



Designation: E573 – 01 (Reapproved 2021)

# Standard Practices for Internal Reflection Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation E573; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These practices provide general recommendations covering the various techniques commonly used in obtaining internal reflection spectra.<sup>2,3</sup> Discussion is limited to the infrared region of the electromagnetic spectrum and includes a summary of fundamental theory, a description of parameters that determine the results obtained, instrumentation most widely used, practical guidelines for sampling and obtaining useful spectra, and interpretation features specific for internal reflection.

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

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>4</sup>

[E131 Terminology Relating to Molecular Spectroscopy](#)

[E168 Practices for General Techniques of Infrared Quantitative Analysis](#)

[E284 Terminology of Appearance](#)

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

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<sup>2</sup> Internal Reflection Spectroscopy, IRS, is the accepted nomenclature for the technique described in these practices. Other terms are sometimes used, which include: Attenuated Total Reflection, ATR; Frustrated Total Reflection, FTR; Multiple Internal Reflection, MIR; and other less commonly used terms. In older literature, one may find references to Frustrated Total Internal Reflection, FTIR. This should not be confused with Fourier Transform Infrared Spectroscopy FT-IR.

<sup>3</sup> Other terms sometimes used for referring to the internal reflection element are: ATR crystal, MIR plate, or sample plate.

<sup>4</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

## 3. Terminology

3.1 *Definitions of Terms and Symbols*—For definitions of terms and symbols, refer to Terminologies E131 and E284, and to Appendix X1.

## 4. Significance and Use

4.1 These practices provide general guidelines for the good practice of internal reflection infrared spectroscopy.

## 5. Theory

5.1 In his studies of total reflection at the interface between two media of different refractive indices, Newton (**1**)<sup>5</sup> discovered that light extends into the rarer medium beyond the reflecting surface (see Fig. 1). In internal reflection spectroscopy, IRS, this phenomenon is applied to obtain absorption spectra by measuring the interaction of the penetrating radiation with an external medium, which will be called the sample (**2,3**). Theoretical explanation for the interaction mechanisms for both absorbing and nonabsorbing samples is provided by Snell's law, the Fresnel equations (**4**), and the Maxwell relationships (**5**).

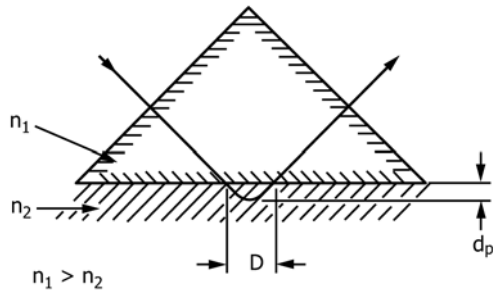
NOTE 1—To provide a basic understanding of internal reflection phenomena applied to spectroscopy, a brief description of the theory appears in Appendix X2. For a detailed theoretical discussion of the subject, see (**4**).

## 6. Parameters of Reflectance Measurements

6.1 Practical application of IRS depends on many precisely controlled variables. Since an understanding of these variables is necessary for proper utilization of the technique, descriptions of essential parameters are presented.

6.2 *Angle of Incidence,  $\theta$* —When  $\theta$  is greater than the critical angle,  $\theta_c$ , total internal reflection occurs at the interface between the sample and the internal reflection element, IRE. When  $\theta$  is appreciably greater than  $\theta_c$ , the reflection spectra most closely resemble transmission spectra. When  $\theta$  is less than  $\theta_c$ , radiation is both refracted and internally reflected, generally leading to spectral distortions.  $\theta$  should be selected far enough away from the average critical angle of the sample—IRE combination that the change of  $\theta_c$  through the

<sup>5</sup> The boldface numbers in parentheses refer to the list of references at the end of these practices.



NOTE 1—The ray penetrates a fraction of a wavelength ( $d_p$ ) beyond the reflecting surface into the rarer medium of refractive index  $n_2$  (the sample), and there is a certain displacement ( $D$ ) upon reflection.  $\theta$  is the angle of incidence of the ray in the denser medium, of refractive index,  $n_1$ , at the interface between the two media.

FIG. 1 Schematic Representation of Path of a Ray of Light for Total Internal Reflection

region of changing index (which is related to the presence of the absorption band of the sample) has a minimal effect on the shape of the internal reflection band. Increasing  $\theta$  decreases the number of reflections, and reduces penetration. In practice, there is some angular spread in a focused beam. For instruments that utilize f4.5 optics in the sample compartment, there is a beam spread of  $\pm 5^\circ$ , but the beam spread in the IRE is smaller because of its refractive index. The value will increase as lower f-number optics are utilized. This beam spread produces a corresponding distribution of effective paths and effective depth of penetrations.

6.3 Number of Reflections,  $N$ — $N$  is an important factor in determining the sensitivity of the IRE. Where multiple reflections are employed, internal reflection occurs a number of times along the length of the IRE depending on its length,  $l$ , thickness,  $t$ , and on the angle of incidence,  $\theta$ , of the radiant beam.

