THE COBLENTZ SOCIETY DESK BOOK OF INFRARED SPECTRA
by A. Lee Smith

This book is a product of the efforts of a large number of people working to solve common problems in the field of molecular spectroscopy, organized as the Coblentz Society. Its history is briefly recounted here.

History of the Coblentz Society

During the late 1940's and early 1950's the then new field of chemical infrared spectroscopy was the subject of rapidly growing interest. Double-beam spectrometers had become commercially available; new techniques, accessories and instrumentation combined with a growing body of applications kept the field in rapid ferment. The summer symposium at Ohio State University, Columbus, and the spring Pittsburgh Conference brought together groups of spectroscopists to exchange information and solutions to problems both by formal papers and informal discussions.

It was apparent that while infrared was not a primary field of research, it provided a common tool to attack diverse problems. Further, a number of problems, such as reference spectra availability and retrieval, were of common concern. From informal discussions held at Columbus in 1953, a Columbus Committee was formed to consider the situation. This committee consisted of Drs. Howard Cary, Bryce Crawford, Jr., R. A. Oetjen, Eugene Rosenbaum, Van Zandt Williams and Norman Wright. The committee reported that there was need of an association of infrared workers to provide the field with a unified voice where necessary, and to keep the field informed on matters of common interest. Recommendations as to the organization and functioning of the society were also made, and suggestions for activities were listed. It is interesting to review this list, which was:

a. Publish reference spectra
b. Keep abreast of related organizations which make decisions that affect infrared
c. Produce an authoritative infrared book
d. Provide consultant and speaker listings
e. Serve as a communication channel between the field and instrument manufacturers
f. Publish specific analyses in compact form
g. Organize symposia on infrared to concentrate IR papers at major scientific meetings

By June of 1954, plans for the new society had been fully developed, including the formation of an executive committee and writing of by-laws. The name chosen was "The Coblentz Society," after Dr. W. W. Coblentz, whose post-doctoral studies at Cornell University in 1904 and subsequent work at the Bureau of Standards had done so much to demonstrate the potential application of infrared spectroscopy to the field of chemistry. Because Dr. Coblentz was a physicist his work was not much read by chemists, and it was not until the 1930's that rapid further development took place.

The objective of the new society was: "To foster the understanding and application of infrared spectra." A corollary of this objective was to promote international interaction between academic and industrial spectroscopy.

The prime movers in the organization of the Coblentz Society were Drs. Norman Wright of Dow Chemical and Van Zandt Williams of Perkin-Elmer. Dr. Wright, a physicist, joined Dow in 1937 with the assignment of designing and building an infrared spectrometer. Four months later, he was recording spectra of chemical interest and in a few more months had demonstrated that infrared represented a powerful new tool for characterization of pure materials and for analysis of mixtures. His subsequent talks to ACS groups and his publications provided a real impetus to the growth of the field. Dr. Wright served as first President of the Coblentz Society.

Dr. Van Zandt Williams was also a physicist, and was initially a member of the infrared group at American Cyanamid, where development work was going on along the same lines as that done at Dow. He later moved to Perkin-Elmer, where he eventually became Executive Vice-President. He retained throughout his career a strong interest in infrared spectroscopy, and served as the first registrar of the Coblentz Society.

Activities

There was no lack of activities for the new society. Arrangements were made with Analytical Chemistry to publish quantitative infrared methods in a condensed format. This program started in October, 1957, and continued for several years under Robert C. Wilkerson. It was subsequently managed by Don E. Nicholson and from 1960 by A. Lee Smith. When submissions became irregular, publication was transferred to Applied Spectroscopy. An index to the methods was published in Applied Spectroscopy, 18, 38, (1964).

A speakers bureau was organized under Mr. Harry Bowman. A list of special collections of spectral data was compiled. In 1956 a program of collecting, compiling, and selling spectra contributed from members' files was proposed. By 1960 almost 2000 spectra had been collected by Clara D. Smith Craver, and the first set of 1000 spectra had been published. A successful symposium on group frequencies had been organized at the 1959 Pittsburgh Conference by W. J. Potts. The Coblentz Symposium thereafter became an annual tradition of this meeting. The editors of several scientific journals were approached by Foil A. Miller regarding publication of infrared spectra.

In 1961-1962 a growing awareness that examiners in the U. S. Patent Office did not consider an infrared spectrum to be characteristic of a material for patent purposes culminated in Coblentz Society participation in a symposium at the 1962 National ACS Meeting in Washington, D.C.. Ellis R. Lippincott, on behalf of the Society, presented a definitive paper on "The Limitations and Advantages of Infrared Spectroscopy in Patent Problems" which was published in the Journal of the Patent Office Society, May, 1963, Vol. XLV, pp. 380-415.

On March 1, 1961, a symposium in honor of Dr. Coblentz was held at the Pittsburgh Conference which featured talks by Earl Plyler, H. W. Thompson, Bryce Crawford, and R. C. Lord. The passing of Dr. Coblentz on September 15, 1962, in Washington, D. C., was noted in the February 18, 1963 Newsletter. In 1963 the Coblentz Award, to be given to an outstanding young spectroscopist, was established, and John Overend chosen as the first awardee. Also in 1963, Dr. Coblentz's original monograph, "Investigations of Infrared Spectra, Parts 1-7" was reprinted under the direction of Dave Kendall.

The National Standard Reference Data Program of the National Bureau of Standards, instituted in 1963, defined a need for specifications for evaluation of infrared reference data. The Office of Standard Reference Data contracted with the Coblentz Society in 1965 to write such specifications, which were developed and published in Analytical Chemistry, Aug., 1966, p. 27A. With only modest modifications these have become adopted as international standards by IUPAC. The specifications are summarized on pp. 11-24 and include updated recommendations to accommodate both dispersively measured and interferometrically measured spectra. For complete details see Analytical Chemistry, 47, 945A (1975).

Early educational activities of the Society included producing 8 mm films on techniques and instrument operation, and holding technique clinics at the Pittsburgh Conference. More recent courses, under the direction of Jeanette Grasselli, have been expanded to include full day workshops on computer assisted spectroscopy. In a cooperative venture between the Society and SAVANT, Howard J. Sloane began production of audio-visual courses on IR techniques in 1982.

There are now three major annual awards sponsored or co-sponsored by the Coblentz Society. These are the Coblentz Award, for an outstanding young spectroscopist, the Ellis R. Lippincott medal, sponsored jointly by the Society for Applied Spectroscopy for presentation to an individual who is judged to have made a significant contribution to vibrational spectroscopy and the Williams-Wright Award which honors an industrial spectroscopist who has made significant contributions in the application of infrared spectroscopy.

The spectrum publication program has reached 10,500 published spectra in its general collections. From these collections, five widely used special applications books have been recently published. These are available directly from the Society. Details are given in the bibliography section.

The affairs of the Society are managed by an eight-member board which elects its own presidents. The wide base of leadership is shown by the following list of presidents of the group:

Coblentz Society Presidents

Norman Wright	1955-1958
Foil Miller	1959
R. A. Friedel	1960-1961
R. N. Jones	1962-1963
A. Lee Smith	1964-1965
Nelson Fuson	1966-1967
Freeman Bentley	1968
Charles Angell	1969-1970
James R. Scherer	1971
Robert P. Bauman	1972-1973
James R. Durig	1974-1975
Robert J. Jakobsen	1976
Peter R. Griffiths	1977
Ira Levin	1978
Bernard J. Bulkin	1979-1980
William C. Harris	1981-1982
Albert B. Harvey	1983-1984
Bruce Chase	1985

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3,360 infrared spectra run by different laboratories over a 30 year period. Additions are issued two or three times a year. This is the most extensive collection of spectra of petroleum hydrocarbons on high purity compounds. Also included are N and S compounds found in petroleum. 700 Raman spectra are available. Approximately 500 are from mercury lamp excitation, and 200 are laser-excited spectra.

Coblentz Society Spectra
POB 9952, Kirkwood, MO 63122

10,500 spectra in loose-leaf notebooks and on 16 mm microfilm. These spectra were collected from government and industrial research laboratories and include a high proportion of currently significant compounds. They were prepared in a cooperative program between the Coblentz Society and the Joint Committee on Atomic and Molecular Physical Data. Since 1967 they have been evaluated under specifications developed by the Society for the National Reference Data System of the National Bureau of Standards.

