Designation: E1252 – 98 (Reapproved 2013)$^{\varepsilon 1}$

Standard Practice for
General Techniques for Obtaining Infrared Spectra for Qualitative Analysis[1]

This standard is issued under the fixed designation E1252; 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.

ε^1 NOTE—Warning statements were editorially corrected in January 2013.

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

1.3 *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:*[2]

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E334 Practice for General Techniques of Infrared Microanalysis

E573 Practices for Internal Reflection Spectroscopy

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

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

E1642 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 E131.

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

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[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is 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.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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 E573. 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 E573 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. (**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 to 1330 cm^{-1} and by CS_2 in the region 1330 to 400 cm^{-1} in cells of about 0.1 mm thickness. (Other solvents can be used.)

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

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	Remarks
		(μm)	(cm^{-1})	(μm)	(cm^{-1})			($\sim$μm)	
Glass	SiO_2+	$\sim$2.5	$\sim$4000	0.35–2	28 570–5000	insoluble	1.5–1.9		HF, alkali[B]
Quartz (fused)	SiO_2	$\sim$3.5	$\sim$2857	0.2–4	50 000–2500	insoluble	1.43	4.5	HF[B]
SIlicon Nitrate	Si_3N_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_2O_3	$\sim$5.5	$\sim$1818	0.2–5.5	50 000–1818	insoluble	1.77	0.55	Good strength, no cleavage
ALON	$9Al_2O_3$.5AlN			0.2–5.5	50 000–1700		1.8	0.6	
Spinel	$MgAl_2O_4$			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_2SO_4 and Alkali[B]
Lithium Fluoride	LiF	$\sim$6.0	$\sim$1667	0.2–7	50 000–1429	slightly	1.39	1.39	Acid[B]
Zirconia	ZrO_2			0.36–7	27 000–1500	insoluable	2.15		HF and H_2SO_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			0.25–8	40 000–1250		1.9	0.6	
Yttria (La-doped)	$0.09La_2O_3$-$0.91Y_2O_3$			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	$\sim$8.0	$\sim$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	GaP			0.5–11	20 000–910				
Lead Fluoride	PbF_2			0.3–12	3450–833		1.7	1	
Servofrax[F]	As_2S_3			1–12	10 000–833	insoluble slightly (hot)	2.59	0.67	Alkali[B] , softens at 195°C
Barium Fluoride	BaF_2	$\sim$11	$\sim$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 Floride	KF			0.16–15	62 500–666	soluble	1.3	0.3	Extremely deliquescent: not recommended for routine use
Rock salt	NaCl	$\sim$16	$\sim$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_2Se_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 soluable 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	$\sim$22	$\sim$455	0.6–25	16 6667–400	insoluble	2.0	3.8	Soft, darkens in light[H] reacts with metals
Potassium Bromide	KBr	$\sim$25	$\sim$400	0.2–27	50 000–370	soluble	1.53	8.6	Soluble in alcohol; fogs
Cadmium Telluride	CdTe	$\sim$28	$\sim$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_2ClBr			0.4–32	25 000–310	slightly	2.0–2.3	0.6–24	Toxic
Silver Bromide	AgBr	$\sim$35	$\sim$286	2–35	5 000–286	insoluble			Soft, darkens in light[H] , reacts with metals
KRS-5	Tl2BrI	$\sim$40	$\sim$250	0.7–38	14 286–263	slightly	2.38	4.0	Toxic, soft, soluble in alcohol, HNO_3[B]
Cesium Bromide	CsBr	$\sim$35	$\sim$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	$\sim$52	$\sim$192	0.3–50	33 330–220	soluble	1.74	8.0	
Low-density polyethylene	$(CH_2CH_2)n$			20–220	500–45	insoluble	1.52		Very soft, organic liquids penetrate into polymer at ambient temperature
Type 61[I]	$(CH_2CH_2)n$			2–220	5 000–45	insoluble	1.52		Softens at 90°C
Type 62[I]	$(CF_2CF_2)n$[J]			2–220	5 000–45	insoluble	1.52		Useful to 200°C for short durations
Diamond	[J]			2-4 and 6-300	4500-2500 and 1667-33	insoluble	2.4	10	K_2Cr_2O7 , H_2SO_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, SO_2, HNO_3, $Pb(NO_3)_2$).