NOTE 2—The length of an IRE is defined as the distance between the centers of the entrance and exit apertures.

6.3.1 Absorption occurs with each reflection (see Fig. 2), giving rise to an absorption spectrum, the intensity of which depends on  $N$ . For single-pass IREs,  $N$  can be calculated using the following relationship:

$$N = \left(\frac{l}{t}\right) \cot\theta \quad (1)$$

For double-pass IREs:

$$N = 2 \left(\frac{l}{t}\right) \cot\theta \quad (2)$$

Many single-pass IREs employ approximately 25 reflections.

NOTE 3— $N$  must be an odd integer for IREs in the shape of a trapezoid, and an even integer for IREs in the shape of a parallelogram.

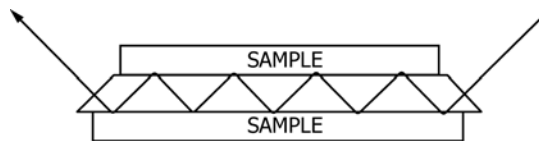


FIG. 2 Multiple Internal Reflection Effect

6.4 Relative Refractive Index,  $n_{21}$ , of the Sample,  $n_2$ , and IRE,  $n_1$ ; ( $n_{21} = n_2/n_1$ )—Refractive index matching controls the spectral contrast. If the indexes of the sample and the IRE approach each other, band distortions can occur. Therefore, it is necessary to select an IRE with a refractive index considerably greater than the mean index of the sample.

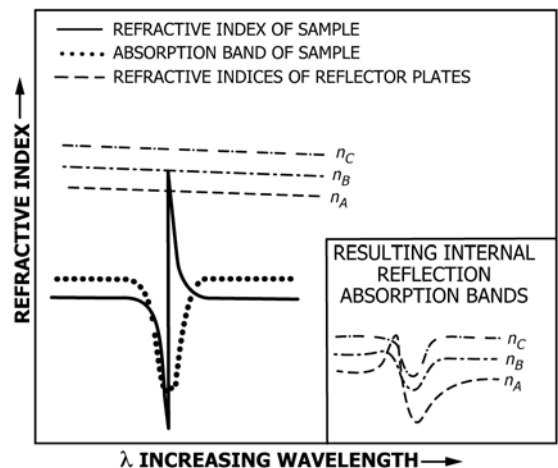
6.4.1 The refractive index of a material undergoes abrupt changes in the region of an absorption band. Fig. 3 (6) shows the change in refractive index of a sample across an absorption band as a function of wavelength. When an IRE of index  $n_A$  is selected, there may be a point at which the index of the sample is greater than that of the IRE. At this wavelength, there is no  $\theta$  at which total internal reflection can take place, and nearly all of the energy passes into the sample. The absorption band resulting in this case will be broadened toward longer wavelengths, and hence appear distorted. When an IRE of index  $n_B$  is selected, there is no point at which the index of the sample exceeds it. On the long wavelength side, however, the refractive indexes approach each other. This results in an absorption band that is less distorted, but that is still broadened on the long wavelength side. With an IRE of index  $n_C$ , a considerably higher refractive index than that of the sample, the index variation of the sample causes no obvious distortion of the absorption band.

6.5 Depth of Penetration,  $d_p$ —The distance into the rarer medium at which the amplitude of the penetrating radiation falls to  $e^{-1}$  of its value at the surface is a function of the wavelength of the radiation, the refractive indexes of both the IRE and the sample, and the angle of incidence of the radiation at the interface.

6.5.1 The depth of penetration,  $d_p$ , can be calculated as follows:

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{1/2}} \quad (3)$$

where:  $\lambda_1 = \frac{\lambda}{n_1}$  = wavelength of radiation in the IRE.



Solid Line—Refractive index of sample.  
Dotted Line—Absorption band of sample.  
Dashed Lines—Refractive indices of reflector plates.

FIG. 3 Refractive Index Versus Wavelength

The depth of penetration increases as the angle of incidence decreases, and becomes infinitely large as  $\theta$  approaches the critical angle (see Figs. 4 and 5) (7).

6.6 *Effective Path Length,  $d_e$* —The effective pathlength, or relative effective thickness,  $d_e$ , for the beam for each reflection is defined by Harrick (4) in detail, and is different for  $\perp$ -polarized than for  $\parallel$ -polarized radiation. For bulk materials, when  $\theta = 45^\circ$ ,  $d_{e\perp} = \frac{1}{2} d_{e\parallel}$ , and the average effective thickness is about equal to the penetration depth,  $d_p$ . For larger angles,  $d_e$  is smaller than  $d_p$  and for smaller angles,  $d_e$  is larger than  $d_p$ . The total effective pathlength is equal to  $N$  times the effective pathlength,  $d_e$ . An example of the effect of  $\theta$  on  $N \cdot d_e$  is shown in Fig. 6.