The spectra are on prism and grating spectrometers; mull and solution spectra are favored, but neat samples and halide pellet spectra are also included. Selected spectra for specific uses are being published in a "Special Collections" series. The Coblentz Society Desk Book, 900 all-grating spectra grouped by chemical classes, with text, is designed as a reference and teaching aid. Other collections are Plasticizers and Other Additives, Halogenated Hydrocarbons, Gases and Vapors, and Regulated and Major Industrial Chemicals.

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1. Molecular Formula List of Compounds, Names and References to Published Infrared Spectra
   AMD-31   92,000 compounds
   AMD-31-S15   53,000 compounds

2. Serial Number List of Compounds, Names and References to Published Infrared Spectra
   AMD-32
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2nd Edition, J.G.Grasselli and W.M.Ritchey, Editors, CRC Press Inc., 18901 Cranwood Parkway, Cleveland, OH, 44128, 1975.

Contains coded infrared spectra for 22,000 compounds. It lists strong bands in the infrared and includes Raman, UV, NMR and mass spectral data when available.

Index of Vibrational Spectra of Inorganic and Organometallic Compounds, Vol.1
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INFRARED DATA RETRIEVAL

Computer search systems are available for retrieving infrared spectra from coded band data to match against unknowns. The public file for this purpose is the ASTM tape, AMD-33, corresponding to the publications cited above. Two computerized systems are available in time-sharing. Other systems are dedicated for specific computers or for software accompanying computer-assisted spectrometers.

Available Publicly on Time-Shared Computers

Name	Spectra	Availability	Contact for Details
IRGO	150,000	Subscription and mail-in search service	Dr. Clara Craver, Chemir Labs., 761 W. Kirkham, St. Louis, MO 63122 Tel. (314) 962-6704
SPIR	143,000	Subscription, Canada only	NRC, 100 Sussex Dr., Ottawa, Ontario, Canada
CIS	3,000	Subscription	Chem. Info. Sys., Inc. 7215 York Rd., Baltimore, MD

Available for Dedicated Computers

Name	Spectra	Availability	Contact for Details
First-1	143,000	Purchase, for batch run on IBM 370	Mr. B. Blackney, DNA Systems, POB 1424, Saginaw, MI 48605 Tel. (517) 793-0185
Spec-Finder[R]	100,000	Purchase	Sadtler Labs., 3316 Spring Garden St., Phila, PA

THE SPECTRUM PUBLICATION PROGRAM

This program was initiated in the summer of 1956 with a questionnaire to members which, like subsequent questionnaires, showed overwhelming interest in the publication of "more and better" spectra. The first 5,000 spectra were published with no criteria beyond enlarging the spectral data base in either of two ways:

If a compound's spectrum was already published, the Coblentz spectrum of that compound added data in either accuracy, physical state or spectral range; or

If no spectrum was available, the spectrum to be published was checked for consistency with that expected for its structure and for quality adequate to permit identification of the compound.

More comprehensive evaluation of infrared spectra was started under the impetus of the wide availability of grating spectrometers and increased interest in spectral reference data by the National Bureau of Standards. In fact, the Office of Standard Reference Data of the National Bureau of Standards was established about the same time that practical experience had been gained with grating infrared spectrometers. It was possible to produce 'good' spectra in quantity, but a consensus was needed on what a 'good' spectrum should be for broad scientific reference purposes.

The OSRD funded several full-day working meetings of the Board of Managers of the Coblentz Society to develop specifications for evaluated infrared spectra. After extensive consideration of many parameters, the Board generated the "Specifications for Evaluation of Infrared Spectra" and published them in Analytical Chemistry, 38, 27A (1966).

Five thousand spectra have been published cooperatively by the Joint Committee on Atomic and Molecular Physical Data and the Coblentz Society since then. These spectra were evaluated under the OSRD specifications which provide for Class II or Research Quality spectra and for Class III or Analytical Quality spectra.

The specifications for Research Quality Spectra have been recently modified to accommodate both dispersively measured and interferometrically measured spectra. These modifications are added to the original criteria where needed in the following summary of evaluation specifications. For complete details see Analytical Chemistry, 47, 945A (1975).

Specifications for Evaluation of Infrared Spectra

For purposes of evaluation, infrared spectra can be classified into three categories: Class I, standard spectra; Classes II and III, reference spectra.

CLASS I spectra, critically defined physical data, are designated as "standard spectra" because they are of a sufficiently high quality to be acceptable as physical constants of the substances under precisely defined conditions of measurement, and further refinements in spectrophotometric technique are not expected to change them significantly. Spectra of this quality may be obtainable for condensed phase systems within two to five years. It was the unanimous opinion of the Board of Management of the Coblentz Society that the specifications and format of such Standard Spectra should be defined by international agreement, and the Commission on Molecular Structure and Spectroscopy of IUPAC is now studying this problem.

CLASS II spectra, research quality spectra, are obtained on good infrared spectrophotometers, grating or interferometric, operated by competent technicians under conditions appropriate to a research laboratory. The purity of the compounds must be specified with respect to the type and quantity of any spectroscopically detectable impurity present, and independent verification of the compound's identity is required.

CLASS III are the absorption spectra of individual compounds, polymers, and resins of known composition that have been obtained with sufficient accuracy to be useful in the identification of unknown materials.

The Board of Management of the Coblentz Society recommends that spectra in Classes II and III be called 'reference spectra', and that they be so designated in the published charts and in associated literature. It strongly recommends that the use of the word 'standard' be reserved solely for spectra of Class I.

The panel of spectroscopists established to evaluate infrared spectra cannot be expected to establish in all cases the correctness of the reputed chemical structures simply from the infrared spectra alone. Their prime responsibility is to rule on the technical quality of the spectra and to check for gross incompatability with the assigned structure. Thus, users of Class III spectra must recognize that many of these spectra will have been

drawn from large collections that were not compiled with definitive documentation in mind, so that some incorrectly assigned spectra may pass through the evaluation process. This problem is eliminated for Class II spectra, which are required to have independent composition validation.

Specifications pertinent to spectrophotometer operation, presentation of data, sample preparation and sample purity for reference spectra are presented below. Where numerical limitations apply, as for resolution, frequency accuracy and noise, both Class II and Class III specifications are cited.

I. Spectrophotometer Operation

A. Resolution

The resolution should be consistent with the operating specifications for the spectrophotometer. For Class III spectra, the minimum acceptable performance is that obtainable from a sodium chloride prism spectrometer in good operating condition.

For dispersively measured Class II spectra the spectral slit width should not exceed 2 cm^{-1} through at least 80% of the wavenumber range and at no place should it exceed 5 cm^{-1}. See Figure 4, p.19.

For interferometrically measured spectra the resolution is judged by comparison with the standard reference spectrum to ascertain whether it meets Class II or Class III specifications. The optical retardation must be at least 0.5 cm, and the apodization function stated.

B. Wavenumber Accuracy

For Class III, charts showing evidence of wavenumber calibration error in excess of ± 30 cm^{-1} at 3000 cm^{-1} or ± 5 cm^{-1} below 2000 cm^{-1} are not acceptable. IUPAC recommendations are for ± 15 cm^{-1} limit at 3000 cm^{-1}. Primary calibration data are given in Figure 3 and Tables 3 and 4, pp. 18 and 19.

For Class II, the abscissa as read from the chart should be accurate to ± 5 cm^{-1} at wavenumbers greater than 2000 cm^{-1} and to ± 3 cm^{-1} at wavenumbers less than 2000 cm^{-1}. Calibration corrections within these limits are encouraged and should be indicated on the chart.

Proof of the wavenumber accuracy is provided by a spectrum of the standard reference material. Fiduciary marks should be recorded on each chart shortly after the beginning and near the end of each uninterruptedly scanned segment of the spectrum. These marks are required to guard against errors from paper shrinkage and from mismatch between the printed chart grid and the spectrophotometer.

C. Noise Level

Charts should not exhibit more than 2% average peak-to-peak noise for Class III or 1% average peak-to-peak noise, or 0.25% r.m.s. for Class II.

D. Energy

It is recommended that the spectrometer be purged with dry air to ensure that at least 50% of the source energy is available throughout the spectrum (except at the 2350 cm^{-1} and 670 cm^{-1} CO_2 absorption areas.)

E. Other Performance Criteria

1. Charts exhibiting evidence of more than 5% stray radiation in any region of the spectrum are unacceptable for Class III. For Class II the limit is 2% stray radiation in regions higher than 500 cm^{-1}.

2. Charts exhibiting evidence of a dead servo-system or of excessive overshoot should be rejected. The spectrophotometer and recorder time constant must be compatible with the scan rate. See Operating Parameters.

