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

This standard is issued under the fixed designation E 1252; 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 spectral range from 4000 to 50 cm⁻¹ and includes techniques that are useful for qualitative analysis of liquid-, solid-, and vapor-phase samples by infrared spectrometric techniques for which the amount of sample available for analysis is not a limiting factor. These techniques are often also useful for recording spectra at frequencies higher than 4000 cm⁻¹, in the near-infrared region.

1.2 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 and health practices and determine the applicability of regulatory limitations prior to use. Specific precautions are given in 6.5.1.

2. Referenced Documents

2.1 ASTM Standards:

E 131 Terminology Relating to Molecular Spectroscopy
E 168 Practices for General Techniques of Infrared Qualitative Analysis
E 334 Practice for General Techniques of Infrared Microanalysis
E 573 Practices for Internal Reflection Spectroscopy
E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers
E 1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests
E 1642 Practice for General Techniques of Gas Chromatography Infrared (GC/IR) Analysis

3. Terminology

3.1 Definitions—For definitions of terms and symbols, refer to Terminology E 131.

4. Significance and Use

4.1 Infrared spectroscopy is the most widely used technique for identifying organic and inorganic materials. This practice describes methods for the proper application of infrared spectroscopy.

5. General

5.1 Infrared (IR) qualitative analysis is carried out by functional group identification (1-3)³ or by the comparison of IR absorption spectra of unknown materials with those of known reference materials, or both. These spectra are obtained (4-8) through transmission, reflection, and other techniques, such as photoacoustic spectroscopy (PAS). Spectra that are to be compared should be obtained by the same technique and under the same conditions. Users of published reference spectra (9-16) should be aware that not all of these spectra are fully validated.

5.1.1 Instrumentation and accessories for infrared qualitative analysis are commercially available. The manufacturer’s manual should be followed to ensure optimum performance and safety.

5.2 Transmission spectra are obtained by placing a thin uniform layer of the sample perpendicular to the infrared radiation path (see 9.5.1 for exception in order to eliminate interference fringes for thin films). The sample thickness must be adequate to cause a decrease in the radiant power reaching the detector at the absorption frequencies used in the analysis. For best results, the absorbance of the strongest bands should be in the range from 1 to 2, and several bands should have absorbances of 0.6 units or more. There are exceptions to this generalization based on the polarity of the molecules being measured. For example, saturated hydrocarbons are nonpolar, and their identifying bands are not strong enough unless the C-H stretch at 2920 cm⁻¹ is opaque and the deformation bands are in the range from 1.5 to 2.0 absorbance units (A) at 1440 to 1460 cm⁻¹. Spectra with different amounts of sample in the radiation path may be required to permit reliable analysis. If spectra are to be identified by computerized curve matching, the absorbance of the strongest band should be less than 1;
otherwise, the effect of the instrument line shape function will cause errors in the relative intensities of bands in spectra measured by dispersive spectrometers and by FT-IR spectrometers with certain apodization functions (specially triangular).

5.2.1 Techniques for obtaining transmission spectra vary with the sample state. Most samples, except free-standing thin films, require IR transparent windows or matrices containing the sample. Table 1 gives the properties of IR window materials commonly employed. Selection of the window material depends on the region of the IR spectrum to be used for analysis, on the absence of interference with the sample, and adequate durability for the sample type.

5.3 Spectra obtained by reflection configurations commonly exhibit both reflection and absorption characteristics and are affected by the refractive indices of the media and the interfaces. Spectral interpretation should be based on references run under the same experimental conditions. In particular, it should be realized that the spectrum of the surface of a sample recorded by reflection will often differ from the spectrum of the bulk material as recorded by transmission spectroscopy. This is because the chemistry of the surface often differs from that of the bulk, due to factors such as surface oxidation, migration of species from the bulk to the surface, and possible surface contaminants. Some surface measurements are extremely sensitive to small amounts of materials present on a surface, whereas transmission spectroscopy is relatively insensitive to these minor components.

