

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY

**RECOMMENDATIONS FOR THE
PRESENTATION OF INFRARED ABSORPTION
SPECTRA IN DATA COLLECTIONS—A.
CONDENSED PHASES**

Prepared for publication by

E. D. BECKER

US Department of Health, Education and Welfare,
Bethesda, Maryland, U.S.A.

PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

U. K.	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, U.K.
U. S. A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon of Canada Ltd., 75 The East Mall, Toronto, Ontario, Canada
A U S T R A L I A	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, N.S.W. 2011, Australia
F R A N C E	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
FEDERAL REPUBLIC OF G E R M A N Y	Pergamon Press GmbH, 6242 Kronberg/Taunus, Pferdstasse 1, Federal Republic of Germany

Copyright © 1978 International Union of Pure and Applied Chemistry

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner

This report was first published in *Pure & Applied Chemistry*, Vol. 50, No. 3 and supplied to subscribers as part of their subscription

COMMISSION 1.5 - MOLECULAR STRUCTURE AND SPECTROSCOPY

RECOMMENDATIONS FOR THE PRESENTATION OF INFRARED ABSORPTION SPECTRA IN DATA COLLECTIONS. A. CONDENSED PHASES

PREAMBLE

These recommendations relate to the infrared spectra of condensed phase materials that are intended for permanent retention in data collections. They are revised from "Tentative Specifications for the Measurement and Evaluation of Infrared Spectra for Documentation Purposes," published in IUPAC Information Bulletin No. 34 in 1969. Further action concerning that report has been held in abeyance pending the assessment of new developments in the technique of infrared spectrophotometry resulting from the emergence of interferometric techniques of spectra measurement. These recommendations are based on two reports published by the Coblenz Society (1,2) of which the latter takes account of the interferometric method of measuring the spectra.

Although these recommendations are directed toward infrared spectra prepared for reference collections, many of them are also pertinent to spectra presented in journals.

The Coblenz Society has designated three levels of quality evaluation for infrared spectra:

I. Critically Defined Physical Data. This is a quality level in which all instrumental sources of error have been assessed and their tolerances specified. This applies specifically to the absolute band intensities and shapes; these are factors that are not considered in II and III. It is unlikely that substantial collections of spectra of this category will be amassed. No specifications have yet been written but it can be anticipated that small collections of spectra in this category covering limited wavenumber ranges will be obtained to serve as reference standards for infrared intensity measurements.

II. Research Quality Analytical Spectra. This category represents a quality level which can be achieved by good infrared spectrophotometers operated by competent technicians under conditions appropriate to a research laboratory.

III. Approved Analytical Spectra. This represents a minimal quality level for spectra that are to be retained for permanent cataloging.

There are, of course, many other spectra of high quality that cannot be classified into the above categories because certain information is lacking. These may be referred to as Unevaluated Spectra.

The recommendations in this report are based on the Coblenz Society's Research Quality Analytical Spectra category but the lower tolerances acceptable for the Approval Analytical Spectra are noted parenthetically where the tolerance differences are purely numerical. Other differences between the two quality characteristics mainly concern the documentation of the chemical structure and related matters. These are important where the spectra are deposited in atlases, but are less relevant where the spectra are used for other purposes, e.g. in a chemical journal in which it may be presumed that the documentation of the sample origin and structure will be referenced in the same article.

It is recommended that the Coblenz categorization of spectral quality be retained in the IUPAC specifications.

SPECIFICATIONS

These recommendations relate to both dispersively and interferometrically measured spectra unless otherwise indicated. When used without qualification the term spectrophotometer designates either a dispersive or an interferometric instrument. For interferometrically measured spectra all evaluation is based on the spectrogram, not on the interferogram.

-
- (1) Anal. Chem. 38, No. 9, 27A (1966).
 - (2) Anal. Chem. 47, No. 11, 945A (1975).

COMMISSION 1.5 - MOLECULAR STRUCTURE AND SPECTROSCOPY

RECOMMENDATIONS FOR THE PRESENTATION OF INFRARED ABSORPTION SPECTRA IN DATA COLLECTIONS. A. CONDENSED PHASES

PREAMBLE

These recommendations relate to the infrared spectra of condensed phase materials that are intended for permanent retention in data collections. They are revised from "Tentative Specifications for the Measurement and Evaluation of Infrared Spectra for Documentation Purposes," published in IUPAC Information Bulletin No. 34 in 1969. Further action concerning that report has been held in abeyance pending the assessment of new developments in the technique of infrared spectrophotometry resulting from the emergence of interferometric techniques of spectra measurement. These recommendations are based on two reports published by the Coblenz Society (1,2) of which the latter takes account of the interferometric method of measuring the spectra.