3. For Class II, spectra of reference standards which document the performance of the spectrophotometer in respect to band shapes and relative band intensities are necessary. (Discussed under Operating Parameters.)

II. Presentation

A. Information to Appear on the Chart

Both the structural and the molecular formulas of the compound should appear with the chart. It is also recommended that the compound name be included, and preferably this should conform with the nomenclature used by Chemical Abstracts. The make and model of the spectrophotometer must be recorded as well as the date on which the spectrum was obtained. For dispersion instruments the dispersing element must be identified (e.g., NaCl prism, grating).

The physical condition of the sample must be stated, (e.g., Nujol mull, solution, pure liquid, etc.). For measurements on solutions the solvent used in each re-

gion of the spectrum must be recorded on the published chart. The path length and concentration should also be given, but spectra lacking this information may be accepted at the discretion of the evaluator. The path length of pure liquid samples and concentrations in pelleted disk spectra should be given if possible.

B. Spectral Range

The chart must cover 3700 to 700 cm^{-1} for Class III and 3700 to 450 cm^{-1} for Class II. Gaps caused by solvent interference or by obscuration from mulling agents may be permitted for Class III spectra at the discretion of the evaluator, but must be designated as such on the published chart.

C. Intensity

It is anticipated that many spectra will be recorded on a linear transmittance ordinate grid, but spectra recorded on paper having a logarithmic ordinate grid are preferable, since this permits the direct interpolation of absorbance intervals.

The absorption bands must be strong enough to be useful in characterizing the material. Spectra are generally unacceptable if they show:

1. No bands more intense than 0.6 absorbance unit
2. Many bands exhibiting total absorption
3. An average I_o less than 60 to 75% transmittance

For Class II any band over 1.5 absorbance units should be reproduced on a less absorbing sample and the curve should extend to at least one weaker band. Multiple traces on any chart should be kept to a minimum.

D. Wavenumber Readability

For Class III, band peak positions must be readable on the published chart to ± 15 cm^{-1} at 3000 cm^{-1} and ± 2.5 cm^{-1} below 2000 cm^{-1}. In selecting among alternative spectra for a given compound, preference is given to linear wavenumber over wavelength presentation unless there are strong reasons to decide otherwise. The peak position for linear wavelength charts must be readable to 0.02 micrometers.

For Class II, sharp peaks should be readable to within ± 5 cm^{-1} at wavenumbers greater than 2000 cm^{-1} and within 2 cm^{-1} at wavenumbers less than 2000 cm^{-1}. Only spectra recorded with the abscissal scale linear in wavenumber are acceptable; scale changes at designated abscissal positions are allowed.

E. Recording

It is preferred that the spectrum exhibit no gaps in wavenumber, but evaluator's discretion is permissible for Class III. Hand retraced spectra are unacceptable.

For Class II, recording should be continuous with no gaps in wavenumber, but it is permissible for spectra to extend over more than one chart. Discontinuities in ordinate (absorbance), if present, should not exceed 0.01 absorbance unit.

F. Atmospheric Absorption

Bands resulting from atmospheric absorption should ordinarily be no greater than the allowable noise level (1% for Class II and 2% for Class III).

III. Sample Identification and Preparation

A. Compound Identification and Purity

Purchase of a material from a reputable chemical supply house, or preparation according to an accepted procedure are not, in themselves, acceptable as proof of structure. Additional physical and chemical evidence sufficient to satisfy an expert in the field should be supplied to the evaluator. Preferably this evidence should come from measurements on the same batch that was used for the infrared spectrum.

For Class II, spectra should show no inconsistencies with the postulated structure and should not exhibit an obvious impurity band. Some relaxation of this requirement may be permitted in the case of isotopically labeled substances in which complete isotopic exchange cannot reasonably be achieved. In such cases the bands associated with the minor isotopic species should be indicated on the chart.

The prime responsibility for the correctness of the structure lies with the laboratory contributing the spectrum, and the name of the laboratory should be recorded on the chart. In exceptional cases spectra contributed anonymously may be published, but such spectra should be labeled "Chemical Structure not Authenticated."

No spectrum can be rated as Class II unless either the evaluator is supplied with a reasonably detailed description of the preparation and purification history of the measured sample, together with adequate evidence for the correctness of the assigned chemical structure, or two curves derived from samples obtained from inde-
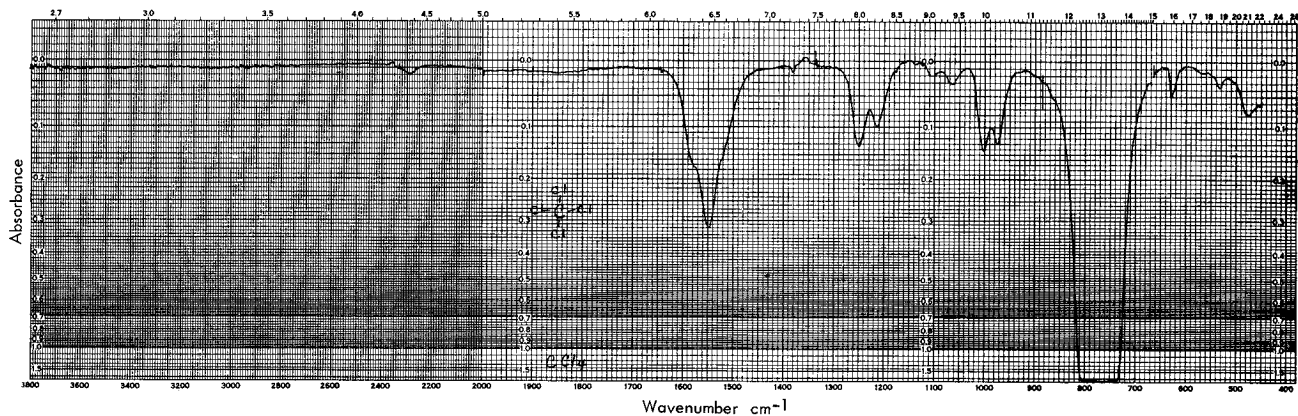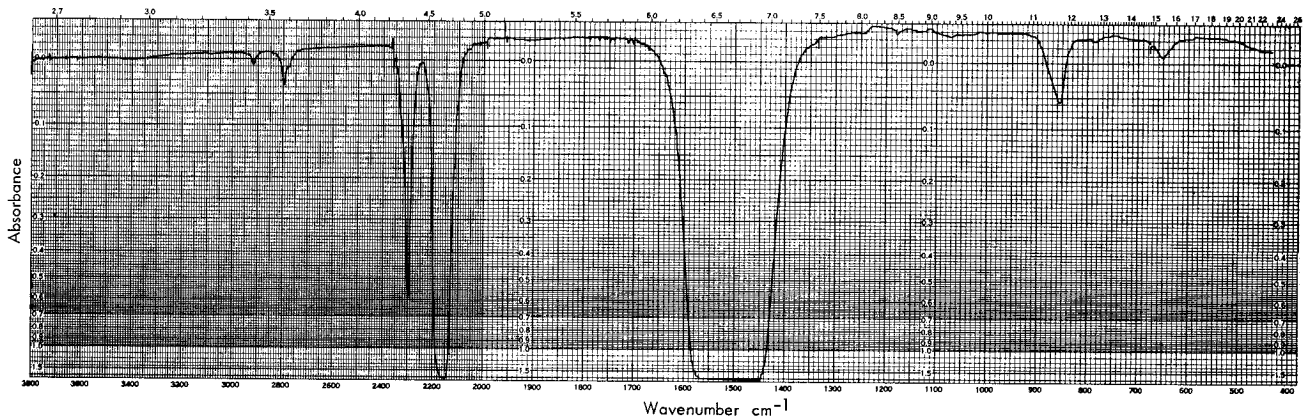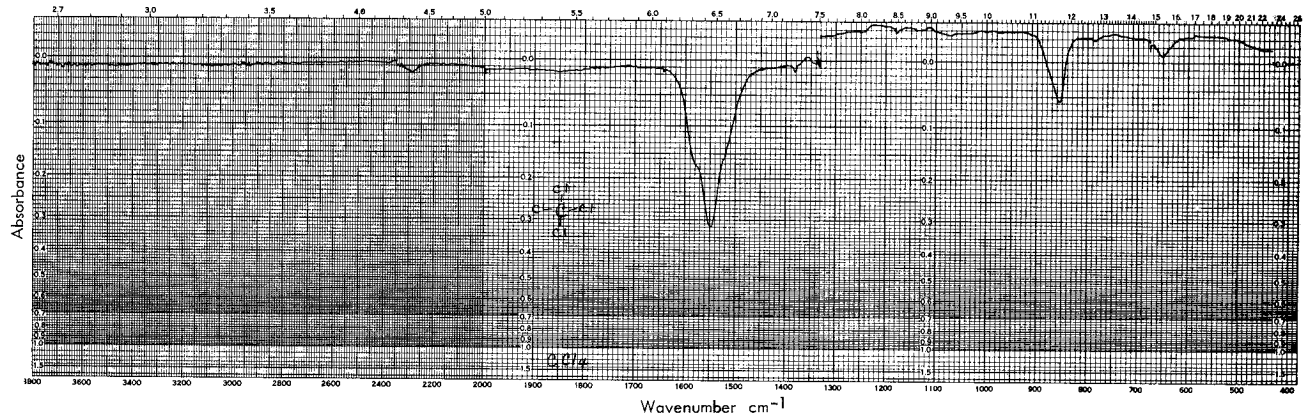
FIGURE 1. RECOMMENDED SOLVENTS FOR SPLIT SOLUTION

pendent sources are available which are in reasonable agreement.