5.3.1 Reflection spectra are obtained in four configurations:
5.3.1.1 Specular reflectance (7.5),
5.3.1.2 Diffuse reflectance (7.6),
5.3.1.3 Reflection-absorption (7.7),
5.3.1.4 Internal reflection (7.9). Refer to Practices E 573. This technique is also called Attenuated Total Reflection (ATR), and
5.3.1.5 Grazing angle reflectance.
5.4 Photoacoustic IR spectra (11.2).
5.5 Emission spectroscopy (11.4).

TEST METHODS AND TECHNIQUES

6. Analysis of Liquids

6.1 Fixed Cells—A wide range of liquid samples of low to moderate viscosity may be introduced into a sealed fixed-path length cell. These are commercially available in a variety of materials and path lengths. Typical path lengths are 0.01 to 0.2 mm. See 5.2 for considerations in selection of cell materials and path lengths.

6.2 Capillary Films—Some liquids are too viscous to force into or out of a sealed cell. Examination of viscous liquids is accomplished by placing one or more drops in the center of a flat window. Another flat window is then placed on top of the liquid. Pressure is applied in order to form a bubble-free capillary film covering an area large enough that the entire radiation beam passes through the film. The film thickness is regulated by the amount of pressure applied and the viscosity of the liquid. A capillary film prepared in this manner has a path length of about 0.01 mm. Volatile and highly fluid materials may be lost from films prepared in this manner.

Demountable spacers can be used when a longer path length is required to obtain a useful spectrum.

6.3 Internal Reflection Spectroscopy (IRS)—Viscous materials can be smeared on one or both sides of an internal reflection element (IRE). See Practices E 573 for detailed information on this technique.

6.4 Disposable IR Cards—These can be used to obtain spectra of non-volatile liquids. A very small drop, usually less than 10 µL of the liquid, is applied near the edge of the sample application area. If the sample does not easily flow across the substrate surface, it may be spread using an appropriate tool. The sample needs to be applied in a thin layer, completely covering an area large enough that the entire radiation beam passes through the sample. Note that any volatile components of a mixture will be lost in this process, which may make the use of a disposable card a poor choice for such systems.

6.5 Solution Techniques:

6.5.1 Analysis of Materials Soluble in Infrared (IR) Transparent Solvent: The Split Solvent Technique—Many solid and liquid samples are soluble in solvents that are transparent in parts of the infrared spectral region. A list of solvents commonly used in obtaining solution spectra is given in Table 2. The selection of solvents depends on several factors. The sample under examination must have adequate solubility, it must not react with the solvent, and the solvent must have appropriate transmission regions that enable a useful spectrum to be obtained. Combinations of solvents and window materials can often be selected that will allow a set of qualitative solution-phase spectra to be obtained over the entire IR region. One example of this “split solvent” technique utilizes carbon tetrachloride (CCl₄) and carbon disulfide (CS₂) as solvents.

Note 1—Warning: Both CCl₄ and CS₂ are toxic; keep in a well ventilated hood. Use of these solvents is prohibited in many laboratories. In addition, CS₂ is extremely flammable; keep away from ignition sources, even a steam bath. Moreover, CS₂ is reactive (sometimes violently) with primary and secondary aliphatic amines and must not be used as a solvent for these compounds. Similarly, CCl₄ reacts with aluminum metal. Depending on conditions such as temperature and particle size, the reaction has been lethally violent.

6.5.1.1 Absorption by CCl₄ is negligible in the region 4000 to 1330 cm⁻¹ and by CS₂ in the region 1330 to 400 cm⁻¹ in cells of about 0.1 mm thickness. (Other solvents can be used.) Solutions are prepared, usually in the 5 to 10 % weight/volume range, and are shaken to ensure uniformity. The solutions are transferred by clean pipettes or by syringes that have been cleaned with solvent and dried to avoid cross-contamination with a previous sample. If the spectrum of a 10 % solution contains many bands that are too deep and broad for accurate frequency measurement, thinner cells or a more dilute solution must be used.