[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_2Cl_4	5000-1042^B	0.1
		5000-1408^B	1.0
chloroform^C	$CHCl_3$	5000-3125, 2941-1299, 1136-870^B	0.1
		5000-3226, 2941-2532, 2222-1587^B	1.0
chloroform-d$_1$^{C}	$CDCl_3$	5000-1000 cm^{-1B}	0.1
		5000-3225, 2778-2439, 2000-1538^B	1.0
methylene chloride^C	CH_2Cl_2	5000-1449, 1205-854, 625-200^B	0.1
		5000-3225, 2000-1538, 1111-1000, 625-500^B	1.0
methylene chloride-d$_2$ ^{C}	CD_2Cl_2	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_3CN	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_3CN	5000-2380, 2000-1250, 800-714, 645-400^B	0.1
		5000-3448, 1852-1333, 645-400^B	1.0
acetone	$(CH_3)_2CO$	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	$(CH_3)_2SO^E$	5000-3333, 2703-1539, 1266-1149, 870-769, 645-200^B	0.1
dimethyl-d$_6$ sulfoxide 1,4-dioxane	$(CD_3)_2$ SO^E $O(CH_2$-$CH_2)_2O$	5000-2381, 1961-1190, 606-400	0.1
		5000-3125, 2632-2040, 1923-1539, 800-666, 588-385	0.2
water	H_2O	5000-3846, 2857-1754, 1492-1000	0.025
heavy water	D_2O	5000-2778, 2000-1299	0.07

[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 H_2O from the atmosphere if not well capped.

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 1—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 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 CCl_4 and CS_2 solutions can be presented on the same hard copy over the region 4000 to 400 cm^{-1} , or the presentation can be over the 4000 to 1330 cm^{-1} region for the CCl_4 solution and over the 1330 to 400 cm^{-1} region for the CS_2 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 to 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 CS_2 (|~ 1400 to 1600 cm^{-1}), CCl_4 (| ~730 to 800 cm^{-1}), and $CHCl_3$ (about 790 to 725 cm^{-1}) when using a 0.1-mm path length.

NOTE 2—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 to 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 3—A spectrum obtained using the disposable IR Card[4] 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 Practice E334.

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 µm) 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 to 1300 cm^{-1} and mineral oil is used for the region 1300 to 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).

TABLE 3 Mulling Agents

NOTE 1—For the least amount of absorption from the mulling agent use Nujol™ in the region of approximately 1350 to 400 cm^{-1} and Fluorolube™ in the region 4000 to 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] Formerly trademarked by Stanco Incorporated, New York, NY, expired 1996.

[B] Trademark by Gabriel Performance Products, LLC, in Baton Rouge, LA.

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 E334).

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 transmission spectroscopy. For details and applications, see (**17-29**).

7.6.3 Another method utilized to obtain solid samples for use in DRIFT spectroscopy relies on an abrasive pad sampler, made of silicon carbide, diamond, or other hard substance. These disposable sample holders, available from a number of sources, offer a simple means of sampling hard inorganics (for example, minerals) and organics (for example, thermoset resins).

7.7 *Reflection-Absorption Spectroscopy*—This technique is used to obtain absorption spectra of insoluble coatings on reflecting substrates, such as smooth metallic surfaces. Spectra of coatings as thin as 1 µm can be obtained using a spectral reflectance attachment. (For details and applications, see (**30-33**).)

7.8 *Total Reflectance*—Accessories are available that can measure both diffuse and specular components of the infrared reflectance spectrum. One special type of accessory is an integrating sphere, which captures reflected energy from all angles, and often incorporates a purpose-built detector having a large surface area. Under certain conditions, the specular component of the reflected energy can be reduced or even removed before the energy reaches the detector. This type of accessory if useful for measuring the total reflected energy from a sample, for examining samples (such as fabrics) that are not easily handled in any traditional manner.