For Class III, the purity of the samples should be such that only bands of minor intensity due to impurities are present, and these bands should be identified on the published chart. The permitted intensity of impurity bands is at the discretion of the evaluator, but should not normally exceed 10% of the absorbance of the major band of established structural significance. Not more than three impurity bands should appear, but the evaluator makes allowance for compounds that are readily hydrolyzed, oxidized, or isomerized. It should be noted that the presence of correctly identified impurity bands in the spectra of unstable materials is not necessarily a detriment, since one of the uses of reference spectra is for the detection and identification of common impurities.

B. Sample Preparation

1. Liquid State Samples

For analytical purposes it is preferable that the sample be run in liquid solution, normally at concentrations in the range 5% to 10% weight per volume. Solvent bands should be compensated, but not more than 75% of the energy should be removed from the beam by such compensation, and then only over a short region of the spectrum. Any solvent bands resulting from incomplete compensation should be indicated on the chart. A suitable solvent combination is carbon tetrachloride (3800 -1335, 650-430 cm^{-1}) and carbon disulfide (1350-430 cm^{-1}); both solvents should be used at path lengths in the range 0.03-0.3mm. See Figure 1.

Cases may arise that require the use of other solvents, and solubility limitations or other concentration dependent factors may necessitate the use of cells of longer path length. These conditions are acceptable provided the reference beam energy is not attenuated by more than 75%.

It is also desirable that the spectrum of the liquid be recorded. Solution spectra and liquid spectra are to be regarded as complementary, and not as substitutes for one another.

The spectra of liquids not soluble in transparent solvents should be measured as capillary films.

2. Solid State Samples

Solution spectra in the most transparent solvents are

preferred, provided the solvents and path lengths can be chosen to leave no significant gaps due to solvent obscuration.

For insoluble compounds mulls are preferred to pressed pellets unless it can be established that the pellet gives an undistorted spectrum.

For Class II, solid state spectra must meet the following criteria for isotropic materials. The background absorbance should be less than 0.20 near 3800 cm^{-1} and less than 0.10 near 2000 cm^{-1}. No gross abnormalities should be evident in the background. Compensation in the reference beam by a blank mull or pellet should be indicated, and in no case should it reduce the reference beam intensity by more than 50%. The Christiansen effect should not be apparent, but minor distortion resulting from this effect may be permitted at the discretion of the evaluator. Interference fringes should not be apparent.
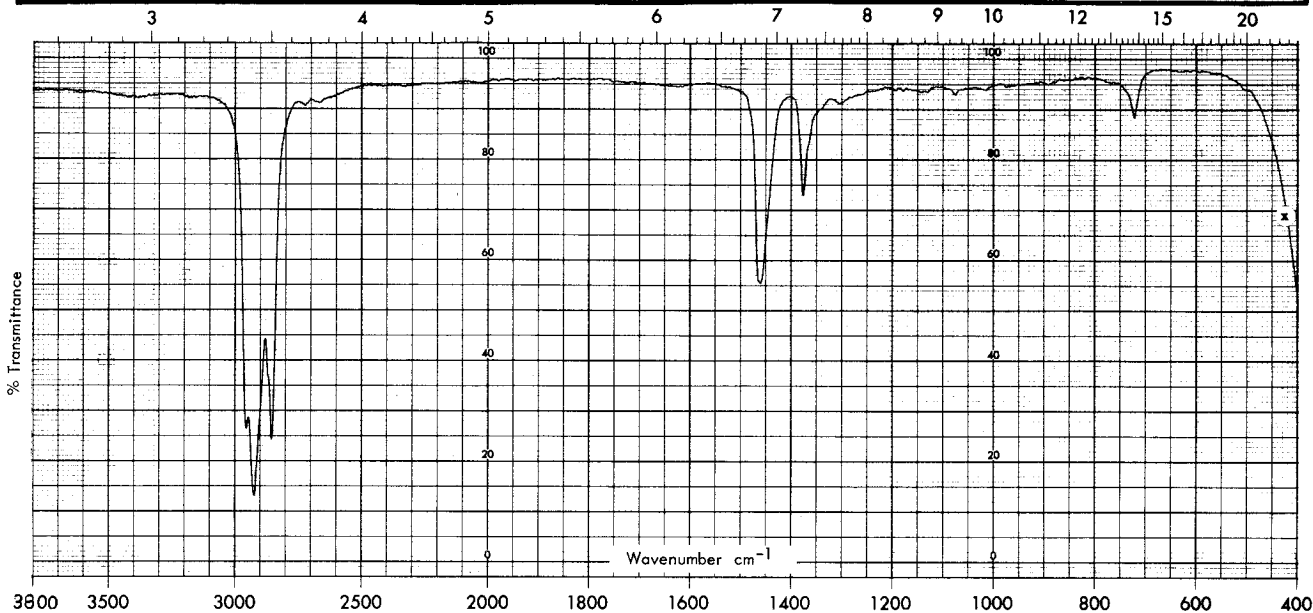
Pellets should exhibit no bands due to absorbed water greater than 0.03 absorbance unit. Mulls should be made with perhalogenated oils for the range 3800-1335 cm^{-1}, and the intensity of the overtone band near 2300 cm^{-1} should not exceed 0.02 absorbance unit. Liquid paraffin (Nujol or the equivalent) should be used below 1350 cm^{-1}, and the intensity of the band near 720 cm^{-1} should not exceed 0.05 absorbance unit. See Figure 2. If there are suitable bands present, they should be overlapped in the two mull spectra and one of the bands should be identified in both mull spectra; this aids in establishing the intensity ratio between the two sections of the spectrum.

For non-isotropic materials such as single crystals or crystalline polymers, spectra should be accompanied by a record of the orientation of the sample with respect to the radiation beam and, in the case of dispersively measured spectra, the orientation with respect to the grating rulings should also be indicated.

Amorphic and partially crystalline polymers of ill-defined molecular and conformational structure should not be included as pure materials.

For Class III, there must be at least 25% nominal transmission at 3700 cm^{-1} and at least 40% nominal transmission at 2000 cm^{-1} in the absence of specific compound absorption. There must be no gross abnormalities or discontinuities. Spectra should not exhibit appreciable pseudo-structure attributable to interference fringes, and any such fringe patterns should be identified on the published chart. The Christiansen effect should

Mineral oil		10,115
	PREP. **neat** PATH REGION SOLVENT **capillary**	NSRDS-COBLENTZ CLASS III **structure verified** STATE **liquid** M.P. B.P.
	SPECTROMETER **Perkin-Elmer 180**	CONTRIBUTOR **Standard Oil of Ohio** DATE RECORDED

