



Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis¹

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1. Scope

1.1 This practice covers the spectral range from 4000–50 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 Spectroscopy²
- E 168 Practices for General Techniques of Infrared Quantitative Analysis²
- E 334 Practices for General Techniques of Infrared Microanalysis²
- E 573 Practices for Internal Reflection Spectroscopy²
- E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers²
- E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One²
- E 1642 Practice for General Techniques of Gas Chromatography Infrared (GC/IR) Analysis²

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

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 The boldface numbers in parentheses refer to a list of references at the end of the text.

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*⁴—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 (CCl_4) and carbon disulfide (CS_2) as solvents.

NOTE 1—**Warning:** Both CCl_4 and CS_2 are toxic; keep in a well ventilated hood. Use of these solvents is prohibited in many laboratories. In addition, CS_2 is *extremely* flammable; keep away from ignition sources, even a steam bath. Moreover, CS_2 is reactive (sometimes violently) with primary and secondary aliphatic amines and must not be used as a solvent for these compounds. Similarly, CCl_4 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 CCl_4 is negligible in the region 4000-1330 cm^{-1} and by CS_2 in the region 1330-400 cm^{-1} in cells of about 0.1 mm thickness. (Other solvents can be used.) Solutions are prepared, usually in the 5–10 % 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.

6.5.1.2 A spectrum obtained by the split-solvent technique in cells up to 0.5 to 1.0 mm-thickness, can be compensated for all solvent bands to yield the spectrum of only the sample itself. When a spectrometer that is capable of storing digital data is employed, the desired spectrum is obtained by a computer-assisted subtraction of the stored data for the solvent from the data for the solution. The user should refer to the

⁴ The 3M disposable IR Card is manufactured by 3M Co., Disposable Products Division.

E 1252

TABLE 1 Properties of Window Materials (in order of long-wavelength limit)