7.9 *Internal Reflection Spectroscopy*—Bulk samples, including polymer films and liquids, can be analyzed by this technique if the surface is representative of the sample interior. For further information, see Practices E573. In the case of materials with hard surfaces where it may be difficult to get good contact between the internal reflection element (IRE) and the sample using the IRS technique, it is possible to improve the surface contact by warming both the IRE and the material while in contact under pressure. However, this technique will often ruin the IRE.

8. Analysis of Vapor-Phase Samples

8.1 *Use of Simple Gas Cells:*

8.1.1 Samples that are gases at ambient conditions of temperature and pressure, or even liquids that have a vapor pressure as low as 0.1 torr (~13 Pa) at ambient temperature, are readily examined by IR. A spectrum satisfactory for routine qualitative identification can be recorded of most gases by purging, in a hood, a small-volume cell (one having, for example, 1 3-mm pathlength) with the sample gas to flush out the air. The stopcocks are then closed. Longer pathlengths can be used if the goal is to identify impurities in the gaseous sample.

8.1.2 A 5 or 10-cm glass cell equipped with windows of KBr, CsI, or other suitable material, is frequently used to record vapor-phase IR spectra. Several pressures may be employed so that the shapes of both weak and strong bands can be observed. Band shapes and intensities in gas phase spectra vary with both the total pressure and with the nature of the diluent. It is a useful procedure, therefore, to obtain gas spectra adjusted to some constant dilution with an inert IR transparent gas, such as nitrogen, for example, to a total pressure 600 torr. This aspect is particularly important if quantitative analyses are contemplated. Moreover, infrared spectra of strongly intermolecular hydrogen bonded molecules, such as carboxylic acids (monomer-dimer) are especially affected by both pressure and temperature.

8.1.3 Certain gases such as NO_2 or SO_2 react with the alkali halide windows, causing the formation of ionic species on the window surface. In this case, ZnSe or another substance which is not attacked by SO_2 or NO_2 , should be used as window material if the artifact-bands interfere excessively with the sample spectrum.

8.1.4 A 10-cm glass cell equipped with high-density polyethylene windows several millimetres thick can be used to record vapor-phase IR spectra in the region 500 to 50 cm^{-1} and below.

8.2 *Use of Multipass Gas Cells:*

8.2.1 Long path length cells are required in order to record IR spectra of chemicals with low vapor pressure at ambient temperatures. The same type of cell is employed in order to detect parts per million (ppm) levels of contaminants (impurities) in air or other gas. In the latter case, the H_2O and CO_2 present in air can be compensated by placing a comparable cell filled with ordinary air in the reference beam with the appropriate path length setting. For instruments capable of storing digital spectra, the same cell can be used to obtain the reference air spectrum, and then this spectrum can be subtracted from the sample spectrum. The usual path length employed in trace analyses is ~20 m. A comparable path length setting is required for chemicals with low vapor-pressure at ambient temperatures.

8.2.2 A disadvantage of utilizing multipass cells is that the optics are in contact with the sample, and this can cause even the gold-coated mirrors to deteriorate. Another disadvantage is that certain samples adhere to the large cell surface area, causing a built-in memory when a different sample is introduced into the cell. Extensive flushing with dry air or dry nitrogen with repeated cell evacuation is often necessary to clean out the cell. Gentle heating with a heat lamp may also aid in reducing memory effects. In addition, the cell windows often become coated with materials used to seal the cell window. Ignoring these factors will result in obtaining IR spectra of the sample plus contaminants from previous runs.

8.3 *Use of Heated Gas Cells:*

8.3.1 Vapor-phase IR spectra of solids and high boiling liquids can be examined at an elevated temperature (200°C and above), using a relatively short path length vapor cell (0.1 to 0.75 m). The IR spectra recorded in this manner are especially useful in the identification of GC-IR fractions of unknown materials, since most GC-IR spectra are conveniently recorded at high temperatures (see Practices E1642).