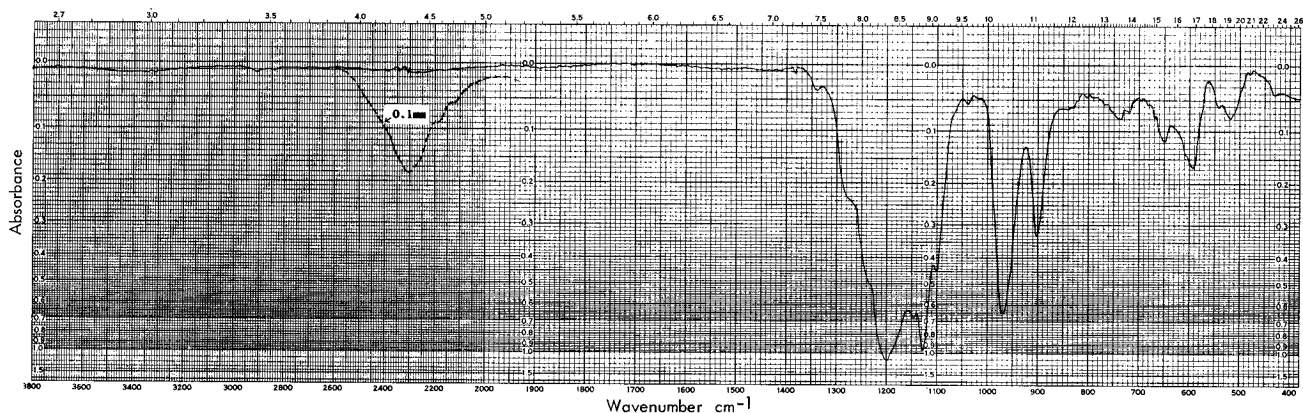| Fluorolube		10,114
	PREP. **neat** PATH REGION SOLVENT **capillary**	NSRDS-COBLENTZ CLASS III **structure verified** STATE **liquid** M.P. B.P.
	SPECTROMETER **Dow KBr foreprism-grating:** **Blazed at 3.5, 12.0, 20.0** **Changed at 5.0, 7.5, 14.9**	CONTRIBUTOR **The Dow Chemical Company** DATE RECORDED **4.7.66**

FIGURE 2. RECOMMENDED MULLING AGENTS FOR SOLIDS

not be great enough to distort the band contours significantly. In spectra of alkali halide pellets, the water absorption bands must not exceed 0.1 absorbance unit.

3. Gas and Vapor State Samples

Specifications for gas and vapor state vary considerably with the purposes for which the spectra are to be used. The following general guide lines will be replaced by more specific recommendations in 1978.

The pressure of the absorbing gas should be selected so as to display the significant features in the spectrum, while showing a minimum number of bands so strong that structure is lost. Very intense absorptions should be rescanned at lower pressure, but the number of additional tracings on a single chart should be kept to a minimum for readability.

It is desirable that the pressure of the absorbing gas be stated; and if an inert diluent gas is used, it should be identified and the total pressure given. The path length of the cell should be preferably 5 to 10 cm, and should be stated.

Users of gas and vapor spectra must recognize that such spectra are strictly qualitative, since the intensity of an absorption may depend strongly on the total pressure as well as on the partial pressure of the absorbing species. (Intensities may change by a factor of 5 or more upon pressurizing a gas from zero to one atmosphere with an inert diluent.) Furthermore, the intensities of different bands do not respond equally to pressure.

On the other hand, the exact frequency of sharp spikes is likely to be important for qualitative analysis. Thus, it is especially important for gas and vapor spectra that wavenumber calibration accuracy be established and maintained.

IV. Spectrophotometer Performance Checks

The approved standard reference material is a mixture containing 98.4 parts by weight of indene, 0.8 parts by weight of camphor, and 0.8 parts by weight of cyclohexanone. (Figs. 3 & 4) This is the indene mixture recommended by the International Union of Pure and Applied Chemistry (IUPAC) for the wavenumber calibration of medium resolution spectrophotometers when used for measurements on condensed phase systems over the range 4000 - 600 cm^{-1}. The indene-camphor-cyclohexanone mixture should be stored in sealed ampoules which should be opened immediately before use.

Information about commercial sources of this material is available from the Coblentz Society. At this time it may be obtained from the Perkin-Elmer Corp., Norwalk, CT, or from the Aldrich Chemical Co., Milwaukee, WI, catalog number 19, 167-1. The 1/1/1 mixture for far-IR calibration is Aldrich no.19, 148-5.

Calibration spectra on secondary standards are acceptable subject to their approval, provided they are calibrated over the full wavenumber range and are compatible with the need to satisfy research quality criteria.

A. Wavenumber Calibration

The recommended wavenumber calibration points are the absorption maxima of the standard indene/camphor/cyclohexanone mixture listed in Table I. Suitable path lengths are 0.2 mm for the range 3800-1580 cm^{-1} and 0.03 mm for the range 1600-600 cm^{-1}. A mixture containing equal parts by weight of indene, camphor, and cyclohexanone at a path length of 0.1 mm may be used for the range 600-300 cm^{-1}. See Table II.

B1. Dynamic Error Test for Dispersively Measured Spectra

For dispersively measured spectra the following dynamic error test is suitable for use with most grating spectrophotometers.

The spectrum of the indene/camphor/cyclohexanone (98.4/0.8/0.8) mixture is remeasured from 1350-850 cm^{-1} at one fourth of the scan rate used for the reference spectrum, with other operating conditions unchanged. The heights from the baseline of the bands at 1288.0, 1226.2, 1205.1, 1018.5 and 914.7 cm^{-1} are measured in absorbance units on both the fast and slowly scanned charts. The peak height ratios $A_{1226.2}/A_{1288.0}$; $A_{1205.1}/A_{1226.2}$ and $A_{914.7}/A_{1018.5}$ should not differ by more than ± 0.02 between the fast and slow runs.

B2. Aliasing Error Test for Interferometrically Measured Spectra

The following aliasing (folding) test should be made for spectra measured interferometrically. The transmission spectrum of a 0.05 mm layer of liquid water is determined over the range 3800-3000 cm^{-1}. The false energy at 3400 cm^{-1} should not exceed 0.5% transmission on the run.
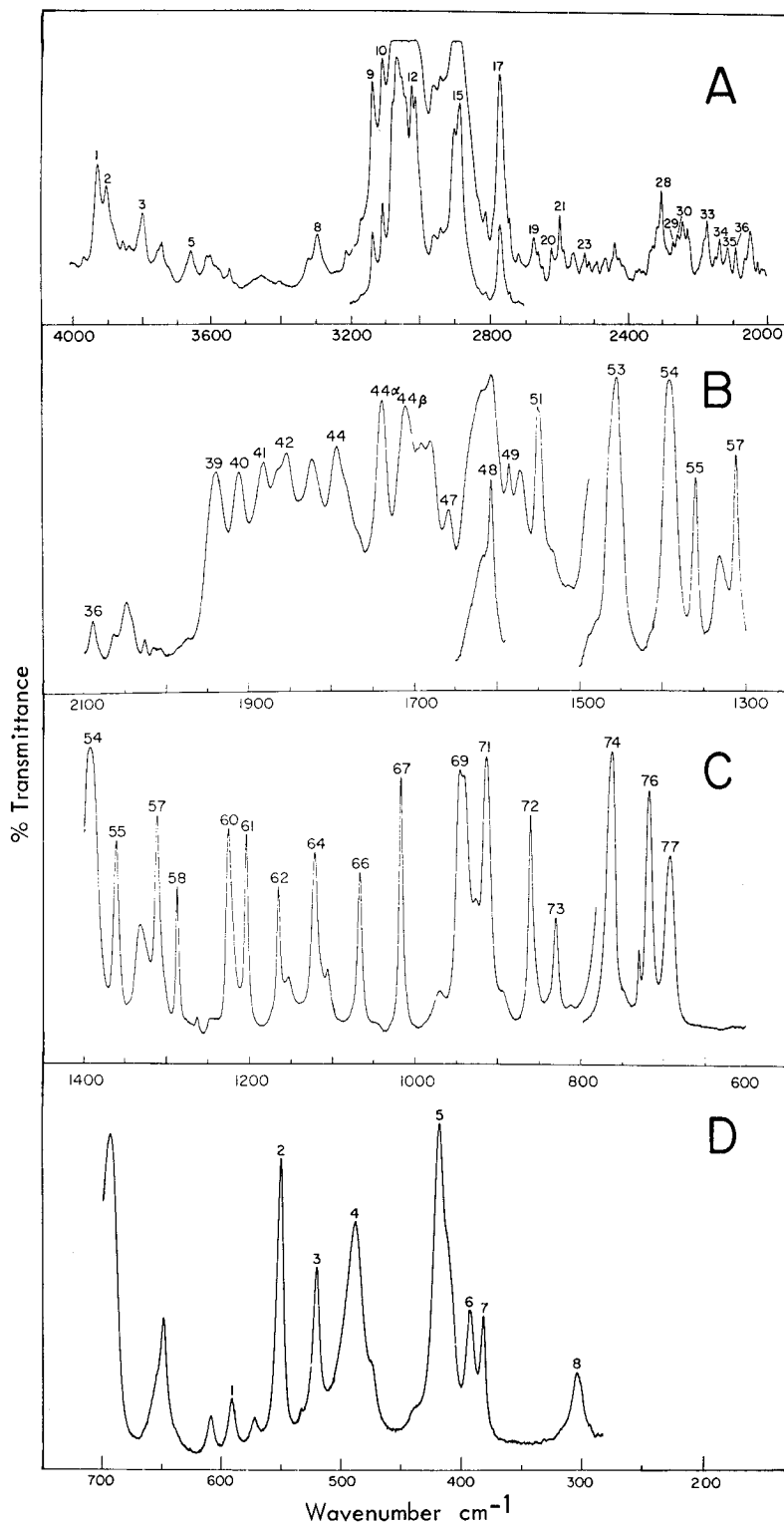
Figure 3. IUPAC definitive spectra of indene-camphor-cyclo-
hexanone mixtures: A–C, 98.4/0.8/0.8 mixture; D, 1/1/1.
See Tables I and II for cm^{-1} of numbered absorption maxima.