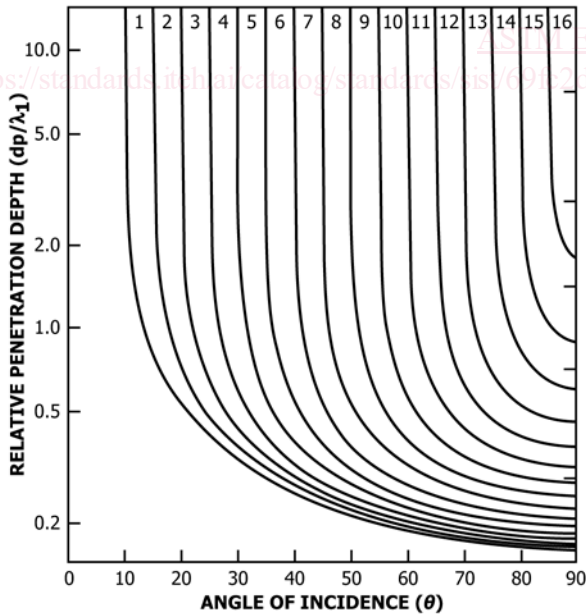
6.7 *Absorption Coefficient,  $\alpha$* —As in transmission spectroscopy, the absorptivity of a material affects the fraction of the incident radiation that is absorbed, and hence the spectral contrast. The internal reflectance of bulk materials and thin films, for small absorptivities, is as follows:

$$R = 1 - \alpha d_e \quad (4)$$

The reflectance for  $N$  reflections is:

$$R^N = (1 - \alpha d_e)^N \quad (5)$$

NO.	$\theta_c$	$n_{21}$	NO.	$\theta_c$	$n_{21}$
1	10°	.174	9	50°	.766
2	15°	.259	10	55°	.819
3	20°	.342	11	60°	.866
4	25°	.423	12	65°	.906
5	30°	.500	13	70°	.940
6	35°	.574	14	75°	.966
7	40°	.643	15	80°	.985
8	45°	.707	16	85°	.996



NOTE 1—Fractional penetration depth of electromagnetic field in rarer bulk medium for total internal reflection versus angle of incidence for a number of interfaces. The penetration depth is infinitely large at the critical angle and is about one tenth the wavelength at grazing incidence for relatively high index media.  $\lambda_1 = \lambda/n_1$  is the wavelength in the denser medium.

FIG. 4 Relative Penetration Depth Versus Angle of Incidence

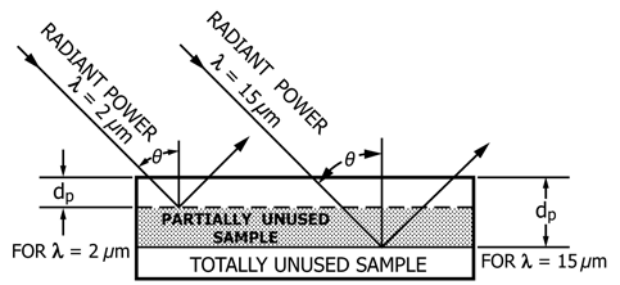
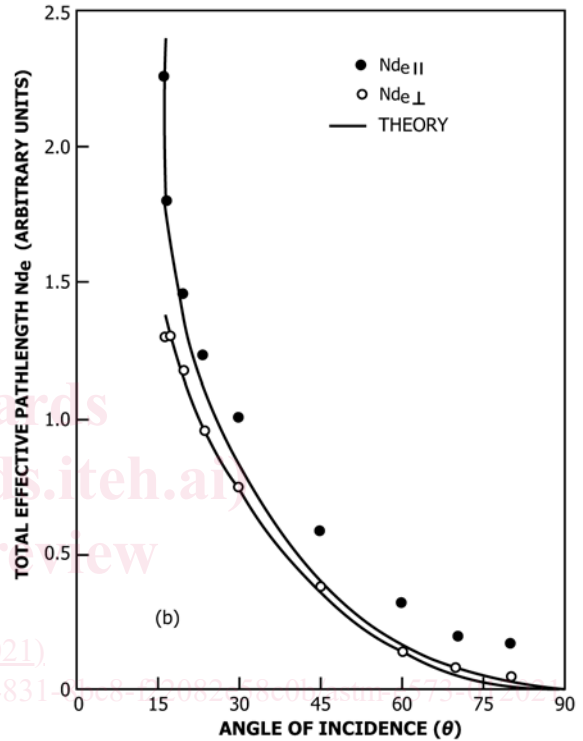


FIG. 5 Variation of Penetration Depth with Wavelength of Radiation in Sample (7)



NOTE 1—Total effective pathlength versus angle of incidence for polystyrene stain on silicon surface. The sharp drop with angle of incidence is largely, although not entirely, due to decrease of  $N$  with  $\theta$ . Points represent experimental measurements and solid curves are theoretical calculations (4).