Window Material	Chemical Composition	Cutoff Range ^A		Useful Transmission Range		Water Solubility	Refractive Index	at (~μm)	Remarks
		(μm)	(cm ⁻¹)	(μm)	(cm ⁻¹)				
Glass	SiO ₂ ⁺	~2.5	~4000	0.35–2	28 570–5000	insoluble	1.5–1.9		HF, alkali ^B
Quartz (fused)	SiO ₂	~3.5	~2857	0.2–4	50 000–2500	insoluble	1.43	4.5	HF ^B
Silicon Nitrate	Si ₃ N ₄			0.3–4.5	33 000–2200				
Silicon Carbide	SiC			0.6–5	16 600–2000				
Calcite	CaCO ₃			0.2–5	50 000–2000		1.65, 1.5	0.589 ^C	Reacts with acids
Sapphire	Al ₂ O ₃	~5.5	~1818	0.2–5.5	50 000–1818	insoluble	1.77	0.55	Good strength, no cleavage
ALON	9Al ₂ O ₃ ·5AlN			0.2–5.5	50 000–1700		1.8	0.6	
Spinel	MgAl ₂ O ₄			0.2–6	50 000–1600		1.68	0.6	
Strontium Titanate	SrTiO ₃			0.39–6	25 000–1700	insoluble	2.4		HF ^B
Titanium Dioxide	TiO ₂			0.42–6	24 000–1700	insoluble	2.6–2.9		H ₂ SO ₄ and Alkali ^B
Lithium Fluoride	LiF	~6.0	~1667	0.2–7	50 000–1429	slightly	1.39	1.39	Acid ^B
Zirconia	ZrO ₂			0.36–7	27 000–1500	insoluble	2.15		HF and H ₂ SO ₄ ^B
Silicon	Si			1.5–7 and 10–FIR	6600–1430	insoluble	3.4	11.0	Reacts with HF, alkali ^D
Yttria	Y ₂ O ₃			0.25–8	40 000–1250		1.9	0.6	
Yttria (La-doped)	0.09La ₂ O ₃ -0.91Y ₂ O ₃			0.25–8	40 000–1250		1.8	0.6	
IRTRAN I ^E	MgF ₂			2–8	5 000–1 250	slightly	1.3	6.7	HNO ₃ ^B
Magnesium Oxide	MgO			0.4–8	25 000–1300	insoluble	1.6	5	Acid and NH ₄ salts ^B
Fluorite	CaF ₂	~8.0	~1250	0.2–10	50 000–1000	insoluble	1.40	8.0	Amine salt and NH ₄ salts ^B
Strontium Fluoride	SrF ₂			0.13–11	77 000–909	slightly	1.4		
IRTRAN III ^E	CaF ₂			0.2–11	50 000–909	insoluble	1.34	5.0	Polycrystalline, no cleavage
Gallium Phosphide	GaP			0.5–11	20 000–910				
Lead Fluoride	PbF ₂			0.3–12	3450–833		1.7	1	
Servofrax ^F	As ₂ S ₃			1–12	10 000–833	insoluble slightly (hot)	2.59	0.67	Alkali ^B , softens at 195°C
Barium Fluoride	BaF ₂	~11	~909	0.2–13	50 000–769	insoluble	1.45	5.1	
AMTIR	GeAsSe Glass			0.9–14	11 000–725	insoluble	2.5	10	Hard, brittle, attacked by alkali, good ATR material
IRTRAN II ^E	ZnS			1–14	10 000–714	insoluble	2.24	5.5	Insoluble in most solvents
Indium Phosphide	InP			1–14	10 000–725				
Potassium Fluoride	KF			0.16–15	62 500–666	soluble	1.3	0.3	Extremely deliquescent: not recommended for routine use
Rock salt	NaCl	~16	~625	0.2–16	50 000–625	soluble	1.52	4.7	Soluble in glycerine ^G
Cadmium Sulfide	CdS			0.5–16	20 000–625				
Arsenic Triselenide	As ₂ Se ₃			0.8–17	12 500–600	slightly	2.8		Soluble in bases
Gallium Arsenide	GaAs			1–17	10 000–600	insoluble	3.14		Slightly soluble in acids and bases
Germanium	Ge			2–20	5 000–500	insoluble	4.0	13.0	
Sylvite	KCl			0.3–21	33 333–476	soluble	1.49	0.5	Soluble in glycerine ^G
IRTRAN IV ^E	ZnSe			1–21	10 000–476	insoluble	2.5	1.0	Polycrystalline
Sodium Bromide	NaBr			0.2–23	50 000–435	Soluble	1.7	0.35	
Sodium Iodide	NaI			0.25–25	40 000–400	Soluble	1.7	0.5	
Silver Chloride	AgCl	~22	~455	0.6–25	16 667–400	insoluble	2.0	3.8	Soft, darkens in light ^H reacts with metals
Potassium Bromide	KBr	~25	~400	0.2–27	50 000–370	soluble	1.53	8.6	Soluble in alcohol; fogs
Cadmium Telluride	CdTe	~28	~360	0.5–28	20 000–360	insoluble	2.67	10	Acids, HNO ₃ ^B
Thallium Chloride	TlCl			0.4–30	25 000–330	slightly	2.2	0.75	Toxic
KRS-6	Tl ₂ CIBr			0.4–32	25 000–310	slightly	2.0–2.3	0.6–24	Toxic
Silver Bromide	AgBr	~35	~286	2–35	5 000–286	insoluble			Soft, darkens in light ^H , reacts with metals
KRS-5	Tl ₂ Brl	~40	~250	0.7–38	14 286–263	slightly	2.38	4.0	Toxic, soft, soluble in alcohol, HNO ₃ ^B
Cesium Bromide	CsBr	~35	~286	0.3–40	33 333–250	soluble	1.66	8.0	Soft, fogs, soluble alcohols
Potassium Iodide KI				0.15–45	66 600–220				
Thallium Bromide	TlBr			0.45–45	22 000–220	slightly	2.3	0.6–25	Toxic
Cesium Iodide	CsI	~52	~192	0.3–50	33 330–220	soluble	1.74	8.0	
Low-density polyethylene	(CH ₂ CH ₂) _n			20–220	500–45	insoluble	1.52		Very soft, organic liquids penetrate into polymer at ambient temperature
Type 61 ^I	(CH ₂ CH ₂) _n			2–220	5 000–45	insoluble	1.52		Softens at 90°C
Type 62 ^I	(CF ₂ CF ₂) _n ^J			2–220	5 000–45	insoluble	1.52		Useful to 200°C for short durations
Diamond				2-4 and 6-300	4500-2500 and 1667-33	insoluble	2.4	10	K ₂ Cr ₂ O ₇ , H ₂ SO ₄ ^B

^A 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.

^B Reacts with.