Note 2—New syringes should be cleaned before use. Glass is the preferred material. If plastic is used as containers, lids, syringes, pipettes, and so forth, analytical blanks are necessary as a check against contamination.

NOTE 2—New syringes should be cleaned before use. Glass is the preferred material. If plastic is used as containers, lids, syringes, pipettes, and so forth, analytical blanks are necessary as a check against contamination.

The 3M disposable IR Card is manufactured by 3M Co., Disposable Products Division.
<table>
<thead>
<tr>
<th>Window Material</th>
<th>Chemical Composition</th>
<th>Cutoff Range (µm)</th>
<th>Useful Transmission Range (cm⁻¹)</th>
<th>Water Solubility</th>
<th>Refractive Index (at ~µm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>SiO₂</td>
<td>0.25–2</td>
<td>40 000–1250</td>
<td>insoluble</td>
<td>1.5–1.9</td>
<td>HF, alkali&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Quartz (fused)</td>
<td>SiO₂</td>
<td>0.2–5</td>
<td>6 000–20 000</td>
<td>insoluble</td>
<td>1.65, 1.5</td>
<td>0.589&lt;sup&gt;c&lt;/sup&gt; Reacts with acids</td>
</tr>
<tr>
<td>Silicon Nitrate</td>
<td>Si₃N₄</td>
<td>0.2–5</td>
<td>25 000–769</td>
<td>insoluble</td>
<td>1.77</td>
<td>0.55 Good strength, no cleavage</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>SiC</td>
<td>0.6–5</td>
<td>50 000–1600</td>
<td>1.68</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>0.2–5</td>
<td>50 000–20 000</td>
<td>1.65</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Sapphire</td>
<td>Al₂O₃</td>
<td>0.2–5</td>
<td>50 000–18 180</td>
<td>1.8</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>ALON</td>
<td>NaAlO₂·5Al₂O₃</td>
<td>0.2–5</td>
<td>50 000–17 000</td>
<td>1.8</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Spinel</td>
<td>Mg₆Al₄O₁₆</td>
<td>0.2–6</td>
<td>50 000–16 000</td>
<td>1.68</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Strontium Titanate</td>
<td>SrTiO₃</td>
<td>0.2–6</td>
<td>25 000–17 000</td>
<td>2.4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>TiO₂</td>
<td>0.42–6</td>
<td>24 000–17 000</td>
<td>2.6–2.9</td>
<td>H₂SO₄ and Alkali&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Lithium Fluoride</td>
<td>LiF</td>
<td>0.2–7</td>
<td>50 000–14 290</td>
<td>1.39</td>
<td>1.39 Acid&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Zirconia</td>
<td>ZrO₂</td>
<td>0.3–6</td>
<td>27 000–15 000</td>
<td>2.15</td>
<td>10 HF and H₂SO₄&lt;sup&gt;d&lt;/sup&gt; Reacts with HF, alkali&lt;sup&gt;c&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td></td>
<td>2.4 and 500 000–2500</td>
<td>1.52</td>
<td>10</td>
<td>K₂Cr₂O₇ , H₂SO₄&lt;sup&gt;d&lt;/sup&gt; Softens at 90°C</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Cutoff range is defined as the frequency range within which the transmittance of a 2 cm thick sample is greater than 0.5. FT-IR spectrometers may be able to work outside this range.

<sup>b</sup> Reacts with.

<sup>c</sup> Ordinary and extraordinary rays.

<sup>d</sup> Long wavelength limit depends on purity.

<sup>e</sup> Trademark of Eastman Kodak Co.

<sup>f</sup> Trademark of Servo Corp of America.

<sup>g</sup> Window material will react with some inorganics (for example, SO₂, HNO₃, Pb(NO₃)₂).

<sup>h</sup> These materials should be stored in the dark when not being used, and should not be placed in contact with metal frames.

<sup>i</sup> Trademark of 3M.

<sup>j</sup> Microporous polytetrafluoroethylene.