



Designation: E 932 – 89 (Reapproved 1997)

Standard Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers¹

This standard is issued under the fixed designation E 932; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the necessary information to qualify dispersive infrared instruments for specific analytical applications, and especially for methods developed by ASTM.

1.2 This practice is not to be used as a rigorous test of performance of instrumentation.

1.3 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 131 Terminology Relating to Molecular Spectroscopy²

E 168 Practices for General Techniques of Infrared Quantitative Analysis²

E 387 Test Method for Estimating Stray Radiant Power Ratio of Spectrophotometers by the Opaque Filter Method²

E 1252 Practice for General Techniques for Qualitative Infrared Analysis²

3. Terminology

3.1 *Definitions and Symbols*—For definitions of terms and symbols, refer to Terminology E 131 and *Compilation of ASTM Standard Definitions*.³

4. Significance and Use

4.1 This practice is intended for all infrared spectroscopists who are using dispersive instruments for qualitative or quantitative areas of analysis.

4.2 The purpose of this practice is to set forth performance guidelines for testing instruments used in developing an analytical method. These guidelines can be used to compare an instrument in a specific application with the instrument(s) used in developing the method.

4.3 An infrared procedure must include a description of the

instrumentation and of the performance needed to duplicate the precision and accuracy of the method.

5. Apparatus

5.1 For the purposes of this practice, dispersive instruments include those employing prisms, gratings, or filters to separate infrared radiation into its component wavelengths.

5.2 For each new method, describe the apparatus and instrumentation both physically and mechanically, and also in terms of performance as taught in this practice. That is, the description should give numerical values showing the frequency accuracy and the frequency and the photometric precision. State the spectral slit width maximum or slit width program if one is used. Where possible, state the maximum and minimum resolution if those data are a part of the instrument display. Show typical component spectra as produced by the instrument to establish the needed resolution.

5.3 If a computer program is used, describe the program. Include the programming language and availability, or whether the program is proprietary to a manufacturer.

6. Reference to this Practice in Standards

6.1 Reference to this practice should be included in all ASTM infrared methods. The reference should appear in the section on apparatus where the particular spectrometer is described.

7. Parameters in Spectroscopy

7.1 Dispersive infrared spectrometers have a source of quasi-monochromatic radiation together with a photometer for measuring relative radiant power. Accurate spectrometry involves a large number of interrelated factors that determine the quality of the radiant power passing through a sample and the sensitivity and linearity with which this radiant power can be measured. Assuming proper instrumentation and its use, the instrumental factors responsible for inaccuracies in spectrometry are resolution, linearity (Practices E 168), stray radiant power (Test Method E 387), and cell constants (Practice E 1252). Rigorous measurement of these factors is beyond the scope of this practice, and a more practical approach is described for the accessible factors.

8. Instrument Operation

8.1 The analyst selects the proper instrumental operating

¹ This practice is under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.03 on Infrared Spectroscopy.

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² *Annual Book of ASTM Standards*, Vol 03.06.

³ Available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

conditions in order to get satisfactory performance (1-3).⁴ Because instrument design varies, the manufacturer's recommendations are usually best. A record of operating conditions should be kept so that data can be duplicated by future users.

8.2 In addition to operating conditions, the following should be checked and recorded:

8.2.1 *Ambient temperature,*

8.2.2 *Pen response time,*

8.2.3 *Scanning speed,*

NOTE 1—In some instruments these functions are integrated in the scan modes.

8.2.4 *Noise level, and*

8.2.5 *Mechanical repeatability.*

8.3 Each of the above factors is important in the measurement of analytical wavenumber and photometric data. There is usually some lag between the recorded reading and the correct reading. Proper selection of operating conditions and good, reproducible, sample handling techniques minimize these effects or make the effects repeatable. For example:

8.3.1 Variation in temperature of the monochromator or sample may cause changes in wavenumber precision and accuracy.

8.3.2 Scanning too fast will displace the apparent wavenumber towards the direction scanned and will decrease the peak absorbance reading for each band.