Path Lengths

4000–1500 cm^{-1}	0.20mm
3200–2700	0.03
1650–1600	0.03
1500– 780	0.03
800– 600	capillary
700– 280	0.05

Table I.—Indene-Camphor-Cyclohexanone (98.4/0.8/0.8) Mixture — Recommended Calibration Bands[a]

Band No.	Wavenumber (cm⁻¹)	Band No.	Wavenumber (cm⁻¹)
1	3927.2 ± 1.0	44α	1741.9
2	3901.6	44β	1713.4
3	3798.9	47	1661.8
5	3660.6 ± 1.0	48	1609.8
8	3297.8 ± 1.0	49	1587.5
9	3139.5	51	1553.2
10	3110.2	53	1457.3 ± 1.0
12	3025.4	54	1393.5
15	2887.6	55	1361.1
17	2770.9	57	1312.4
19	2673.3	58	1288.0
20	2622.3	60	1226.2
21	2598.4 ± 1.0	61	1205.1
23	2525.5	62	1166.1
28	2305.1	64	1122.4
29	2271.4	66	1067.7 ± 1.0
30	2258.7	67	1018.5
33	2172.8	69	947.2
34	2135.8 ± 1.0	70	942.4
35	2113.2	71	914.7
36	2090.2	72	861.3
39	1943.1	73	830.5
40	1915.3	74	765.3
41	1885.1	76	718.1
42	1856.9	77	692.6 ± 1.0
44	1797.7 ± 1.0		

Tables I and II contain wavenumber values for bands in Figure 3, p.18.

Table II.—Indene-Camphor-Cyclohexanone (1/1/1) Mixture — Recommended Calibration Bands[a]

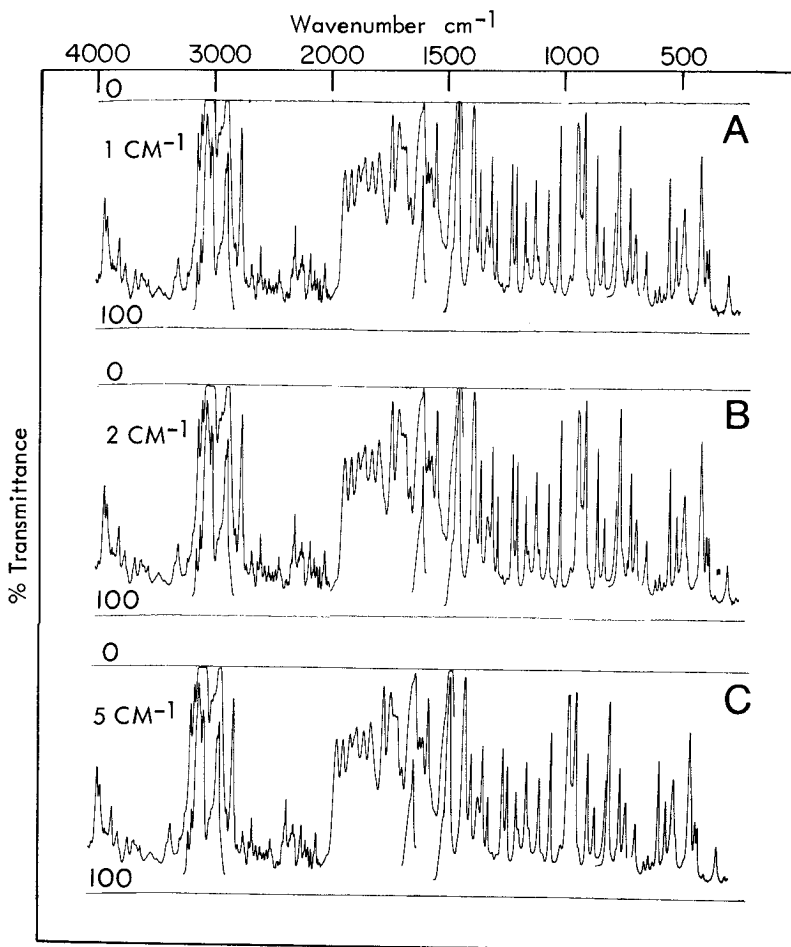| Band No.	Wavenumber (cm⁻¹)
1	592.1
2	551.7
3	521.4
4	490.2 ± 1.0
5	420.5
6	393.1
7	381.6
8	301.4

Figure 4. Resolution differences at 1, 2 and 5 cm⁻¹ slit widths shown by spectra of the indene calibration blend (98.4/0.8/0.8 from 4000-700 cm⁻¹; 1/1/1 from 700-280 cm⁻¹). Compare the band ratio differences for sharp peaks throughout the spectra.

(Figure 4 is adapted from Jones and Nadeau, Canadian Journal of Spectroscopy, 20, 35-42, March/April, 1975.)

C. Resolution Test for Dispersively Measured Spectra

In the neighborhood of 1200 cm^{-1} the spectral slit width can be determined approximately from the ratio A$_{1205.1}$/A$_{1226.2}$ computed in the dynamic error test, as given in:

TABLE III

Approximate Resolution
Collated From Indene Band Ratios

A$_{1205.1}$/A$_{1226.2}$	Spectral Slit Width (cm^{-1})
0.80	4.0 – 5.0
0.85	3.0 – 3.5
0.90	2.0 – 2.5
0.95	1.0 – 1.5
0.97	<1.0

For interferometrically measured spectra the nominal resolution can be computed provided both the apodization function and the optical retardation are reported. For both dispersively and interferometrically measured spectra the resolution of the spectrum of the indene/camphor/cyclohexanone reference sample should match the spectrum shown in Curve B of Figure 4 over 80% of the wavenumber range, and at no point be less than that of Curve C to meet Class II specifications.

D. False Radiation

The indene/camphor/cyclohexanone reference spectrum should show virtually total absorption at 3050.0, 1609.6 and 765.4 cm^{-1} if measured at the designated path lengths. The test spectra at these wavenumbers should therefore match the spectrophotometer transmission zero within the allowed tolerances. A 0.4 mm layer of pure indene is virtually totally absorbing at 392, 420 and 551 cm^{-1} and this can be used to establish the false radiation below 600 cm^{-1}. It should not exceed 2% transmission at wavenumbers greater than 600 cm^{-1}; the permissible amount at lower wavenumbers is left to the discretion of the evaluator.

E. Check on 100% Transmittance Line

Each set of spectra should be accompanied by a 100%T (I$_o$) check obtained by scanning the wavenumber range of the submitted spectra with no cell in either beam under the standard operating conditions used to obtain the spectra. The 100 % T trace should be flat within 0.01 nominal absorbance units. Minor exceptions are allowed at the discretion of the evaluator.