^C Ordinary and extraordinary rays.

^D Long wavelength limit depends on purity.

^E Trademark of Eastman Kodak Co.

^F Trademark of Servo Corp of America.

^G Window material will react with some inorganics (for example, SO₂, HNO₃, Pb(NO₃)₂).

^H These materials should be stored in the dark when not being used, and should not be placed in contact with metal frames.

^I Trademark of 3M.

^J Microporous polytetrafluoroethylene.

TABLE 2 Commonly Employed IR Solvents

NOTE 1—Data obtained from IR spectra recorded in the Analytical Laboratories, Instrumental Group, Dow Chemical Company, Midland, MI. It is recommended that the user of these tables record the spectrum for any solvent used in this application, since minor impurities may exhibit total absorption in the region of interest when using relatively long path length cells.

Compound ^A	Structure	Transmission Windows (cm ⁻¹)	Path Length (mm)
carbon tetrachloride	CCl ₄	5000-909, 666-36 ^B	0.1
		5000-1316 (absorption~ 1666-1429)	0.1
		5000-1666, 1499-1299	1.0
		250-36	2.0
perchloroethylene	C ₂ Cl ₄	5000-1042 ^B	0.1
		5000-1408 ^B	1.0
chloroform ^C	CHCl ₃	5000-3125, 2941-1299, 1136-870 ^B	0.1
chloroform-d ₁ ^C	CDCl ₃	5000-3226, 2941-2532, 2222-1587 ^B	1.0
		5000-1000 cm ^{-1B}	0.1
methylene chloride ^C	CH ₂ Cl ₂	5000-3225, 2778-2439, 2000-1538 ^B	1.0
		5000-1449, 1205-854, 625-200 ^B	0.1
methylene chloride-d ₂ ^C	CD ₂ Cl ₂	5000-3225, 2000-1538, 1111-1000, 625-500 ^B	1.0
		5000-2500, 2000-1449, 1333-1177, 625-400 ^B	0.5
bromoform ^C	CHBr ₃	5000-3125, 2941-1250, 1111-800, 500-200	0.1
		5000-3125, 2941-1408, 1111-1000	1.0
carbon disulfide ^D	CS ₂	5000-2350, 2100-1600, 1400-410 ^B	0.1
		5000-2439, 2000-1666,	1.0
		1351-909, 800-704	2.0
		333-278, 238-36	
acetonitrile	CH ₃ CN	5000-3225, 2778-2500, 2000-1587, 1299-1099, 1000-952, 909-787, 714-400 ^B	0.1
		5000-3333, 2000-1666, 1298-1141, 704-400 ^B	1.0
acetonitrile-d ₃	CD ₃ CN	5000-2380, 2000-1250, 800-714, 645-400 ^B	0.1
		5000-3448, 1852-1333, 645-400 ^B	1.0
acetone	(CH ₃) ₂ CO	3448-3125, 2703-1852, 1053-952, 885-813, 746-588 ^B	0.1
		3448-3225, 870-813, 746-606, 357-200 ^B	1.0
dimethyl sulfoxide	(CH ₃) ₂ SO ^E	5000-3333, 2703-1539, 1266-1149, 870-769, 645-200 ^B	0.1
		5000-2381, 1961-1190, 606-400	0.1
dimethyl-d ₆ sulfoxide 1,4-dioxane	(CD ₃) ₂ SO ^E O(CH ₂ -CH ₂) ₂ O	5000-3125, 2632-2040, 1923-1539, 800-666, 588-385	0.2
		5000-3846, 2857-1754, 1492-1000	0.025
water	H ₂ O	5000-2778, 2000-1299	0.07
heavy water	D ₂ O		

^A Recommended handling and storage is in ventilated hood for these organic solvents.

^B Some bands may be present, but their absorption is readily compensated by placing solvent in a variable path length cell in the reference beam, or by spectral subtraction using computer techniques for full-range utility in the ranges given.

^C These compounds decompose and are often stabilized with a small amount of a compound such as ethanol. These compounds will react with amines.

^D Carbon disulfide will react with primary and secondary amines, sometimes violently. It is highly flammable and toxic.

^E Picks up H₂O from the atmosphere if not well capped.

