetings and doing some homework. If you are interested, there is nothing wrong with nominating yourself. Please send your suggestions to Dr. R. W. Hannah, Secretary, The Coblenz Society, Inc., c/o The Perkin Elmer Corporation, Main Ave., Station 94, Norwalk, CT 06856.

COBLENZ VOLUME 10 READY

Volume 10 in the Coblenz Society series of evaluated infrared reference spectra is now available from Sadler Research Laboratories, Inc., 3316 Spring Garden St., Philadelphia, PA 19104. Cost is $325 for 1000 spectra, and $60 for a cumulative index of Coblenz spectra. Spectra in microfilm format are available at the same price. These spectra have been selected and evaluated by experienced spectroscopists to meet Coblenz Society criteria. Previously published spectra are not duplicated unless the new spectrum is more accurate, better resolved, has greater spectral range or shows the sample in a different physical state.

NOTES

Fisk Infrared Institute director Nelson Fusan was seriously injured in an auto accident in late July, and was unable to participate in the Institute. Dana Mayo, director of the MIT infrared summer course, was hospitalized with phlebitis. Both courses were held as scheduled, however. We wish both these gentlemen a speedy recovery.

The last issue of ANALYTICAL CHEMISTRY (Vol. 47, No. 11, p. 945A) contains revised specifications for the evaluation of Research Quality (Class II) infrared spectra (including those generated on Fourier transform spectrometers).


INFRARED PAPERS AT FACSS MEETING

Several sessions of papers at the October 6-10 FACSS meeting in Indianapolis are of interest to infrared spectroscopists. Speakers and titles are given below. The program also includes sessions on NMR, General Analytical Chemistry, Analytical Instrumentation, X-ray Spectrometry, Thin-layer Chromatography, Atomic Absorption and Emission Spectroscopy, SEM and Electron Probe, Chromatography, Electroanalytical Chemistry, Trace Analysis, Pharmaceutical Analysis, Polymer Characterization, and Process Analysis. Further information can be obtained from Dr. Ira Holcomb, Park-Davis & Co., Detroit, MI 48232 (313-567-5300).

Jeanette G. Grasselli, Chairwoman
Tuesday, October 7

10:20
"A Computer-Spectrometer Interactive System for Raman and Infrared Spectroscopy"
Walter F. Edgell, Edward Schmidlin, T. J. Kurtakosse, Purdue University

10:40
"Infrared Microsampling Revisited"
Robert J. Obrmski, Howard J. Sloane, Beckman Instruments, Inc.

11:00
"Infrared Spectroscopy Study of the Interaction of Silanes with Antimony Oxide"
G. A. Pasteur, H. Schonhorn, Bell Laboratories

11:20
"Triple and Multiple Beam Spectroscopy"
Ivan S. Hirschfeld, Block Engineering, Inc.

11:40
"Catecholamine Determination by Resonance Raman Spectra of the Aminochromes"
Michael D. Norris, Department of Chemistry, University of Michigan

12:00
"Optimal Least Square Smoothing of Spectroscopic Data"
J. Petzold, V. Ternonia, Faculty of Agronomy, B5800 Gembloux, Belgium

12:20
"Evaluation of Least-Squares Smoothing for Digitally Recorded Spectra"
Timothy A. Nieman, Department of Chemistry, University of Illinois C. G. Enke, Department of Chemistry, Michigan State University

Continued . . .
SPECTROSCOPIC VIBRATIONS - A new column in which innovations in vibrational spectrometry are described.

Probably the most important trend in instrumental infrared spectroscopy can be seen in the addition of dedicated data systems to infrared and Raman spectrometers. For several years the users of computerized Fourier transform (FT-IR) spectrometers have effectively demonstrated that several of the apparent advantages of FT-IR are in fact derived from their data system rather than their interferometer. Now manufacturers (such as Spex and Perkin-Elmer) and users (such as Dr. James Mattson of the University of Miami) are recognizing that similar advantages can be found when a minicomputer is interfaced to a conventional spectrometer.

Perhaps the greatest single application for a computerized spectrometer in the analytical laboratory is the method of analyzing mixtures by sequentially removing the information due to each component. This technique goes under several different names, such as "spectral stripping" or "scaled absorbance subtraction," and tremendously increases the utility of infrared spectrophotometry both for the quantitative analysis of mixtures containing several components and for the qualitative analysis of samples with one or two trace impurities or additives. It may readily be forecast that the next few years will see an increasing number of data systems on the market, and perhaps even a reduction in cost.