NOTE 2—Some instruments provide for automatic monitoring and correction of this effect.

8.4 Mechanical repeatability of the monochromator and recording system as well as positioning of chart paper are important in wavenumber measurement.

8.4.1 Chart paper should be checked for uniformity of the printed scale length as received and rechecked at time of use, particularly if the paper has been subjected to pronounced humidity changes. Instructions on obtaining proper mechanical repeatability may be given in the manufacturer's literature.

8.5 In the case of computerized dispersive instruments, any spectrum printed from a computer file must be obtained as prescribed by the manufacturer and should be identical to the original data.

PRECISION AND ACCURACY

9. Definitions

9.1 *wavenumber precision*—a measure of the capability of a spectrometer to return to the same spectral position as measured by a well-defined absorption or emission band when the instrument is reset or rescanned. The index used in this practice is the standard deviation.

9.2 *wavenumber accuracy*—the deviation of the average wavenumber reading of an absorption band or emission band from the known wavenumber of that band.

10. Nature of Test

10.1 For the purpose of calibration, most methods employ pure compounds and known mixtures at specified analytical

wavenumbers. The wavenumbers are either read from a dial, optical display, chart paper, or a computer file.

11. Reference Wavenumbers in the Infrared Region (2)

11.1 The recommended wavenumber calibration points are the absorption maxima of a standard (98.4/0.8/0.8 by weight) indene/camphor/cyclohexanone mixture listed in Table 1. Suitable path lengths are 0.2 mm for the range from 3800 to 1580 cm^{-1} and 0.03 mm for the wavenumber range from 1600 to 600 cm^{-1} . A mixture containing equal parts by weight of indene, camphor, and cyclohexanone (1/1/1 by weight) at a path length of 0.1 mm may be used for the range from 600 to 300 cm^{-1} . See Table 2 and Fig. 1.

11.2 Polystyrene is also a convenient calibration standard for the wavenumber range from 4000 to 400 cm^{-1} . Polystyrene films, approximately 0.03 to 0.05 mm thick, can be purchased from instrument manufacturers. The recommended calibration peaks are listed in Fig. 2.

NOTE 3—The correction of frequency for the refractive index of air is significant in the wavenumber calculation only when wavelengths have been measured to better than 3 parts in 10 000. Reference (3) tabulates additional reference wavenumbers of interest.

11.3 For low-resolution prism or filter instruments operated in single-beam mode, the position of the atmospheric carbon dioxide band near 2350 cm^{-1} can be useful. This band may be resolved into a doublet. The 2350- cm^{-1} value is for the approximate center between the two branches. The atmospheric carbon dioxide band near 667 cm^{-1} is useful in the low-wavenumber region.

12. Dynamic Error Test

12.1 For dispersively measured spectra, the following dynamic error test is suitable for use with most grating and prism spectrometers. (4 and 5)

TABLE 1 Indene-Camphor-Cyclohexanone (98.4/0.8/0.8) Mixture—Recommended Calibration Bands⁵

Band No.	Wavenumber, cm^{-1}	Band No.	Wavenumber, cm^{-1}
1	3927.2 ± 1.0	44 α	1741.9
2	3901.6	44 β	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		

⁴ The boldface numbers refer to the list of references at the end of this practice.

TABLE 2 Indene-Camphor- Cyclohexanone (1/1/1) Mixture—Recommended Calibration Bands⁵

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

12.2 The spectrum of the (98.4/0.8/0.8) indene/camphor/cyclohexanone mixture is remeasured from 1350 to 850 cm⁻¹ at one fourth of the scan rate used for the reference spectrum and 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 absorbance ratios A1226.2/A1288.0, A1205.1/A1226.2, and A914.7/A1018.5 should not differ by more than ± 0.02 between the fast and slow runs.