<https://standards.iteh.ai/catalog/standards/sist/3c1ecb99-476e-41ec-ae5a-e2cc5407ee55/astm-e1252-98>

manufacturer's manual for each instrumental system to perform the computer-assisted manipulation of the spectral data necessary for hard copy presentation. Spectra from both CCl₄ and CS₂ solutions can be presented on the same hard copy over the region 4000-400 cm⁻¹, or the presentation can be over the 4000-1330 cm⁻¹ region for the CCl₄ solution and over the 1330-400 cm⁻¹ region for the CS₂ solution. The former choice is preferable because both band frequencies and band intensities are affected differently by the different solvents (due to solvent-solute interaction).

6.5.1.3 Split solution spectra are acceptable without solvent compensation, but recognition of the solvent bands that are present is mandatory when such spectra are compared with those recorded, either with solvent compensation or with computer-assisted solvent subtraction. The IR spectrum of a solution over the entire 4000-400 cm⁻¹ region can be useful, but it is not recommended for solutions of unknown materials because pertinent spectral data may be masked by solvent absorption. It is not possible to compensate fully absorbing bands such as CS₂ (~1400 to 1600 cm⁻¹), CCl₄ (~730 to 800 cm⁻¹), and CHCl₃ (about 790 to 725 cm⁻¹) when using a 0.1-mm path length.

NOTE 3—Attempted compensation of such totally absorbing bands can obscure sample bands.

6.5.1.4 Often the same IR spectrum can be recorded using 1 % solutions in 1.0-mm sealed cells as with 10 % solutions in 0.1-mm cells. Interferences from the solvents, however, are larger with 1-mm cells (see Table 2). In cases where there is strong intermolecular association, such as intermolecular hydrogen bonding between solute molecules, the resulting IR spectra obtained with 1 % solutions will be different from the ones obtained with the 10 % solutions, because of the different concentration of unassociated solute molecules, and in the different concentrations of intermolecularly hydrogen bonded dimeric, trimeric, tetrameric, etc., solute molecules.

6.5.1.5 A distinct advantage is gained by recording IR spectra under a set of standard conditions, such as 5-10 % solutions in a 0.1-mm path length sealed cell. This practice allows approximate quantitative analyses to be readily performed at a future date on samples where the utmost accuracy is not required. Moreover, for qualitative analyses, the spectra recorded will have comparable band intensities, assuming that identical concentrations and path lengths are employed and that the instrumental parameter settings are identical.

6.5.1.6 Spectra that are to be used for computer searches should be measured carefully. The search algorithms typically normalize the strongest spectral feature to an arbitrary absorbance level. Because of this, the spectrum of the solute should be measured using a concentration/path length combination that results in the strongest solute band having an absorption that does not exceed an absorbance of 1.0.

6.5.2 *Analysis of Materials Soluble in Volatile Organic Solvents: Use of Disposable IR Cards*—Many solid samples are soluble in volatile organic solvents which easily wet the sample application area of an IR transparent window or a disposable IR card. Any solvent may be utilized that totally dissolves the component(s) of interest, is volatile enough to quickly evaporate after sample application, is not reactive with the sample, and does not react with the sample application area.

NOTE 4—A spectrum obtained using the disposable IR Card⁴ can be compensated for the polymer bands to yield the spectrum of only the sample. When a spectrometer that is capable of storing digital data is employed, the desired spectrum is obtained by a computer-assisted subtraction of the stored data for the blank sample card from the data for the applied sample. The user should refer to the manufacturer's manual for each instrumental system to perform the computer-assisted manipulation of the spectral data necessary for hard copy presentation.

6.5.2.1 A solution of the sample in appropriate solvent is prepared usually in the 10 % or greater weight/volume range, and is shaken to ensure uniform solution. A drop of the solution is applied to the center of the sample application area using a clean pipette, or syringe. If necessary, the sample can be spread out on the substrate surface using the blunt applicator tip such as from an disposable pipette. The solvent(s) used for sample dissolution are allowed to evaporate, leaving a deposit of the solid or liquid sample on the sample application area. In many cases, the solvents used will evaporate quickly. If evaporation time needs to be reduced, a gentle stream of clean dry air or nitrogen can be blown across the surface or the card can be heated gently in an oven or with an infrared heat lamp for very short duration.