Peter Griffiths

COMPUTER PROCESSING OF DATA FROM DISPERSIVE INFRARED INSTRUMENTS

Over the past few years, computer processing of infrared spectra has more and more become a means of solving problems considered difficult, at best, by traditional techniques. The thrust in this direction has been associated with a high degree with Fourier Transform spectroscopy or, rather, with the computer which is resident in these systems and which is necessary for performing the transformation from the interferogram to an interpretable spectrum. It must be emphasized that many of the capabilities which have been attributed to the interferometer should really have been credited to the software within the computer.

For a number of years, dispersive instruments have been coupled with computers to solve traditional problems, e.g., quantitative analyses of multi-component mixtures. Also, searching of large data files for identification purposes has been carried out routinely by a number of laboratories. Whether associated with performing difference spectroscopy by computer subtraction of one spectrum from another, and the gain in signal to noise obtained by spectral accumulation or averaging, have made it clear that computers in the infrared laboratory are finally coming of age. One of the first of many to realize that these operations could be performed using a properly interfaced and programmed dispersive infrared instrument-computer system was Dr. James Mattson of Miami University. Their work on water solutions, which involved subtraction of the water background in order to study rates of deposition of proteins from body sera on charged germanium internal reflection plates, is documented in the literature [1]. This experiment is extremely difficult to perform by traditional dispersive spectroscopy, not only the optical alignment of two internal reflection units, but also the area of sample-internal reflection crystal contact and the quality of the internal reflection crystal must be precisely matched. Even when these details are carefully attended to, the results are often frustratingly poor. However, the ability to obtain and store the background and sample
spectra within the computer using the same accessory, and to calculate and display the difference, eliminates many of the experimental difficulties and produces a much more usable final result.

An example which ably demonstrates the computer's role in extending the problem-solving capability of infrared was recently described by Dr. Jack Koenig et al of Case-Western Reserve (2). In this publication Dr. Koenig and his coworkers describe how they obtained the spectrum of crystalline trans-1,4-polychloroprene by subtracting the spectrum of the melted sample, which exists in the amorphous form only, from the spectrum of the naturally occurring room temperature mixture of amorphous and crystalline polymer. A Fourier Transform instrument was used. The spectra shown in Figures 1 and 2 are virtually identical to Dr. Koenig's spectra but were obtained utilizing a new mid-priced microprocessor-controlled dispersive infrared instrument (3). Data for the room temperature


TOURING THE LABS

The Organic Spectrochemistry Laboratory at the National Research Council of Canada, Ottawa, Canada

OUR HOST - Norman Jones

Our Organic Spectrochemistry Section at the National Research Council of Canada (NRCC) is part of the Division of Chemistry and is located at 100 Sussex Drive, Ottawa. The NRCC is an organization operated by the Federal Government of Canada and, in a general way, can be compared with the U.S. National Bureau of Standards in Washington. Spectroscopy has always been prominent at the NRCC. Also in the Division of Chemistry we have a Chemical Spectroscopy Section directed by Dr. Harold Bernstein; his group is currently concentrating on resonance Raman spectroscopy. There is also a strong spectroscopic content to the work of Dr. Whalley's High Pressure Section which deals with high pressure phases of crystalline solids and especially ice polymorphs. The NMR activities at NRCC are now centered mainly in the Division of Biological Sciences where Dr. Ian Smith's Molecular Biophysics Section uses 13C, 2H, and 19F labelled molecules to investigate biochemical processes in membranes. The NRCC's major contribution to spectroscopy, however, is linked to the laboratory of Dr. Gerhard Herzberg. The work of his group on vibrational studies of small molecules led to an award of the Nobel Prize in Chemistry to Dr. Herzberg in 1971. Formally part of the Division of Physics, this group has now been reorganized as part of the Herzberg Institute of Astrophysics. All of these research groups work independently. Save for Dr. Whalley, our laboratories are in the same building; we have always had the good fortune of maintaining excellent relations among ourselves and many of our day-to-day technical problems get solved through the stimulus of the informal discussions which take place spontaneously during the coffee and luncheon breaks which bring us together in our cafeteria. The remainder of this article will deal only with my own Organic Spectrochemistry Section but to give you a balanced account of spectroscopy at NRCC, I must begin with this brief outline of the broader picture.