NOTE 4—The indene/camphor/cyclohexanone should remain in sealed, refrigerated ampoules.

13. Selection of Slit Width or Slit Program

13.1 One of the most important parameters the analyst must select is the spectral slit width. The slit width affects resolution and the signal-to-noise ratio (S/N). Generally, a narrower slit width gives higher resolution and lower S/N ratio. These must be optimized for any given analysis.

13.2 The preferred manner of expressing resolution is in terms of spectral band width, but methods of measuring this quantity in all spectral regions are not available.

13.2.1 Spectral band width is not constant throughout the spectrum and therefore must be determined in each region of interest. In the neighborhood of 1200 cm⁻¹, the spectral band width can be determined approximately from the ratio A1205.1/A1226.2 of the (98.4/0.8/0.8) indene/camphor/cyclohexanone mixture, computed in the dynamic error test, as given in Table 3.

13.3 In each infrared method, typical spectra of the components, or a spectrum of a suitable mixture of components, should be included to illustrate the resolution found to be adequate to perform the analysis. These spectra should be direct copies of the plotted spectra and not redrawn curves.

PHOTOMETRY

14. Linearity of Absorbance

14.1 In a spectrometric method, photometric data are used to determine concentrations. Linearity of absorbance is a function of instrument response. The relationship must be determined in the concentration range of interest.

14.2 Procedure for testing linearity and establishing working curves are described in Practices E 168.

14.3 Some methods for quantitative analysis do not require linear response. The ultimate criterion for these is whether a method gives correct answers for known samples.

15. Measurement Procedure for Frequency Accuracy and Precision

15.1 From Tables 1-3, select calibration wavenumbers, preferably bracketing each analytical wavenumber and read each wavenumber ten times.

15.2 Average the observed readings for each wavenumber. The wavenumber accuracy is the difference between the true wavenumber and the average observed wavenumber.

NOTE 5—To check the wavenumber accuracy of a non-scanning instrument, balance the instrument at the true value of the absorbance maximum. Adjust the wavenumber drive until maximum apparent absorbance is found. Always approach the line or band from the same direction. Repeat ten times.

15.3 Calculate the precision of each observed wavenumber using the following equation:

$$s = \sqrt{\frac{\sum(X_i - \bar{X})^2}{n - 1}} \quad (1)$$

where:

s = estimated standard deviation of the series of results,

X_i = individual observed value (wavenumber, absorbance, or transmittance)

\bar{X} = average (arithmetic mean) of the observed values, and

n = number of observations.

15.4 Results should be specified in the following order: true peak position of reference material, average wavenumber determined, and wavenumber standard deviation.

16. Measurement Procedure for Photometric Precision

16.1 Photometric precision represents the capability of the photometer system to reproduce the same value in successive determinations. The index of precision used in this practice is the standard deviation.

16.2 Photometric precision is determined on a calibration sample by measuring the absorbance or transmittance of the same sample ten times, following the same procedure used to obtain the data for the linearity test.

16.3 Tabulate the individual readings of apparent absorbance or transmittance. Calculate the standard deviation of the ten readings using the equation in 15.3. Report the average reading and the standard deviation.

17. Stray Radiate Power

17.1 Stray radiant power (SRP) causes an error in the spectrometer zero transmittance reading. If measured at the designated path lengths, the indene/camphor/cyclohexanone reference spectrum should show essentially zero transmittance at 3050.0, 1609.6 and 765.4 cm⁻¹. The test spectra at these wavenumbers should therefore match the spectrometer transmittance zero within the manufacturers' tolerances. A 0.4-mm layer of pure indene is almost totally absorbing at 392, 420, and 551 cm⁻¹ and this can be used to establish the stray radiant power below 600 cm⁻¹. This should not exceed 2 % transmittance at wavenumbers greater than 600 cm⁻¹; the permissible amount at lower wavenumbers is left to the discretion of the evaluator.