6.5.3 *Analysis of Aqueous Solutions: Internal Reflection Cells*—Water is not generally recommended as an infrared solvent because it is strongly absorbing throughout most of the useful mid-IR region and because it attacks many of the window materials commonly used in transmission cells. When aqueous solutions are the most convenient form to handle particular materials, however, internal reflection cells with a short enough effective pathlength to permit recording of spectra from the near infrared to about 850 cm^{-1} (except between about 3800 and 2900 cm^{-1} and between about 1700 and 1600 cm^{-1}) can be used. These cells are commonly cylindrical or rectangular. The water background can be subtracted in FT-IR and computer-assisted dispersive instruments. The spectrum of the solute obtained by this method will usually be quite different from the spectrum of the dry solute so that a library of aqueous solution spectra is ordinarily required for the identification materials dissolved in water.

6.5.4 *Analysis of Water-Containing Solutions: Disposable IR Card*—This technique would be appropriate for samples such as latexes, mayonnaise, and other colloidal or emulsion type samples. For many such samples there is also an organic modifier present, such as a surfactant or organic liquid, which

facilitates wetting of the sample application area. In these cases a drop of the sample is applied to the sample application area as in 6.5.2.1, or it is smeared on as in 6.4.

7. Analysis of Solids

7.1 *High-Pressure Diamond Anvil Cells*—Samples can often be run in a high-pressure diamond anvil cell in accordance with Practices E 334.

7.2 Alkali Halide Pressed Pellet Technique:

7.2.1 This technique involves grinding a solid sample, mixing it with an alkali halide powder, and pressing the resulting mixture into a pellet or disk. Scattering of IR radiation is reduced by having the sample particles embedded in a matrix of comparable refractive index. Alkali halides are used because they have properties of cold flow and absence of absorption in a wide spectral region. KBr is the most commonly used, but KCl and CsI are also used for better matching of refractive index, extended spectral range, or to avoid ion exchange with another halide salt sample. The pellet technique is applicable to many organic materials, but there are limitations associated with several chemical types of materials. Amine salts, carboxylic acid salts, and some inorganic compounds may react with alkali halides and produce a spectrum that does not represent the original sample.

7.2.2 Because the spectrum obtained depends on particle size, it is important to prepare both sample and reference materials in the same manner in order to ensure that the particle size distributions are reproduced. It should also be noted that the crystal structure of a compound may be changed by grinding or by the high pressure exerted in forming the pellet, causing an alteration of the IR spectrum.

7.2.3 Both the sample and the alkali halide powder must be dry in order to produce a clear pellet. Usually, the ratio of the quantities of sample to KBr powder should be the range from 1/50 to 1/1000, depending on the type of sample. The solid sample is ground using a mortar and pestle or a mechanical vibrating mill until the particle size is smaller than the wavelength of the IR radiation (for example, $<2 \mu\text{m}$) to minimize the scattering of IR radiation. The mortar and pestle should be made of agate, alumina, or boron carbide to avoid contamination of the sample during grinding. Adequate grinding will usually produce a glossy layer adhering to the mortar. The KBr (or other alkali halide) is added and thoroughly mixed with the sample. The KBr sample mixture is then placed in a special die and compressed to a small disk with a thickness of about 1 mm. The amount of force applied depends on the diameter of the die. The best pellets are formed by evacuating the die filled with the KBr sample mixture before applying pressure. This process minimizes the amount of water in the pressed pellet.

7.2.4 For routine qualitative analysis of many compounds, adequate grinding and mixing can be realized by grinding the KBr-sample mixture in a vibrating mill for 30 to 60 s.

7.2.5 Alkali halide powder may be used as a gentle abrasive to collect samples of surface layers of materials such as paint. Pellets made from these powders have been used to study environmental exposure of surface finishes, and for forensic comparison of automotive finishes.

7.2.6 A miniature press is often employed to press pellets as

small as 0.5-mm diameter. The quality of the spectrum obtained is improved by placing the small pellet in a beam condenser in the IR spectrometer sample compartment. This results in an additional focusing of the IR beam, usually by a factor of 4 to 6 in the linear dimension.

7.3 Polymer Matrix Technique—Powdered low-density polyethylene can be used as the matrix material in the region 500-50 cm^{-1} . Because absorption bands in the far IR usually have low intensity, a relatively high sample-to-polyethylene powder ratio is required. The well-dispersed sample-polyethylene mixture is placed in a die and heated to 90°C. This results in a pressed film with evenly dispersed sample. This procedure is applicable only to compounds that are stable at 90°C.