FIG. 6 Total Effective Pathlength Versus Angle of Incidence

6.7.1 If  $\alpha d_e \ll 1$ ,  $R^N \approx 1 - N \cdot \alpha \cdot d_e$ , that is, the reflection loss is increased by a factor of  $N$ . The relationships between the absorption coefficient,  $\alpha$ , and the absorptivity,  $a$ , are given by Eq X2.13 and Eq X2.14.

6.8 *Sampling Area*—When multiple reflections are used, the sampling area is somewhat analogous to the pathlength in transmission spectroscopy. The amount of absorption by a sample in contact with a multiple-reflection IRE is proportional to the area of contact within the sensitive region. Sampling area is proportional to  $1/\cos \theta$  and increases with increasing  $\theta$ .

6.8.1 The sensitive region of an IRE sampling face varies, depending on the IRS system in which it is used. A small region or the entire area of the sampling faces can be sensitive, as seen for the dispersive systems shown in Fig. 7. It must be

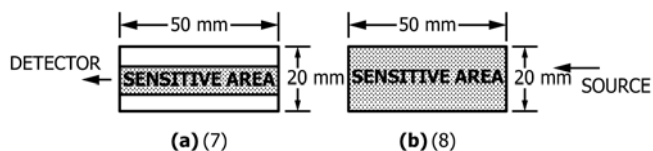


FIG. 7 Sensitive Sampling Areas of IRE Plates

emphasized that, in general, there is no relationship between the size of the sensitive sampling area and the optical efficiency of the IRS system, provided that the slit height of the dispersive spectrophotometer is filled. In fact, it is preferred that an IRE have insensitive edges so that gasket materials or sample holders do not cause spectral interference. It is important that samples be positioned so that they lie completely across the width of the sensitive area. For accessories utilizing single-reflection prisms and hemicylinders, the entire sample face should be covered. If this area is not completely covered by the sample, radiation bypasses the sample and the effect will be similar to a transmission cell with an air bubble in it. Knowing the sensitive sampling area on an IRE is important when the sample is limited and it is desirable to place the sample on the IRE in the most efficient manner (8). The sensitive region of an IRE sampling face may differ quite radically when used in an interferometer. The focused image is nearly circular and may not fill the vertical dimension of the crystal but often will overflow the width of the IRE face. This results in vignetting and introduces small wavenumber errors in Fourier Transform spectroscopy. The problem of overfilling the entrance aperture can be minimized by utilizing beam condensing optics, but this will increase the angular spread of the incident rays.

NOTE 4—It is recommended that an IRE with a vertical dimension only slightly larger than the focused beam diameter be used. This ensures that the sensitive area encompasses the full crystal face.

6.9 *Efficiency of Contact*—In order to obtain an internal reflection spectrum, it is necessary to bring the sample to a distance within the penetration depth,  $d_p$ . Physical contact of the sample with the IRE may be sufficient to obtain a qualitative spectrum. However, if the exact contact conditions are not reproduced, a source of error may result, particularly when interpretation requires a direct comparison with similarly obtained spectra, or when quantitative measurements are made.

6.10 *Electric Field Strength*—Spectral contrast is affected by the strength of the electric field, that is, the amplitude of the standing wave, in the rarer medium at the reflecting interface between two media. The field strength of the  $\parallel$ -polarized component is greater than that of the  $\perp$  component, and both of these field strengths decrease with increasing  $\theta$ .

## 7. Instrumentation

7.1 *Internal Reflection Attachments*—The internal reflection attachment, IRA, holds the IRE. It directs some portion of the radiation beam into the IRE, and then redirects the emerging energy into the spectrophotometer slits or onto the FT-IR detector without displacing or defocusing the beam while maintaining the same beam spread. The IRA is placed into the sampling compartment of a spectrometer. Most commercially available infrared spectrophotometers can be equipped with a

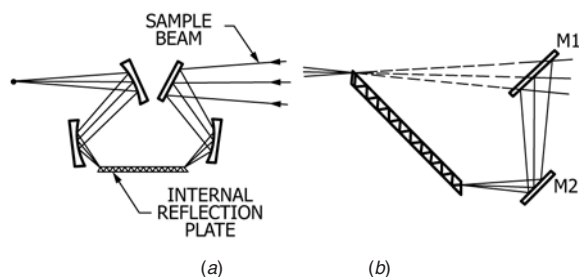
reflection attachment for obtaining internal reflection spectra (Note 4). The optical efficiency of internal reflection infrared systems can be nearly equal to theoretical. However, in some IRAs only half of the spectrophotometer energy may be available. Schematic diagrams of two types of fixed-angle IRAs are presented in Fig. 8. For double-beam operation, it is preferred that an IRA identical to that used in the sample beam be used in the reference beam in order to compensate for surface scatter, atmospheric absorptions, or absorptions in the IRE. When using an IRA in a FT-IR spectrometer, a reference spectrum (or background) is usually recorded using the same IRE with no sample in contact with the crystal. Very careful cleaning and sampling procedures (more than usual) are required here. Spectral verification of IRE cleanliness is essential. Internal reflection equipment includes the following:

7.1.1 The IRAs designed to be placed into the sampling compartment of a spectrophotometer. These are of the following types: (a) variable-angle single internal reflection; (b) fixed-angle multiple internal reflection ( $\theta$  usually set at  $45^\circ$ ), and (c) variable-angle multiple internal reflection ( $\theta$  is either continuously variable, usually between  $30^\circ$  and  $60^\circ$ , or a choice of angles is preset by the manufacturer, usually at  $30^\circ$ ,  $45^\circ$ , and  $60^\circ$ . In order to have the  $\theta$  that is specified on the attachment, an IRE for that same  $\theta$  must be used.) (d) platforms for supporting fixed-angle plates in a horizontal position, and (e) IRAs for supporting prism IREs of various geometry.

7.1.2 *Goniometers*—Goniometers are essential for absolute intensity measurements.

7.1.3 *Horizontal ATR Attachments*—This family of accessories is based on single-pass IRE geometries, which may be of fixed-angle or variable-angle construction. They are designed so that only one crystal face is accessible to the user in a horizontal plane. Some designs have the crystal set into the top surface of the accessory; others have a range of interchangeable plates, each with a different crystal material or sampling geometry. Plates are available to examine solid samples and often can accommodate a device to apply pressure to the sample. Other plates have a “boat” configuration and are designed to accept liquid samples. Some accessories are designed to vary the temperature of the sample.

7.1.3.1 Liquid samples that are inhomogeneous (for example, engine oils) may suffer from separation or deposition of heavier components onto the surface of the crystal. This results in a spectrum that shows an excessive contribution from



NOTE 1—(a) utilizes trapezoid IREs, and (b) utilizes parallelepiped IREs.

FIG. 8 Fixed-Angle Multiple-Reflection Internal Reflection Attachments

the settled material contacting the plate. Pressure applied to a non-adhering sample by using a pressure plate cannot be easily controlled. Use of pressure causes some polymeric samples to exude semiliquid onto the plate.

7.1.3.2 A variety of micro ATR accessories are commercially available. These include IRAS using single bounce prisms, spheres and hemicylinders as well as single pass multiple bounce prisms and parallelograms. Sampling areas can be 0.5 mm to 2 mm in diameter. Common IRE materials used for these include zinc selenide, diamond, silicon and germanium. Some of these allow the application of very high pressures for achieving sample-IRE contact.

NOTE 5—It is not the intention of this practice to specify any particular instrumentation for IRS. It is assumed that the equipment used is of the usual commercial quality and that the manufacturer's instructions will be consulted for proper IRA operation.

7.1.3.3 Caution is advised when using these accessories. In some IRA's, the angle of incidence is an average of many angles and is therefore not defined. Spectra will not be comparable to those run at a 45 degree angle of incidence. Spectra obtained at discrete angles of incidence using different IRE materials will sample different layers of a material. With germanium and silicon, the ATR spectrum may be that of a surface coating or exudate in contrast to diamond, zinc selenide and KRS-5 where the spectrum can include surface and substrate materials. In single reflection, accessories where less than the entire sample area is used (that is, the sample is smaller than the sample area), stray light effects can distort the spectrum.

7.2 *Internal Reflection Elements*—Infrared radiation is propagated through the internal reflection element by total internal reflection. Where multiple reflections are employed, the long pathlengths required place stringent demands on both the quality and the preparation of optical materials for IREs. The geometries of more common types and the properties of the best optical materials are presented in 7.3 and 7.4. Additional information is available in the literature (4).

7.3 *Geometry*—Common IREs are classified as follows:

7.3.1 *Single-Reflection IREs* (Note 5):

7.3.1.1 Fixed-angle prisms (Fig. X3.1(a))

7.3.1.2 Variable-angle hemicylinders (Fig. X3.1(b)), and

7.3.1.3 Micro hemicylinders.

NOTE 6—Prior to 1964, single-reflection IREs were the only type commercially available. They are still used, but principally for strongly absorbing materials. For weak absorbers, the angle of incidence must be set close to the critical angle and the kind of distortion depicted earlier (Fig. 3) can result.

7.3.2 *Multiple-Reflection IREs* (Diagrams of common types are shown in Fig. X3.1(c), (d), (e), (f), and (n)):

7.3.2.1 *Single-Pass IRE*—This is the simplest and most common. Radiation introduced through the entrance aperture propagates by multiple internal reflections down the length of the plate to the exit aperture. In these IREs,  $\theta$  is generally fixed at 45°; however, plates are available with  $\theta$  fixed at any angle.

7.3.2.2 *Double-Pass IRE*—In this type, radiation propagates down the length of the plate and is reflected back upon itself by a metalized end reflecting surface. The beam returns at a

slightly different angle of incidence. The average  $\theta$  is usually between 45° and 50°.

