



Standard Practices for Internal Reflection Spectroscopy¹

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1. Scope

1.1 These practices provide general recommendations covering the various techniques commonly used in obtaining internal reflection spectra.^{2,3} 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.

2. Referenced Documents

2.1 ASTM Standards:

E 131 Terminology Relating to Molecular Spectroscopy⁴

E 168 Practices for General Techniques of Infrared Quantitative Analysis⁴

E 284 Terminology of Appearance⁵

3. Terminology

3.1 *Definitions of Terms and Symbols*—For definitions of terms and symbols, refer to Terminologies E 131 and E 284, 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)⁶ 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, θ* —When θ is greater than the critical angle, θ_c , total internal reflection occurs at the interface between the sample and the internal reflection element, IRE. When θ is appreciably greater than θ_c , the reflection spectra most closely resemble transmission spectra. When θ is less than θ_c , radiation is both refracted and internally reflected, generally leading to spectral distortions. θ should be selected far enough away from the average critical angle of the sample—IRE combination that the change of θ_c through the 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 θ 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, θ , of the radiant beam.

NOTE 2—The length of an IRE is defined as the distance between the

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² 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.

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

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

⁵ *Annual Book of ASTM Standards*, Vol 06.01.

⁶ The boldface numbers in parentheses refer to the list of references at the end of these practices.