7.4 Mull Technique:

7.4.1 This technique involves grinding a solid sample with a small amount of a liquid known as a mulling agent. Fluorocarbon oil is used for the region 4000-1300 cm^{-1} and mineral oil is used for the region 1300-50 cm^{-1} . Split mulls using both liquids are necessary to obtain an optimal complete spectrum. Qualitative spectra can be obtained using only one of the mulling agents (usually mineral oil), provided that absorption by the mulling agent used does not mask spectral regions of analytical importance.

7.4.2 Approximately 3 to 10 mg of sample is placed in an agate, alumina, or boron carbide mortar, ground to a particle size less than 2- μm diameter, and spread uniformly over the surface of the mortar. At this stage, the sample should have a glossy appearance. One to a few drops of the mulling fluid is added, and vigorous grinding is continued until all the particles are suspended in the mulling agent and the mixture is a paste of creamy consistency. This paste is then transferred with a

clean rubber policeman onto a flat NaCl, KBr, or other plate (disposable IR cards are useful for the mid-IR to far IR, while low-density polyethylene (LDPE) windows are useful below 200 cm^{-1}) and spread uniformly across the middle section of the plate. A second flat plate is used to squeeze the paste into a thin film by gently rotating the top plate, with the exception that IR cards and LDPE windows do not require this step. At this point, a properly prepared mull should be reasonably transparent to visible light (a frosty or cloudy appearance means that further grinding is needed).

7.4.3 For split mulls, two mortars and pestles are useful for working with the two mulling agents. The difficult part of this process is adjusting the mull film thicknesses so that the band absorbances in both spectral regions yield true relative values. This is accomplished by selecting a sample band that is free from interference in both mulling fluids and in adjusting the film thicknesses so that the absorbances of this band are essentially identical in the spectra of the two mulls. The adjustment of film thicknesses is simplified by the use of an instrument (FT-IR or dispersive), capable of storing digital data and thus enabling the adjustment to be made by computer-assisted calculations based on a sample band that is free from interference. The user should refer to the manufacturer's manual in order to perform the calculations for each type of system employed.

7.4.4 Another technique that has been used to prepare high-quality mulls is to grind the sample and mulling agent with a grinder having two motor-driven rotating ground-glass plates. This method is useful for preparing mulls of many organic materials. It is not recommended for hard materials, since glass may be introduced into the sample as a contaminant. Grinding may also be done manually with large diameter ground glass joints.

7.5 Specular Reflection Spectroscopy—A flat surface will allow an incident beam to be reflected off the surface at an angle of reflection equal to the angle of incidence. The reflectance spectrum measured includes information on the absorbing properties of the material, and often appears to be highly distorted. Application of the Kramers-Kronig transformation to the observed spectrum can be used to extract the normal absorption spectrum from this information (see Practice E 334).

7.6 Diffuse Reflection Spectroscopy:

7.6.1 When used in conjunction with a Fourier Transform infrared spectrometer, this technique is commonly referred to as DRIFT (Diffuse Reflection Infrared Fourier Transform) spectroscopy. It has gained wide acceptance for analysis of a range of materials, due to its simplicity and ease of sample preparation. It is also preferred for samples that strongly reflect or scatter infrared energy.

7.6.2 This technique is generally applicable to solid samples that are ground (as in the preparation of an alkali halide pellet or a mull) and then mixed with KBr, KCl powder, or other optical transparent powdered materials, or combination thereof. Spectra below 400 cm^{-1} can be obtained using polyethylene powder. The mixture is loaded into a sample cup that is then placed in a diffuse reflectance accessory. The resulting spectra can differ significantly from those obtained by

TABLE 3 Mulling Agents

NOTE 1—For the least amount of absorption from the mulling agent use Nujol[®] in the region of approximately 1350-400 cm^{-1} and Fluorolube[®] in the region 4000-1350 cm^{-1} . It is recommended that IR reference spectra be recorded of the mulling agents used in your laboratory.

Mulling Agents	Maximum Peaks of Absorption~ cm^{-1}	
Mineral Oil (Nujol ^A)	2952	
	2921	
	2869	
	2952	
	1460	
	1378	
	721	
	Fluorocarbon Oil (Fluorolube ^B)	1275
		1230
		1196
1141		
1121		
1094		
1034		
961		
896		
830		
735		
650		
594		
543		
519		

^A Trademark.

^B Trademark.