Although these recommendations are directed toward infrared spectra prepared for reference collections, many of them are also pertinent to spectra presented in journals.

The Coblenz Society has designated three levels of quality evaluation for infrared spectra:

I. Critically Defined Physical Data. This is a quality level in which all instrumental sources of error have been assessed and their tolerances specified. This applies specifically to the absolute band intensities and shapes; these are factors that are not considered in II and III. It is unlikely that substantial collections of spectra of this category will be amassed. No specifications have yet been written but it can be anticipated that small collections of spectra in this category covering limited wavenumber ranges will be obtained to serve as reference standards for infrared intensity measurements.

II. Research Quality Analytical Spectra. This category represents a quality level which can be achieved by good infrared spectrophotometers operated by competent technicians under conditions appropriate to a research laboratory.

III. Approved Analytical Spectra. This represents a minimal quality level for spectra that are to be retained for permanent cataloging.

There are, of course, many other spectra of high quality that cannot be classified into the above categories because certain information is lacking. These may be referred to as Unevaluated Spectra.

The recommendations in this report are based on the Coblenz Society's Research Quality Analytical Spectra category but the lower tolerances acceptable for the Approval Analytical Spectra are noted parenthetically where the tolerance differences are purely numerical. Other differences between the two quality characteristics mainly concern the documentation of the chemical structure and related matters. These are important where the spectra are deposited in atlases, but are less relevant where the spectra are used for other purposes, e.g. in a chemical journal in which it may be presumed that the documentation of the sample origin and structure will be referenced in the same article.

It is recommended that the Coblenz categorization of spectral quality be retained in the IUPAC specifications.

SPECIFICATIONS

These recommendations relate to both dispersively and interferometrically measured spectra unless otherwise indicated. When used without qualification the term spectrophotometer designates either a dispersive or an interferometric instrument. For interferometrically measured spectra all evaluation is based on the spectrogram, not on the interferogram.

-
- (1) Anal. Chem. 38, No. 9, 27A (1966).
 - (2) Anal. Chem. 47, No. 11, 945A (1975).

Tests to evaluate these specifications based on measurements on standard reference materials are described in the Coblenz Society's report (2) and the additional references cited therein.

I. SPECTROPHOTOMETER OPERATION

A. Resolution

For dispersively measured spectra the spectral slit width should not exceed 2 cm^{-1} (5 cm^{-1})* through at least 80% of the wavenumber range and at no place should it exceed 5 cm^{-1} (10 cm^{-1}). For interferometrically measured spectra the optical retardation must be at least 0.5 cm (0.2 cm) and the apodization function must be stated.

B. Wavenumber Accuracy

The abscissa, as read from the chart, should be accurate to $\pm 5\text{ cm}^{-1}$ (15 cm^{-1}) at wavenumbers greater than 2000 cm^{-1} and to $\pm 3\text{ cm}^{-1}$ (5 cm^{-1}) at wavenumbers less than 2000 cm^{-1} . Fiduciary marks should be recorded on each chart shortly after the beginning and near the end of each uninterrupted 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

The noise level should not exceed 1% (2%) average peak-to-peak or 0.25% (0.5%) root mean square of a full-scale deflection in internal transmittance.

D. Energy

The spectrophotometer should be purged with dry gas or evacuated to ensure that at least 50% of the source energy is available at all wavenumbers (except in the regions of carbon dioxide absorption near 2350 and 670 cm^{-1} ; if less than 25% of the original energy is available, these narrow regions of the spectrum should be deleted).

E. Other Performance Criteria

1. False radiation. Apparent stray radiation should be less than 2% (5%) transmittance at wavenumbers greater than 500 cm^{-1} .

2. Servo System and Recording System. Spectra should not exhibit evidence of dead spots or of excessive recorder overshoot. The spectrophotometer and recorder time constant should be compatible with the scan rate.

3. Temperature. It is to be assumed that the spectrum is measured at the ambient temperature unless stated otherwise.

II. PRESENTATION

A. Information to Appear on the Chart

Both the structural and the molecular formulae of the compound should appear on the chart.

The make and model of the spectrophotometer should be recorded as well as the date on which the spectrum was measured. For spectra obtained dispersively all changes of gratings and filters should be indicated, including the wavenumber at which they occur. A bar or arrow would be appropriate for this purpose. No mechanical attenuator should be placed in the reference beam additional to the optical attenuator, which is integral to some infrared spectrophotometers. For interferometrically measured spectra, the apodization function must be specified (See I. A). For all spectrophotometers the wavenumber positions at which cell changes occur should be specified.