8.3.2 Recording IR spectra at high temperature, employing a dispersive instrument, requires that the IR radiation from the source be chopped ahead of the sample to avoid recording IR radiation emitted from the hot sample. Unless using very high temperatures, this is not usually a problem when employing an FT-IR spectrometer, provided that the sample is held between the interferometer (which is a wavenumber-selective chopper) and the detector.

9. Analysis of Polymers

NOTE 4—See Refs **(8)** and **(34)** for general methods of IR analysis of polymers. See Refs **(10-14)** for compilations of polymer spectra.

9.1 *Polymers Soluble in Water:*

9.1.1 Film forming polymers which are soluble in water are readily examined in the region 4000-400 cm^{-1} as cast films on flat silver bromide (AgBr) plates (see Table 1 for other window materials). In order to cast a film with a uniform thickness of ∼0.01 mm, a suitably dilute water solution of the polymer is prepared. Silver bromide is less sensitive to strong visible or ultraviolet light than silver chloride (AgCl), but it will darken with time. The plates, therefore, should be stored in the dark when not in use. Only clear transparent AgBr plates should be used for these measurements. Moreover, flat AgBr or AgCl plates should be 2 mm thick in order to eliminate interference fringes. The plates are readily cleaned by redissolving the cast film in water.

9.1.2 Films of water-soluble polymers cast on glass are readily examined by peeling off the film from the glass. Water soluble polymers that do not form good films may be examined using the alkali halide pellet technique (7.2.1).

9.1.3 Also see Practices E573 for details of the internal reflection spectroscopy (IRS) technique.

9.2 *Polymers Soluble in Organic Solvents*—A variety of solvents such as 1,2-dichlorobenzene, toluene, methyl ethyl ketone, dimethylformamide, tetrahydrofuran (Note 3) can be used to cast polymeric films on an alkali halide plate. The solvent is removed by heating in a nitrogen atmosphere using an IR heat lamp or in an evacuated oven. The ideal cast uniform film is ∼0.01 to 0.05 mm thick and has no spectral evidence of solvent. In most cases, solutions of the polymer can be obtained only by heating; this necessitates preheating the KBr or NaCl plate before the polymer solution is applied to prevent fracturing the plate. A CsI plate allows a wider frequency range to be recorded, and it is not as sensitive to thermal shock. Table 4 gives a list of solvents used to dissolve different classes of polymers. Films can also be cast from an organic solvent on an internal reflection element (IRE) and qualitative spectra recorded using the IRS technique. Further, for those materials soluble in solvents which may easily be volatilized at temperatures below 75°C, the disposable IR card method described in 6.5.4 may be used.

TABLE 4 Solvents Used in Casting Polymer Films

Class	Generic Name	Solvents[A]
Acetate Resins	Polyformaldehyde	1,2-dichlorobenzene
Acrylics	ABS terpolymer	1,2-dichlorobenzene
	Acrylic acid-ethylene copolymer	1,2-dichlorobenzene
	Acrylonitrile-butadiene copolymer	1,2-dichlorobenzene
	Polyacrylamide	water
	Polyethylacrylate	1,2-dichlorobenzene
	Ethylacrylate	1,2-dichlorobenzene
	Ethylacrylate-ethylene copolymer	1,2-dichlorobenzene
	Polymethylacrylate	1,2-dichlorobenzene
	Polymethylmethacrylate	acetone
	Methylmethacrylate-styrene copolymer	1,2-dichlorobenzene
	Polyacrylonitrile	dimethyl sulfoxide or dimethylformamide
	Polymethacrylamide	water
	Polysodium acrylate	water
Amino Resins	Melamine-formaldehyde	[B]
	Urea-formaldehyde	[B]
Cellulosics	Cellulose acetate	acetone
	Cellulose acetate butyrate	1,2-dichlorobenzene or acetone
	Cellulose nitrate	acetone
	Cellulose propionate	acetone
	Ethyl cellulose	ethylene dichloride
	Hydroxyethyl cellulose	water
	Methyl cellulose	water
	Sodium carboxymethyl cellulose	water
Coumarone and Terpene Resins	Coumarone-indene resin polyterpene	1,2-dichlorobenzene 1,2-dichlorobenzene
Epoxies	Polymers based on the diglycidyl ether of bisphenol-A (cured)	[B]