7.3.2.3 *Variable-Angle Multiple Reflection Plates, Single- and Double-Pass* (Note 7)—Angle variation may be obtained by use of IRAs that have provisions for repositioning IREs at set angles of incidence. Where a knowledge of  $\theta$  is not as important as the effect of angle change, fixed angle IREs may be used in any baseplate position to effect an angle change. For example, if a KRS-5 IRE with  $\theta = 45^\circ$  is placed into an IRA position for  $\theta = 60^\circ$ , then the actual angle of incidence is 51.3°. If the value of  $\theta$  must be known, it can be calculated using the following equation:

$$\theta = \theta_{IRA} - \sin^{-1} \left( \frac{\sin(\theta_{IRA} - \theta_{IRE})}{n_1} \right) \quad (6)$$

where:

$\theta_{IRA}$  = angle of incidence of the IRA position,

$\theta_{IRE}$  = angle of incidence of the IRE, and

$n_1$  = refractive index of the IRE material.

NOTE 7—For further information on this subject, see (9).

7.3.2.4 *Cylindrical Internal Reflection Element, (CIRE)*, (Fig. X3.1(f))—The CIREs are made from polished cylinders of any suitable IRE material with polished conical ends. The cone angle will vary with the material used but should be roughly complimentary to the desired internal reflection angle. Although it is difficult to precisely describe the paths of all of the rays entering the entrance cone of the CIRE, empirical studies have shown that the equations for number of reflections (1), depth of penetration (3), reflection (5), and absorptions (appendix) hold with reasonable accuracy. The end face of the CIRE matches the circular shape of the FT-IR beam. When used with instruments that refocus the FT-IR beam on the cone ends at the proper angle, the CIRE performs efficiently because it utilizes the entire beam. The CIREs are useful for constructing liquid cells because they can be sealed into a sample chamber by means of O-rings. Such sealed cells can be made to withstand several hundred pounds of pressure.

7.3.2.5 *Prism Internal Reflection Element, (PIRE)* (Fig. X3.1(h))—The PIREs are polished fixed-angle, elongated, four-sided, double-pass prisms constructed from any suitable IRE material. These IRE's are usually mounted vertically in a chamber that can be used for liquid or solid powder sampling. Liquid volume (when used as a sealed liquid cell) or immersion depth (when used as a probe by dipping the IRE into a powder or liquid sample) controls the number of reflections used. The throughput of a nine-reflection 45° angle double-pass ZnSe prism liquid cell is about 40 % at 4000 cm<sup>-1</sup> and 50 % at 1000 cm<sup>-1</sup>.

7.3.2.6 *Use of Optical Fiber as IRE*—If cladding is removed from a short length of an IR transmitting optical fiber, light passing through the fiber becomes an IRE. If that portion of the fiber is immersed in a liquid or resin sample, the spectrum of that material can be obtained.

7.4 *Optical Materials*—A perfect IRE material is not available because some of the desirable properties are mutually exclusive. Important characteristics of useful materials are:

7.4.1 High mean refractive index, preferably  $n = 2.5$  to 3.5,

7.4.2 High transmittance and spectral purity,

- 7.4.3 Ability to take high polish,
- 7.4.4 Toughness and resistance to cold flow, permitting pressing and clamping to optimize contact, and
- 7.4.5 Chemical inertness, offering resistance to chemical attack by samples and cleaning materials.

NOTE 8—Properties of best available and most frequently used IRE materials appear in Table 1. For a more complete coverage of the wide range of optical materials suitable for fabricating IREs, consult (10) and (11)

NOTE 9—Coverage of all internal reflection instrumentation is beyond the scope of these practices. For more extensive coverage of the subject, see (4),(12), and(13).

**8. Internal Reflection Elements**

8.1 *Selection*—The refractive index of the IRE should be chosen so that measurements of bulk materials made at the desired  $\theta$  will not yield distorted spectra. Lower index yields higher transmission because reflection losses at the entrance and exit faces are reduced. For thin films (less than 100 nm), the lowest possible index should be used so that distortion will be absent, while absorption will be enhanced. Hardness and inertness should also be considered. The system to be studied determines to some extent the choice of IRE material since the surfaces must not be attacked chemically. Ionizable acids and bases, for example, will etch the surface of KRS-5. Germanium and silicon, on the other hand, can be washed or soaked in dilute acids and alkalis.

8.2 *Evaluation*—The quality of an IRE is judged by its transmittance and the dependence of transmittance on wavelength. The maximum transmittance expected is determined by

considering the reflection losses at the entrance and exit apertures. If only these losses are considered, then:

$$T_1 \approx (1 - R)^2 \tag{7}$$

where:

$T_1$  = transmittance of the IRE,

and at normal incidence for the entrance or exit beam:

$$R = \frac{(n_1 - 1)^2}{(n_1 + 1)^2} \tag{8}$$

Many IREs exhibit transmittances close to the maximum value predicted by Eq 8 even when as many as 100 reflections are employed.

