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Standard Practices for General Techniques of Infrared Quantitative Analysis[1]

This standard is issued under the fixed designation E168; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These practices cover the techniques most often used in infrared quantitative analysis. Practices associated with the collection and analysis of data on a computer are included as well as practices that do not use a computer.

1.2 This practice does not purport to address all of the concerns associated with developing a new quantitative method. It is the responsibility of the developer to ensure that the results of the method fall in the desired range of precision and bias.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements appear in Section 6, Note A4.7, Note A4.11, and Note A5.6.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E131 Terminology Relating to Molecular Spectroscopy

E334 Practice for General Techniques of Infrared Microanalysis

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

E1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E1655 Practices for Infrared Multivariate Quantitative Analysis

3. Terminology

3.1 For definitions of terms and symbols, refer to Terminology E131.

4. Significance and Use

4.1 These practices are intended for all infrared spectroscopists. For novices, these practices will serve as an overview of preparation, operation, and calculation techniques. For experienced persons, these practices will serve as a review when seldom-used techniques are needed.

5. Apparatus

5.1 The infrared techniques described here assume that the equipment is of at least the usual commercial quality and meets the standard specifications of the manufacturer. For dispersive instruments, also refer to Practice E932. For Fourier Transform and dispersive instruments, also refer to Practices E1421 and E932 respectively, and for microanalysis with these instruments see Practice E334.

5.2 In developing a spectroscopic method, it is the responsibility of the originator to describe the instrumentation and the performance required to duplicate the precision and bias of a method. It is necessary to specify this performance in terms that can be used by others in applications of the method.

6. Hazards

6.1 Users of these practices must be aware that there are inherent dangers associated with the use of electrical instrumentation, infrared cells, solvents, and other chemicals, and that these practices cannot and will not substitute for a practical knowledge of the instrument, cells, and chemicals used in a particular analysis.

[1] These practices are under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and are the direct responsibility of Subcommittee E13.03 on Infrared and Near Infrared Spectroscopy.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

7. Considerations for Quantitative Infrared Measurements

7.1 Quantitative infrared analysis is commonly done with grating, filter, prism, or interferometer instruments. The following guidelines for setting up an analytical procedure are appropriate:

7.1.1 Always operate the instrument in the most stable and reproducible conditions attainable. This includes instrument warm-up time, sample temperature equilibration, and exact reproduction of instrument performance tests for both standards and samples. After calibration, use equivalent settings for analyses. For all infrared instruments, refer to the manufacturer's recommendations for the instrument settings. After calibration, use these same settings for analysis.

7.1.2 The absorbance values at analytical wavenumbers should fall within the acceptably accurate range of the particular spectrometer used. In general, a single absorbance measurement will have the best signal-to-noise ratio when it is in the range from 0.3 to 0.8 absorbance units (AU) (**1**).[3] The sensitivity of Fourier transform (FT-IR) spectrometers is such that lower absorbance values can be used quite effectively, provided that the baseline can be estimated accurately (see Section 12). Absorbances greater than 0.8 AU should be avoided wherever possible because of the possibility of instrumentally-caused non-linearity, both for dispersive (**2**) and FT-IR (**3,4**) spectrometers. Variation of the concentration and sample path length can be used to adjust absorbance values into the optimum range. When multiple components are determined in a particular sample, it is acceptable to use absorbance values outside the optimum range, (**5**) however, absorbances greater than 1.5 AU should be avoided (**2-4**). Weaker absorption bands of high concentration components may be selected to provide absorbance values within the optimal range.

7.1.3 The most accurate analytical methods are implemented with samples in solution. With liquid samples that are not exceptionally viscous, best results are obtained if the cell is not moved after the first sample is introduced into the instrument (the fixed-cell method). The reason is that sample cell position is difficult to reproduce accurately by insertion into typical cell holders. Suitable fittings and tubes can be attached to the cell to allow sample changing in a flow-through manner. When it is not practical to use a flow-through cell, the cell should fit tightly in the holder so that lateral and tilting motions are restricted.

7.1.4 Unless there is reason to suspect deposition on or contamination of the cell from the samples, it is generally preferable to wash out the current sample with the next sample, if sufficient sample is available. The volume of sample used to flush the cell should be at least five times (and preferably more, for example, 20 times) the volume between the sample inlet and cell exit points.

7.1.5 For some bands, the wavenumber of the maximum absorbance changes as a function of concentration. Similarly, the position of the baseline points may change with concentration. Selection of baseline points must be done carefully to account for the shift of the absorbance maximum. The question arises whether it is preferable to measure absorbances at fixed wavenumber locations or at the observed maximum of the analytical band. The best approach is empirical testing of both the fixed point and the tracking methods of evaluation.

7.1.6 Whenever possible, working directly in absorbance is preferable. That is, either the instrument or associated data processor makes the necessary conversion from transmittance to absorbance. If spectra cannot be obtained in absorbance, then Eq A12.1 and A12.2 in Annex A12 can be used to convert the data.

7.1.7 Use spectral regions offering the most information on the analyte. Select analytical wavenumbers where the component has a relatively large absorptivity. In addition, other analytes should have minimal effect on the measured absorbance.

7.1.8 The performance of the spectrometer should be sufficiently good to give adequate linearity of response for the desired range of concentrations. The signal-to-noise ratio, S/N, should be acceptable for the desired precision.

7.1.9 Select analytical wavenumbers such that the linearity of the absorbance-concentration relationship is least affected by molecular interaction, dispersion in refractive index, and spectrometer nonlinearity.

8. Theory for a Single-Compound Analysis

8.1 Quantitative spectrometry is based on the Beer-Bouguer-Lambert (henceforth referred to as Beer's) law, which is expressed for the one component case as:

$$A = abc \tag{1}$$

where:

A = absorbance of the sample at a specified wavenumber,
a = absorptivity of the component at this wavenumber,
b = sample path length, and
c = concentration of the component.

Since spectrometers measure transmittance, T, of the radiation through a sample, it is necessary to convert T to A as follows:

$$A = -\log T = -\log\frac{P}{P_0} \tag{2}$$

where:

P_0 = input radiant power at the sample, and
P = radiant power transmitted through the sample.

9. Calibration for a Single-Component Determination

9.1 Proper sample preparation is essential to quantitative analysis. See Annex A4.

9.1.1 Quantitative analysis has two distinct parts: calibration and analysis. For a simple one-component analysis, select an appropriate solvent that is essentially free from interfering absorptions at the analytical wavenumber.

9.1.2 For calibration, measure the absorbances, A, of the analyte solutions at several known concentrations, c. Absorptivities, a, are then calculated, using Eq 1 with the baseline corrections as described in Sections 12 – 14. Alternatively, the absorbances, A, of a single solution in several

[3] The boldface numbers in parentheses refer to the list of references at the end of these practices.