TABLE 4 *Continued*

Class	Generic Name	Solvents[A]
	(uncured)	1,2-dichlorobenzene
	Epoxylated phenolformaldehyde	acetone
Ethylene	Polyethylene	1,2-dichlorobenzene
Polymers	Ethylene-propylene copolymer	1,2-dichlorobenzene
	Polyethylene oxide[C]	acetone or CCl_4 or[B]
Fluorocarbons	Polytetrafluoroethylene	[B]
	Polyvinylfluoride	dimethylformamide
Furane Resins	Furfuraldehyde-phenol resins	methylene chloride or methanol
Isoprene	Polyisoprene	toluene or 1,2-dichlorobenzene
Natural Resins	Accroides	acetone
	Asphalt	methylene chloride
	Copals-fused congo	1,2-dichlorobenzene
	Copals-gum congo	dimethylformamide
	Copals-kauri	1,2-dichlorobenzene
	Copals-manilas	dimethylformamide
	East indias-batu	1,2-dichlorobenzene
	East indias-pale	1,2-dichlorobenzene
	Elemi	1,2-dichlorobenzene
	Shellac	dimethylformamide
	Vinol	acetone
Nylons	Nylon 6	dimethylformamide
	Nylon 6/10	dimethylformamide
	Nylon 7	dimethylformamide
	Nylon 11	dimethylformamide
Phenolics	Phenol-formaldehyde	tetrahydrofuran
	Resorcinol-formaldehyde	tetrahydrofuran
Polycarbonates	Bis-phenol A carbonate polymer	methylene chloride tetrahydrofuran 1,2-dichlorobenzene
Polyesters	Polyethyleneterephthalate	1,2-dichlorobenzene
Polybutylene	Polyisobutylene	1,2-dichlorobenzene
Propylene Polymers	Polypropylene	1,2-dichlorobenzene
	Polypropylene oxide	1,2-dichlorobenzene
Protein	Casein	[B]
Plastics	Zein	[B]
Styrene Polymers	Polystyrene	1,2-dichlorobenzene
	Most styrene copolymers	1,2-dichlorobenzene
Polysulfones		tetrahydrofuran
Polyurethanes	Cured	Hot DMSO[B]
	Uncured	tetrahydrofuran DMSO dimethylformamide
Thiokol	Alkyl sulfide, disulfide alkyl ether copolymers	1,2-dichlorobenzene
Vinyl Polymers	Polyvinyl acetal	1,2-dichlorobenzene
	Polyvinyl acetate	acetone
	Polyvinyl alcohol	water
	Polyvinyl alcohol-acetate	water
	Polyvinyl ethyl ether	1,2-dichlorobenzene
	Polyvinyl butyral	dimethylformamide
	Polyvinyl chloride	1,2-dichlorobenzene
	Polyvinyl chloride-acetate	1,2-dichlorobenzene
	Polyvinyl chloride-methyl acrylate copolymer	1,2-dichlorobenzene
	Polyvinyl formal	acetone or ethylene dichloride
	Polyvinyl propionate	1,2-dichlorobenzene
	Polyvinyl pyrolidone	water
	Poly N-vinyl carbazole	dimethylformamide
	Polyvinyl cyclohexane	1,2-dichlorobenzene
Vinylidene Copolymers	Vinylidene chloride-acrylonitrile	1,2-dichlorobenzene dimethylformamide
	Vinylidene chloride-butyl acrylate copolymer	1,2-dichlorobenzene
	Vinylidene chloride-ethyl acrylate copolymer	1,2-dichlorobenzene
	Vinylidene chloride-vinyl chloride copolymer	1,2-dichlorobenzene
Xylene	Poly-p-xylene	1,2-dichlorobenzene

[A] Other similar type solvents may be used.
[B] For heavily crosslinked or insoluble polyurethane, run as pellets on split mulls or as a film if soluble in DMSO.
[C] Solubility depends upon molecular weight.