F. Cell Blank Check

Each set of solution spectra should be accompanied by a trace obtained under the standard operating conditions with solvent in both cells, using the same cells as for the transmitted spectra. No extraneous bands should appear though it is recognized that solvent bands may not be completely compensated in the cell blank spectrum. The permissible degree of mismatch is left to the judgement of the evaluator.
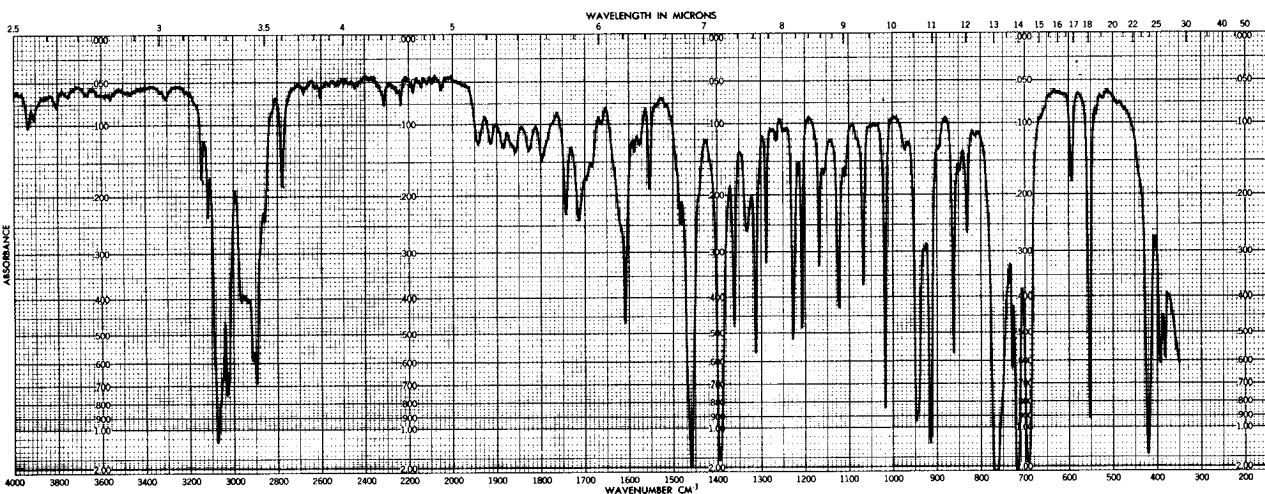

Figure 5. Routine test spectrum of Indene calibration standard 98.4 indene/0.8 camphor/0.8 cyclohexanone at optimum singe-run thickness (0.3mm). Note readability above 2000 cm^{-1} to 5 cm^{-1} and below 2000 cm^{-1} to cm^{-1}. Thicker runs are needed for additional zero checks (p.18).

OPERATING PARAMETERS OF DISPERSIVE SPECTROMETERS

In order to achieve best results with dispersive IR spectrometers, users must take considerable care to optimize the setting of the slit program, response time, gain and scan time. Some of the most modern spectrometers make use of electronically controlled automatically interactive settings to achieve optimum performance under ordinary sampling conditions. However, even for these automated spectrometers it is important for the user to understand the trade-offs in performance among the adjustable parameters, that is, what the "black box" is actually doing.

A paper by A. Lee Smith and W. J. Potts, Jr. (Applied Optics, Vol.6, p. 257, 1967) discusses in detail the significant parameters involved. Key factors are repeated here for convenience. Reference to the original article is highly recommended for a more complete treatment of each of the parameters discussed and for a comprehensive bibliography on the subject.

For dispersive spectrometers it is important to recognize one fundamental limitation: the spectrometer tries to make monochromatic radiation out of a continuous energy spectrum, and never quite succeeds. The spectral slit width, or frequency spread at half-maximum of the radiation passing the exit slit, is proportional to the mechanical slit width for a well adjusted spectrometer, or:
$$\Delta v_{1/2} \propto s$$
Other contributions to the breadth of $\Delta v_{1/2}$ are small compared with the slit term in an energy limited spectrometer during usual operation. The energy distribution in the frequency bundle falling on the detector surface is known as the slit function of the monochromator (Fig.6). The combination of the slit function and the true shape of an absorption band gives, for an infinitely slow scan, the observed line shape (Fig.7).
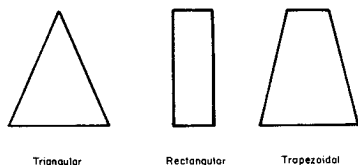

Triangular   Rectangular   Trapezoidal

Fig. 6   Some hypothetical slit functions of monochromators.
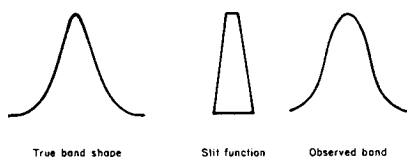

True band shape   Slit function   Observed band

Fig.7   Effect of slit function on line shape.

Clearly, the distortion introduced into the spectrum depends strongly on the slit function of the monochromator. It is also obvious that the narrower the slit, the smaller the net effect of both slit width and slit function on the recorded spectrum. As a rule of thumb, it has been suggested that $\Delta v_{1/2}$ should be less than one-fifth the bandwidth. Bandwidth is defined here as the width of the band envelope at half its maximum absorbance. This requirement implies a spectral slit width of less than 0.8 cm^{-1} for the narrower bands in condensed phases.

Resolution, which may be defined loosely as the ability of the spectrometer to separate two adjacent frequencies, is inversely proportional to slit width. It is usually determined by scanning pairs of lines whose separation is known from previous high resolution studies. Generally, one uses the highest practical resolution in order to achieve more accurate band shapes and intensities consistent with other spectrometer limitations.

Servo Energy

Modern spectrometers use a chopping or beam alternating system to achieve stable operation. Because of the slow response to thermoelectric detectors, the chopping speed is low—usually 5-20 c/s. In the double-beam optical null system an alternating signal at the detector indicates unbalance between the sample and the reference beam. The instrument responds by moving the optical attenuator into (or out of) the reference beam in such a way as to attempt to match exactly the absorption spectrum of the sample, and indeed it is the motion of the attenuator which is actually recorded; however, the fact that a finite signal exists at the detector indicates that the recording pen always lags behind the true sample transmission.

Thus, the system, radiation-detector-amplifier-servo motor-optical wedge, forms a closed loop which is the primary servo loop of the spectrometer. It is imperative for proper spectrometer operation that the energy of this loop be optimized; if it is too low, the attenuator motion will be sluggish and response will be incomplete (Fig.8); if it is too high, the system may overshoot badly on rapidly changing signals and may, in fact, break into oscillation about the equilibrium point. Amplification of the detector signal in the servo loop is controlled by the gain setting. The energy available from the detector for activating the loop varies with the brightness of the source, the efficiency of the de-

tector, and the slit width of the monochromator. Expressed in quantitative terms, the servo energy is proportional to the gain and to the square of the mechanical slit width, or,

$$\text{servo energy} \propto g\,s^2$$

These variables must be adjusted initially to give the proper servo energy, and subsequently maintained in the proper balance by compensating adjustments of gain and slit settings.

Ratio–recording spectrometers do not use an optical attenuator; nevertheless, these spectrometers are still subject to the same basic limitation of slit width, noise, response time, and scan time.

Noise

Noise, or unwanted random fluctuations of the recording pen, usually originates in the detector and first amplifier stage. The noise level sets a practical limit to the gain or degree of amplification of the detector signal. Noise is directly proportional to the gain, or

$$N \propto g$$

Thermoelectric detectors are characteristically inefficient, and the signal–to–noise is therefore low compared to that of a photomultiplier, for example. The principal sources of noise are thermal agitation of electrons in the detector and input transformer (Johnson noise) and tube noise in the first stage of amplification.

Noise is detrimental, since it introduces into the spectrometer record an uncertainty which produces disproportionately large errors in absorbance. For example, 1% noise superimposed on a band showing 20% transmission may give as much as 2.6% error in absorbance; irregularities in the background trace contribute an additional 0.6% for a total error of 3.2%. These errors are greatly magnified for measurements near zero or 100% transmission.

From a qualitative standpoint, noise is undesirable because bands are easily lost in noise (Fig. 9), and further, the unmeasurable but real confidence factor becomes low for a noisy spectrum. Finally, excessive noise interferes with the proper functioning of the speed suppression control. A realistic noise level for general spectrophotometer work is 0.5%T average peak to peak.