Our Organic Spectrochemistry Section was established in 1946 when we set up the first single-beam infrared prism spectrometer for chemical studies in Canada. Our present
equipment includes a Perkin-Elmer Model 180 spectrophotometer operating over the range 4200-32.5 cm$^{-1}$ with direct digital encoding on magnetic tape. We also have a Perkin-Elmer Model 521 spectrophotometer which encodes directly on punched paper tape. There is also a Perkin-Elmer Model 112 single beam grating spectrometer. This instrument was used to produce the reference curves in the "Tables of Wavenumbers for the Calibration of Infrared Spectrometers" published by the International Union of Pure and Applied Chemistry, now a familiar handbook in many spectroscopy laboratories. We also have an infrared reflection spectrophotometer which we have designed and built ourselves. This instrument is used mainly for high precision ATR intensity measurements; it also records digitally on punched paper tape. Our magnetic tape and paper tape records are processed on the IBM 360/67 computer at the NRCC Computation Center.

Our work in the 1950's and early 1960's was largely concerned with establishing infrared group frequencies. We worked mainly with steroids, fatty acids, and esters and relied extensively on deuterium substitution to confirm group assignments. By the mid 1960's it became apparent to us that a search for more "group frequencies" would lead to diminishing returns. Our work in this area has since taken on a more basic approach, and we have turned a critical eye on normal coordinate analysis. Here we are looking mainly at the computational aspects with a view to simplifying the procedures and making them more relevant and comprehensible to chemists. Recently we have completed vibrational analyses of cyclohexanone and cyclopentanone, considered as models for partial structures of natural products; other molecules are also being studied including aromatic esters and porphyrins.

In the 1960's we became increasingly involved with infrared intensity measurements. This interest started with some work on the limitations to the accuracy of rotating sectors to calibrate infrared spectrophotometers. About the same time we became convinced that the future of infrared spectrophotometry lay in digital recording and computer reduction of the data. We published our first paper on band shapes in 1963 using computer analysis of data. It was based on manually punched card input data but our first infrared spectrophotometer with direct paper tape data-logging went into action during the same year. As we have developed computer programs for our own use, we have transposed them into modular units with card input, output, and many of these have found use in other laboratories, particularly the programs dealing with curve fitting and band shape analysis. This project is continuing, and we shall shortly have available a coordinated set of fifty programs packaged on a single tape reel.

By a series of steps that space does not allow us to describe, our band shape and sector photometer studies have led us to an in-depth analysis of the optical behavior of infrared cells. This in turn has encouraged us to study the absorption of thin layers of pure liquids. We are making these measurements both by transmission through precision cells having path lengths down 1 μm and also by attenuated total reflection. In part of this work we are collaborating with Prof. Bryce Crawford at the University of Minnesota. A recent extension of the thin film transmission studies has been the measurement of the absorption of free standing polymer films and the evaluation of the dichroic ratios. So far we have published the infrared spectra of two liquids (benzene and chloroform) which we hopefully regard as the first Coblentz Class I spectra.

Another activity of our laboratory is the operation of the SPIR program for the identification of infrared spectra. This is now on our computer at Ottawa and accessible from terminals across Canada. It uses the FIRST-1 algorithm of DNA Inc. of Saginaw, Michigan, developed by Mr. Duncan Erley and the ASTM data base of approximately 150,000 spectra; private data bases held by the individual users can also be maintained.

Our group consists of four professionals, including myself, and two technicians. As in government laboratories everywhere, we try to maintain a balance between short-term and long-term applications of spectroscopy. We have found sufficient basic research to maintain intellectual stimulation; such stimulation is provided only by basic research at the frontiers of knowledge, and on it the well-being livelihood of our society must ultimately depend.

Q AND A

If you have a question having to do with infrared spectroscopy—techniques, interpretation, or whatever—send it to

Q & A

The Coblentz Society, Inc.
P.O. Box 9952
Kirkwood, MO 63122

If you need an immediate answer, please enclose a self-stamped envelope. Otherwise, the answer (by a knowledgeable member of the infrared community) will be published in the next Newsletter. It is hoped that many Coblentz Society members will participate, either by submitting questions or by sharing their knowledge with the questionner.

Q: For infrared studies, how should deuteration (hydrogen-deuterium exchange) be carried out in practice? The answer may be illustrated with deuteration of liquid hydrocarbons like alkyl benzenes.

A: It isn't really possible to give a blanket answer to this question. In practice, one has to think up a synthesis that will put the D's where they are wanted, and this may require considerable ingenuity. Exchangeable H's (acids, etc.) are easily replaced by simply shaking the organic sample with several successive portions of D$_2$O. In some cases, D$_2$O when catalyzed with acid and/or heated with aromatic materials, will replace hydrogen in certain positions on the aromatic ring. Acidic hydrogens in hydrocarbons may be replaced using a column technique described by Kallos and Westover, Tetrahedron Lett. 1223 (1967). Literature references to many substituted species may be found in the monograph by S. Pinchas and I. Laulicht, "Infrared Spectra of Labeled Compounds," Academic Press, London and New York, 1971.