NOTE 5—Tetrahydrofuran (THF) is used to dissolve certain classes of polymers. It is mandatory that either fresh or inhibited THF be employed. Fresh THF slowly forms peroxides after the bottle has been opened. Violent explosions can occur when THF containing THF peroxide is heated to dissolve the sample. Inhibited THF will exhibit absorption from the inhibitor in the cast polymer film.

9.3 *Latex Suspensions (in Water)*—Suitable films can be prepared from latex suspensions (in water) by casting a thin film (~0.01 mm) on glass, drying, and then removing the dried film from the glass and stretching it over a rigid frame. Even though these materials are not water soluble, the method presented in 9.1 for water-soluble polymers is often used as an alternate method for casting a thin film on a AgBr or AgCl plate. (See 9.5.2 for methods to eliminate interference fringes.)

9.4 *Insoluble Cross-Linked Polymers*—Insoluble cross-linked polymers that cannot be pressed into a thin film can be examined by the KBr pressed pellet or the split mull technique.

Some rubbery polymers can be ground by cooling the polymer with liquid nitrogen or solid carbon dioxide. Other techniques that may be applicable are IRS (see Practices E573), PAS (see 11.2), diffuse reflection, and pyrolysis (see 11.3).

9.5 *Hot-Pressed or Rolled Polymeric Films:*

9.5.1 Hot-pressed films are prepared by placing the polymer between sheets of aluminum foil and pressing at a temperature above the softening point. Hot-pressed or rolled films can be examined by mounting the film flat over a rigid frame. Such films often give rise to interference fringes superimposed on the spectrum of the polymer. Because the spacing of these fringes depends on the thickness and refractive index of the film, this spacing can be used to determine the film thickness if the refractive index is known. When the fringes complicate the interpretation of the polymer spectrum, they can often be reduced or eliminated by roughening the surface of the film; however, this results in some scattering of the IR radiation. Another method is to coat the film surface with a thin layer of mineral oil or fluorocarbon oil, depending on the frequency range of interest (**35**). Another method is to place the film at Brewster's angle to the radiation beam using parallel polarization (**5**).

9.5.2 Interference fringes can be also removed from spectra recorded using FT-IR by modification of the raw interferogram (**36**). Fringes arise from the presence of a weak secondary (and sometimes higher order) centerburst, superimposed on the interferogram. Removal of this extraneous centerburst by generating a straight line in this region of the interferogram results in removal or reduction of the fringes from the spectrum, but at the cost of generating a few weak extraneous features in the spectrum.

10. Analysis of Other Types of Materials

10.1 *Materials Soluble in Water:*

10.1.1 Substances dissolved in water can sometimes be identified directly by obtaining the spectrum of a film of the water solution between AgCl or AgBr plates or in a fixed path length cell with CaF_2 or BaF_2 windows. Absorption by water, however, masks much of the useful region of the infrared spectrum, and separation of the solute may be necessary.

10.1.2 *Use of IRS*—The absorption spectra of aqueous solutions can be obtained by the use of IRS (see 7.9).

10.1.3 *Nonvolatile Solutes*—The water solution is evaporated to dryness, and the residue is examined using the pressed pellet (see 7.2) or the split mull (see 7.3) technique. Inorganic compounds identified using this technique are usually carbonates, phosphates, or sulfates. Nonvolatile organics soluble in CCl_4 and CS_2 are then examined using the method in 6.5.1.

10.1.4 *Extractable Materials*—One method of identifying materials dissolved in water is the extraction of a suitable volume of solution with appropriate solvent (10 mL of solution to 1 mL of extractant). The nonaqueous (bottom) layer is separated and salted with NaCl powder to remove water. The solution is then placed in a 0.1 or 10-mm KBr sealed cell or applied to a disposable IR card as described in 6.2.