8.2.1 *Reasons for Poor Performance:*

8.2.1.1 *Poor Optical Material*—Defects in the quality of IRE materials are magnified because of the long pathlengths and large  $Ns$  employed in IRS. Some pieces of KRS-5 exhibit internal haziness that contributes to energy losses, especially at shorter wavelengths. Other pieces are soft and soluble in organic solvents, leading to rapid deterioration of the surface.

8.2.1.2 *Inadequate Surface Polish*—This causes scattering losses for soft materials such as KRS-5. Harder materials like silicon and germanium are capable of excellent surface polishing, and seldom need reconditioning.

8.2.1.3 *Poor Tolerance on Lengths and Angles*—The length to thickness ratio,  $l/t$ , of the IRE controls  $N$  (usually  $\theta$  is predetermined) (see Eq 1). In single-pass IREs,  $l/t$  is chosen so that the central ray enters and leaves by way of the entrance and exit apertures. If Eq 1 does not yield an integer, then a

**TABLE 1 Properties of Typical Optical Materials for Internal Reflection Elements<sup>A</sup>**

Material	Useful Range, [μm] [cm <sup>-1</sup> ]	Mean Refractive Index	Critical Angle, θ <sub>c</sub>	Properties
Silver chloride	0.45–16 22 000–700	2.0	30	soft, moldable, light-sensitive, easily scratched, insoluble in water
Silver bromide	0.5–35 20 000–500	2.22	27	slightly harder than silver chloride, otherwise similar, insoluble in water and alcohol
Zinc sulfide	0.7–10 14 000–1000	2.22	27	relatively hard and inert, water insoluble, attacked by concentrated acids and bases
Diamond C	0.22–4; 6–FIR 45 000–2 500; 1 600–FIR	2.4	25	hard, expensive, permanent, insoluble in water, acids, and bases
KRS-5, thalious bromide iodide	0.7–40 14 000–250	2.35	24.6	relatively soft, convenient index, favorable combination of properties, soluble in warm water, soluble in bases; insoluble in acids
Zinc selenide	0.5–14.3 20 000–700	2.42	24.6	expensive, brittle, water insoluble, releases H <sub>2</sub> Se, a toxic material when used with acids, soluble in strong acids, dissolves in nitric acid
Cadmium telluride	1.0–22 10 000–500	2.65	22.25	expensive, relatively inert, can be used with aqueous solutions, insoluble in acids
Arsenic triselenide	0.9–11.8 11 000–900	2.8	20.9	brittle, can be soaked in 35 % HCL, 95 % H <sub>2</sub> SO <sub>4</sub> , 10 % nitric acid, attacked by alkali, concentrated nitric acid and aqua regia
Silicon	1.06–6.7; 30–FIR 9 500–1 500; 350–FIR	3.5	15.6	hard, high resistivity material, useful at high temperatures, insoluble in most acids and bases, soluble in HF and HNO <sub>3</sub>
Germanium	2.0–11.4 5 000–900	4.0	14.5	limited range, sensitivity to temperature, becomes opaque at 125°C, insoluble in water, soluble in hot H <sub>2</sub> SO <sub>4</sub> and aqua regia, fine penetration depth
Sapphire	0.4–4.5	1.8	31.8	extremely hard, chemically resistant, low index, short transmission range
Cubic zirconia	0.4–5	2.1	27.3	extremely hard, chemically resistant, nontoxic, good index, relatively short transmission range

<sup>A</sup> For various applications, a wide variety of optical materials have been employed as IREs. These materials include MgO, CaF<sub>2</sub>, ZnSSe (zinc-sulfo-selenide solid solution), NaCl, KCl, and KBr.

single incoming beam will yield two spatially separated beams at the exit aperture that partially or completely miss the exit aperture. (This occurs when the aperture is larger than the source image.) In double-pass IREs (Eq 2), loss of energy occurs if  $N$  is not an integer, since the beam might strike the entrance rather than the exit aperture, and so be directed back toward the source. In this case, the condition for optimum transmission can be satisfied by adjusting  $\theta$ , provided that the instrumentation permits angle variation. The tolerances on all angles of the surfaces from which reflection occurs and through which light is transmitted are strict. This is especially true for high-index IREs, because, if the angle of the exit aperture is off by  $\delta$  degrees, the exit beam is deflected away from the normal to that surface by  $n\delta$ .

8.2.1.4 *Nonparallelism*—If an IRE does not have parallel surfaces, and the deviation from  $\theta$  is by an angle  $\delta$ , then after  $N$  reflections,  $\theta$  within the IRE is changed by  $N\delta$  for a single-pass plate. The exit beam will be deflected  $n \cdot N\delta$  degrees away from the normal to the exit aperture. For double-pass IREs, nonparallelism is not as serious, because any change in  $\theta$  as the beam traverses the IRE is compensated for in its return path. A wavy surface in either single- or double-pass IREs might not be serious if the average flatness is maintained.