The physical condition of the sample should be stated (e.g. solution, liquid, mull, halide pellet matrix, etc.). For measurements on solutions the solvent used in each region of the spectrum should be recorded. The concentration and nominal path length should be given for both solutions and pellets. The nominal path lengths of liquid samples should be indicated; a very thin layer may be described as a capillary film (See III B.1.c). In all cases the cell window or support window should be stated.

B. Spectral Range

The chart should cover the range 3800 (3700) to 450 (700) cm^{-1} without gaps, except under the

*Values in parentheses refer to Approved Analytical Spectra.

conditions defined in I.D. Extensions above and below this range are strongly encouraged. For such extended-range spectra the wavenumber accuracy, false radiation, atmospheric absorption and resolution should be stated.

For special purposes, such as spectra specifically categorized as "far infrared spectra" or "near infrared spectra" the inclusion of the range 3800 (3700) to 450 (700) cm^{-1} need not be mandatory.

C. Intensity Scale

It is preferred that the intensity ordinate values be expressed in absorbance units. Where the charts are plotted on a linear transmittance scale, a logarithmic ordinate grid is preferable so that the absorbance can be interpolated directly. Spectra plotted on a linear absorbance scale or in linear transmittance on a linear percent transmission ordinate grid are acceptable.

Any band over 1.5 absorbance units should be reproduced on a less absorbing sample. A significant fraction of the useful bands should have absorbance greater than 0.2. At least one band in the spectrum should have absorbance exceeding 0.7 (0.6). When multiple traces are required on the same chart their number should be kept to a minimum.

D. Wavenumber Readability

Sharp peaks should be readable to within $\pm 3 \text{ cm}^{-1}$ ($\pm 8 \text{ cm}^{-1}$) at wavenumbers greater than 2000 cm^{-1} and to $\pm 1 \text{ cm}^{-1}$ ($\pm 2 \text{ cm}^{-1}$) at wavenumbers less than 2000 cm^{-1} . Only spectra recorded with the abscissal scale linear in wavenumber are acceptable, but scale changes at designated abscissal positions are allowed. Presentation in a smaller format is allowable provided the absorption maxima are labelled with their wavenumber positions, in figures at least 1 mm high in the final reproduction.

E. Recording

Recording should be continuous with no gaps in wavenumber subject to the exception described in I.D. It is, however, permissible for spectra to extend over more than one chart. Discontinuities in ordinate (absorbance), if present, should not exceed 0.01 absorbance unit. Hand retraced spectra are not acceptable.

F. Atmospheric Absorption

Atmospheric absorption should not exceed the allowable noise level when observed in the double beam mode (See I.D.).

III. SAMPLE IDENTIFICATION AND PREPARATION

A. Compound Identification and Purity

Spectra should show no inconsistencies with the postulated structure. Some relaxation of this requirement may be permitted in the case of isotopically labelled 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.

B. Sample Preparation

1. Liquid State Samples. (a) For analytical purposes it is preferable that the sample be run in liquid solution, normally at concentrations in the range 5% to 10% weight (g) per volume (cm^3). 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. Suitable solvents which between them cover the range 3800–450 cm^{-1} are carbon tetrachloride (3800–1335, 650–450 cm^{-1}) and carbon disulfide (1350–450 cm^{-1}); both solvents should be used at path lengths in the range 0.03 – 0.3 mm.

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%.

(b) For documentation purposes it is 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.

(c) The spectra of liquids not soluble in transparent solvents should be measured as capillary films (See II. A).

2. Solid State Samples. (a) For most analytical purposes solution spectra in transparent solvent are preferred, provided the solvents and path lengths can be chosen to leave no significant gaps due to solvent obscuration. (See III.B.1.a). This does not apply where it is required to characterize the specific crystalline structure as with many natural minerals and biological samples.

(b) Solid state spectra may be recorded from samples incorporated in mulls or pressed disks, but care should be taken to ensure that no interaction occurs between the sample and the supporting medium. The possibility of thermal decomposition or other changes in the crystalline structure must be recognized, as must the possibility of preferred orientation of platy or fibrous crystals.

Solid state spectra should meet the following criteria:

(i) 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%. Only minor distortion resulting from the Christiansen effect may be permitted. 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 (or equivalent) for the range $3800 - 1335\text{ cm}^{-1}$ and the intensity of the overtone band near 2300 cm^{-1} should not exceed 0.02 absorbance unit. Liquid paraffin (Nujol or 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. 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.

(ii) Non-isotropic materials. Spectra of non-isotropic materials, such as single crystals or oriented polymers, 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.