10.2 *Gas Chromatographic Effluents—On-Line Method (GC/FT-IR)*—The use of a Fourier transform spectrometer makes possible the obtaining of the vapor-phase absorption spectra of substances as they are being eluted from a gas chromatograph. See Practice E1421 for details of this technique.

10.3 *Liquid Chromatographic Eluents (LC/IR)*—The eluent stream from a liquid chromatograh can be analyzed using infrared spectroscopy. See Practice E334 for experimental techniques.

11. Special Types of Analysis

11.1 *Temperature Effects on Materials*: (See also emission spectroscopy, 11.4).

11.1.1 The IR spectra of a substance obtained over a range of temperatures are helpful in the elucidation of molecular structure. In these variable temperature studies, it is necessary to employ a spectrometer that does not modulate the IR radiation emitted from the sample. (This is not usually a problem when using a Fourier transform spectrometer.) A suitable accessory that can alter the temperature of the sample will be necessary.

11.1.2 This technique can be used to obtain the IR spectra of synthetic polymers and biomembranes in both their crystal and amorphous states, and in some cases to determine the changes in intermolecular association occurring between polymer chains that affect their physical properties (**37** and **38**). Changes into other crystalline solid forms with change in temperature and changes from liquid to solid state amorphous or crystalline forms can also be studied.

11.1.3 Variable temperature experiments are important in determining whether certain band pairs are the result of the presence of rotational isomers in either the vapor, liquid, or solution phases, or in complete vibrational assignments in determining whether one or more bands in the spectrum is (are) suspected of being a hot band(s) (the band will increase in intensity with increased temperature). These experiments also help to differentiate between band pairs resulting from Fermi resonance and those resulting from rotational isomers, since the band intensity ratios for rotational isomers are temperature dependent. The less stable rotational isomers will increase in concentration with increased temperature (**39**). In both qualitative and quantitative analysis, however, the control of temperature is essential, since both frequencies and band intensities are affected by change in temperature on materials such as carbon disulfide (**40**) and polystyrene (**41**).

11.1.4 When performing variable temperature experiments, the heat present in the sample and the sampling accessory can cause problems as a result of emission of infrared energy inside the spectrometer.

11.1.4.1 In most FT-IR spectrometers, the sample location is after the interferometer, and this emitted energy impinges on the detector as an unmodulated signal. This causes a DC offset to the signal (interferogram), and can be severe enough to swamp the detector response. In a noise-limited experiment, such as GC/IR using a heated lightpipe, this becomes an important consideration (see Practice E1642).

11.1.4.2 In addition, some of the emitted energy travels towards the interferometer, and a fraction is sent back along the sample beam after modulation by the interferometer. This can cause spurious features to occur in the sample spectrum because the energy is out-of-phase with the normal source. In general, this effect is a weak one, but can be a significant problem when studying gases at high temperature, since the cell windows become a bright source, and the rotational spectra of the gas may contain sharp absorption lines that are sensitive to phase. In this case some bands may appear as derivative of negative features.

11.1.4.3 When using certain other instrument designs, the sample location can be before the interferometer. In this case the sample/cell emissions are modulated by the interferometer along with the source signal.

11.2 *Use of Photoacoustic Spectroscopy:*

11.2.1 This method requires an IR system equipped with a photoacoustic detector. It is useful for the study of materials in any physical state. The modulated IR radiation absorbed by the sample is converted to heat waves within the sample. These heat waves are transduced to acoustic waves at the gas-solid or gas-liquid interface, or in the gas itself. The acoustic frequencies are dependent upon the modulation frequency of the instrument. The lower the modulation frequency, the greater the depth of penetration into the sample.

11.2.2 Photoacoustic spectra can be obtained using two different types of FT-IR spectrometers. The conventional, rapid scanning, spectrometer records a PA spectrum that has a depth of signal penetration varying with the signal wavelength, as well as the modulation frequency of the interferometer. The use of a step-scanning interferometer, however, allows for the use of a single modulation frequency, which results in the depth of penetration being the same across the spectral range. Alteration of this modulation frequency results in the monitoring of differing penetration depth, which means that spectra can be obtained successively deeper into a surface (depth profiling).