8.2.2 *Quality Checks of an IRE*—Check the quality of an IRE by one or more of the following:

8.2.2.1 Visually inspecting for obvious surface or geometric defects,

8.2.2.2 Employing the IRE as a transmission plate to determine its optical purity,

8.2.2.3 Placing the IRE into a single-beam IRA in a dispersive spectrometer and measuring the transmitted power as a function of wavelength. Scattering, which goes roughly as  $\lambda^{-4}$ , is more severe at shorter wavelengths if the surface polish is inadequate. Spectra of IREs with good and bad surfaces are shown in Fig. 9. Very low overall transmittance of new IREs could indicate poor geometry or poor crystal structure,

8.2.2.4 Mounting the IRE on a goniometer and reflecting a highly collimated laser beam from the surface in question, then noting the angular displacements for flatness and poor tolerance on angles, and

8.2.2.5 Comparing with a reference IRE. When a double-beam internal reflection system is used, it is good practice to

keep a previously tested high-quality IRE in the reference optics so that changes in a sample IRE can be readily observed.

8.2.3 Evaluating an IRE by comparing it with an unused reference IRE, using a double-beam internal reflection system, requires that both the sample and reference beam IRAs be well-aligned. The sample-beam IRA must be realigned whenever a new (or refinished) IRE is to be checked and used because small differences of geometry always exist among IREs. An abbreviated procedure suffices for checking a used IRE in the IRA that had previously been aligned with it.

8.2.3.1 The procedure for evaluating a new IRE in a dispersive spectrophotometer in a double-beam internal reflection system is:

(a) Partially align the IRA-IRE optical system,

(b) Turn the 100 % control of the spectrophotometer to move the recorder pen downscale to about 50 %  $T$ ,

(c) Continue the alignment of the IRA to maximize transmitted energy, and

(d) Turn the 100 % control of the spectrophotometer to place the recorder pen at about 80 %  $T$ . Then run the IRE baseline.

8.2.3.2 The procedure for evaluating a used IRE is as follows:

(a) Use a previously aligned optical system, having a high-quality IRE in the reference beam and no additional external reference beam attenuation,

(b) Place the IRE to be checked in the sample-beam IRA, and turn the 100 % control of the spectrophotometer to place the recorder pen at about 80 %, or as far upscale as possible if this is less than 80 %, and

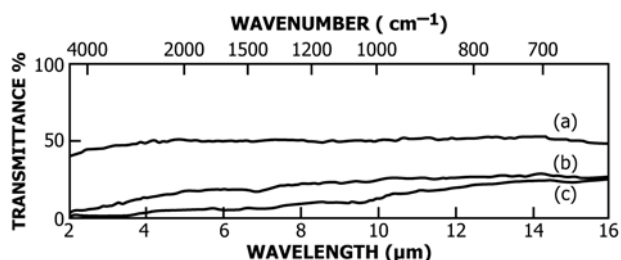
(c) Record the baseline of the IRE.

8.3 *Care and Handling of IREs*—For optimal performance, it is necessary to maintain the cleanliness of the IRE. When cleaning sealed cells (see 10.3.7), chlorinated and ketone solvents should be used with caution, so that cements or glues are not attached. The particular properties of each crystal material dictate special handling precautions. Recommendations for care of most used IREs are as follows:

8.3.1 *Germanium, Silicon, Zinc Selenide, and Zinc Sulfide*—The IREs of these materials are hard and brittle, and subject to mechanical fracture. They do not scratch easily and rarely need repolishing. If necessary, they may be washed or soaked in water or in any organic solvents, without damage to optical properties.

8.3.2 *KRS-5*—This material is relatively soft, and it scratches and deforms fairly easily. Rough or hard samples may dent or scratch the optical faces. The quality of this IRE is variable, some crystals being softer and hazier than others. Commercially available IREs of KRS-5 display wide variations in hardness and resistance to ketone solvents. The best optical materials are hard and insoluble in acetone solvent. Crystals that display acetone solubility scratch, deform, and lose surface polish easily. Warm water, ionizable acids and bases, chlorinated solvents, or amines should not be used on these IREs. Hydrocarbon solvents, ketones, alcohols, and cold water (for short intervals) may be used for cleaning.

NOTE 10—Regarding the toxicity of KRS-5 and KRS-6, no extraordinary hazard is encountered in normal handling as an IRE. Powdered or



NOTE 1—Comparison of the transmittance versus wavelength for a number of KRS-5 single-pass plates with various qualities of surface polish;  $N = 26$ ,  $\theta = 45^\circ$ . (a) Good polish; (b) hazy surface, needs resurfacing; (c) scratched, poor surface polish, needs repolishing. (Courtesy of G. D. Propster, Wilks Infrared Center, Foxboro Corp., South Norwalk, CT.)

FIG. 9 Comparison of Transmittance Versus Wavelength