Response Time

Noise in the spectrometer can be minimized by (a) tuning the ac amplifier to the chopping frequency, a procedure which rejects signals of other frequencies (noise) (b) using an RC network to filter the dc signal resulting from synchronous demodulation of the amplified ac signal, or (c) incorporating inertia or changing the me-
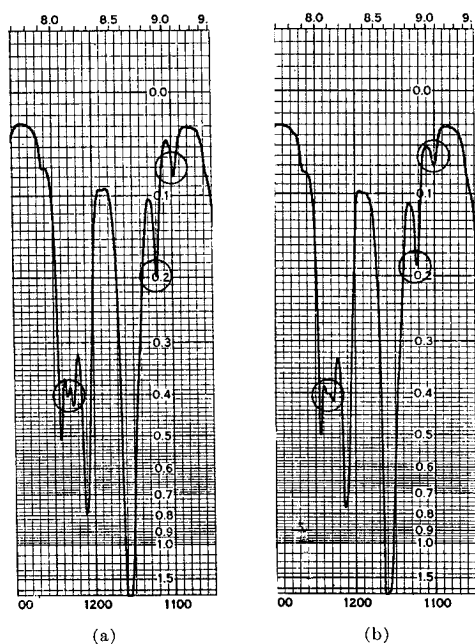

Fig. 8 (a) Scan with normal servo energy. (b) Scan with one-third normal servo energy.
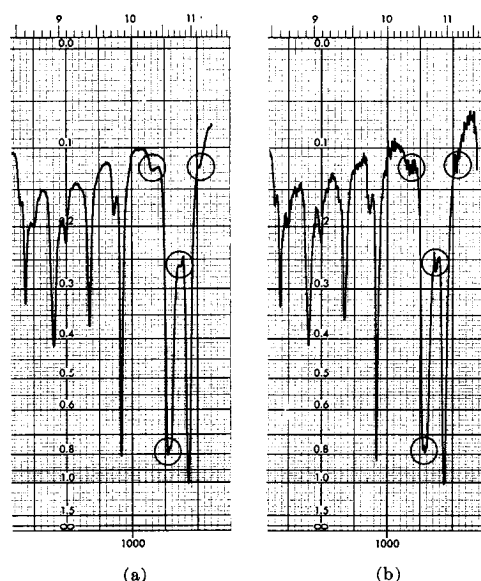

Fig. 9 (a) Normal scan. (b) Same conditions, except one-half normal slit width and gain increased to restore servo energy.

chanical part of the servo system. All these devices have the effect of increasing the time required for a signal to reach its steady state value, this time being the response time or response period of the servo loop.

The relationship between the Johnson noise voltage E_J and the servo system bandpass Δf is given by the Nyquist equation:

$$E_J{}^2 = 4kTR(\Delta f) \times 10^7$$

where k is Boltzmann's constant, T is the absolute temperature, and R is the detector resistance. The bandpass is inversely proportional to the time constant of the servo loop τ, or

$$\Delta f \propto \tau^{-1}$$

(Time constant for a critically damped system is defined as the time required for the servo response to reach within $1/e$ of its steady state value. Response time, or response period, as used here, is equivalent to about four time constants.) As a result of these relations,

$$N \propto g\,\tau^{-\frac{1}{2}}$$

The scanning speed of the spectrometer must be consistent with the response time in order for the recorder to follow accurately the detector signal. If the scan rate is too high, band shapes and intensities will be distorted, and weak bands may be missed completely (Fig.10). It has been suggested that the speed should not exceed
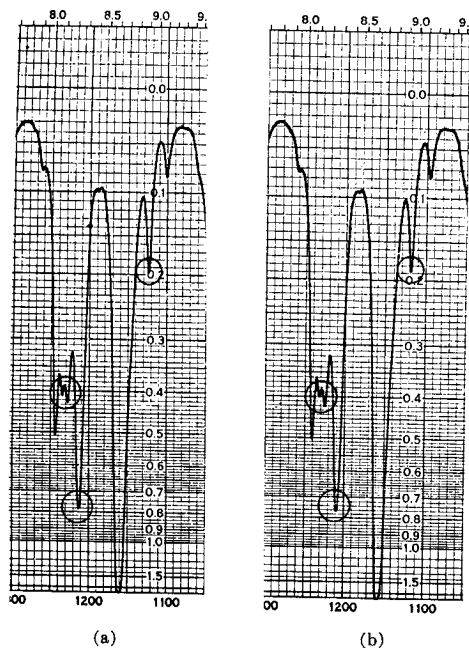
0.4 bandwidths per response period if band intensities are to suffer no more than 2% error from dynamic distortion. Bandwidths in condensed phases range from 2-20 cm^{-1} or more, with the largest number falling in the range 4-7 cm^{-1}.

Any system which adds electrical or mechanical inertia to the servo loop effectively increases its response time. The response time can be determined by measuring with a stopwatch the time required for full-scale deflection of the pen when the sample beam shutter is closed or opened: (that is, equilibrium 100% transmission to equilibrium zero % transmission averaged with the corresponding time for the reverse deflection). This method is an approximation useful only in an underdamped servo system.

Relationship Between the Variables

As stated earlier, the energy passed by the monochromator is proportional to the square of the slit width at any wavelength. If the spectrometer gain g is eliminated from the equations and the condition imposed that servo energy should be constant, the relation becomes:

$$N \propto s^{-2}\tau^{-\frac{1}{2}}$$

This important equation tells us that the noise decreases as the square of the slit opening, but only as the square root of the response time.

Thus, to halve the noise, either open the slits by a factor of the square root of two, or increase the response time (and scan time) by four. Usually the former choice is more expedient. Experience shows that trading a low noise level for higher resolution is usually not profitable; any slight advantage in real resolution is more than cancelled by the increased uncertainty in the recording. A useful table of these relationships has been prepared by A. L. Smith for this book - see below.

Fig. 10 (a) Normal scan with 0.5 sec response time. (b) Same conditions, except 2.0 sec response time.

TABLE IV

	Resolution (Slit Width)	Response Time	Noise Level
a	1 (Normal)	1	1
b	1.41	1	0.5
c	1	4	0.5
d	0.5	1	4
e	0.5	16	1
f	0.5	4	2
g	1	16	0.25
h	2	1	0.25

For example, to reduce noise by a factor of 2, either open the slit $\sqrt{2}$ (line b) and reduce the gain to give the proper servo energy, or increase response (and scan) time by a factor of 4 (line c, Table IV.)

Speed Suppression

Modern optical null spectrometers incorporate special circuitry which causes the wavelength scan motor to run at a speed that is an inverse function of the error signal in the attenuator servo loop. As a result, the spectrometer scan rate decreases when a region of absorption is encountered, the amount of decrease depending on the suppression setting. The slow scan rate persists a second or two after the attenuator comes into balance, whereupon normal scan speed is resumed. This device, if properly used, allows rapid scanning over empty spectral regions and slower scanning in populated regions.

Obviously, a high noise level precludes the use of realistic suppression values; the system will suppress on noise and nothing will be gained. This is another reason why the noise level should not exceed 0.5% T peak to peak.

The operating parameters to be chosen depend upon kinds of spectra desired. General purpose spectra on condensed phases should be run with an optimum compromise on conditions to allow a reasonably low scan time. In the area of special applications, quantitative work improves with a low noise level; energy-reducing

sample conditions require a sacrifice in resolution to give good pen response; and high resolution spectra require an increase in response time and therefore scan time to keep the noise level tolerable. Potts and Smith give a summary of a practical sequence for making these selections repeated here in tables V and VI.

It is obvious that digital recording of spectral data and computer averaging now available on dispersive spectrometers makes it easier to obtain good resolution spectra in energy limited situations. However, adherence to these operating procedures still serves to increase the efficiency and accuracy of spectrometers.

Additional recommended reading on this subject is "Happiness is a Class II Spectrum," by Smith and Potts (Applied Spectroscopy, Vol.26, No.2, 1972).

Table V   Summary of Procedure for Establishing Operating Parameters for General Purpose Spectra

1. Choose slit setting
2. Choose scan time
3. Pick consistent response time
4. Adjust gain for proper servo energy
5. Check noise
6. Adjust balance
7. Add speed suppression and reduce scan time appropriately
8. Run test spectra

Table VI   Summary of Procedures for Establishing Operating Parameters for Special Purpose Spectra

A. *Low noise*
   1. Establish general purpose conditions
   2. Determine noise level reduction factor
   3. Widen slits by $(factor)^{1/2}$ and reduce gain by (factor); or, increase response and scan time by $(factor)^2$
   4. Run test spectrum

B. *Limited energy*
   1. Establish general purpose conditions
   2. Determine energy attenuation factor
   3. Widen slits by $(factor)^{1/2}$; or increase gain by (factor) and increase response time and scan time by $(factor)^2$
   4. Run test spectrum.

C. *High resolution*
   1. Establish general purpose conditions
   2. Determine slit reduction factor
   3. Restore servo energy by increasing gain
   4. Increase response time and scan time to obtain tolerable noise level
   5. Run test spectrum

Note: Figures 6-10 and Tables V and VI are reprinted courtesy of Applied Optics.