11.2.3 The theoretical and experimental aspects of photoacoustic spectroscopy have been discussed in detail (**42-44**), and photoacoustic cells designed specifically for FT-IR application are commercially available. Reviews of PAS/FT-IR of solids and liquids have been written and are recommended reading for those interested in applying this technique (**45**,**46**).

11.3 *Pyrolysis:*

11.3.1 In this technique a sample is heated rapidly in a special cell and the vapor-state decomposition products are studied. The infrared spectrum obtained for the pyrolizate can be complex, since the vapors examined can include many fragments arising from breakdown of the original sample.

11.3.2 Application of the pyrolysis-infrared technique is best regarded as a highly valuable, but last-resort technique. It is valuable because it can be used to obtain spectra of pyrolyzates of intractable samples, such as insoluble thermoset plastics and carbon-filled cross-linked elastomers. The collected pyrolyzate, however, may not represent all of the components in the sample, and the sample may not yield the same spectrum in consecutive runs. Some components of a blend or a copolymer may be missed entirely.

11.3.3 Pyrolysis is a technique-sensitive analytical method. It is necessary, therefore, to standardize carefully in a highly repeatable system for consistent analysis. Consistency of the sample system necessarily means that samples are similar, and that similarity must even extend to the concentration of carbon filler, the inorganic filler, or type of inorganic filler, or combination thereof.

11.3.4 Pyrolysis units for maximum utility in the identification of polymeric compositions should be evacuable, able to control temperature and time, and provide for collection of both vapor-phase pyrolyzate and condensed pyrolyzate. Pyrolysis units that fit these requirements can be purchased from manufacturers. Useful information for utilizing the pyrolysis technique are given (**47-57**).

11.4 *Emission Spectroscopy* (**58**)*:*

11.4.1 Some spectrometers can be modified, using accessories supplied commercially, to measure infrared spectra of samples by emission spectroscopy. In this case, the normal infrared emitting source is either removed or shielded. Optics are then inserted to bring energy emitted by the sample into the interferometer instead. The normal instrument functions then are used to record a single beam spectrum of the emitted signal.

11.4.2 The overall energy profile of the emitted signal is comparable to the blackbody emission profile for the material, which thus is dependent of the temperature of the sample. It is often useful to measure a ratioed emission spectrum, using the spectrum of carbon black recorded under the same experimental conditions. Carbon black can be considered as being close to a perfect black body emitter. It is also possible to generate theoretical black body curves for comparison. The ratio of the theoretical to experimental blackbody curves shows the instrument absorption function being superimposed on the spectrum.

11.4.3 This technique is valuable when measuring the spectrum of samples at elevated temperatures, since the black body response (in terms of both intensity and frequency of maximum intensity) increases with temperature. If the sample temperature is high enough, above approximately 100°C, then a room temperature pyroelectric DTGS detector can be used to measure the signal. Below this temperature, however, a liquid-nitrogen cooled MCT detector is required, so that a suitable temperature differential exists between the sample and the detector. Emission spectra of materials at room temperature have been reported, but they are generally low in intensity, and show very little energy above about 1500 cm^{-1}.

11.4.4 Emission spectroscopy can be used to obtain infrared spectra from thin films, coatings, and single fibers, as well as from bulk materials. In the case of a coating on the surface of a strong emitter, the observed spectrum is sometimes obtained by reabsorption of the blackbody energy being emitted by the bulk and will therefore show characteristics similar to a transmission spectrum.

12. Keywords

12.1 alkali halide pressed pellets; attenuated total reflection spectroscopy; diffuse reflection spectroscopy; disposable IR cards; DRIFT spectroscopy; emission spectroscopy; gas chromatographic effluent spectra; gas phase spectra; heated gas cells; infrared solution spectra; infrared spectroscopy; latex suspensions; liquid phase spectra; photoacoustic spectroscopy; polymer analysis; qualitative infrared analysis; solid phase spectra; split mull technique; vapor phase spectra

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