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New developments in internal reflection spectroscopy

PART II: THE HORIZON™

INTERNAL REFLECTANCE spectroscopy[1] is widely used for studying a variety of liquids, pastes, and solids. It is well suited for analyzing optically thick or opaque samples that cannot be examined via conventional transmission spectroscopy. It is particularly useful for ultramicrosampling.[2,3]

Internal reflectance attachments were originally designed for use with dispersive spectrometers. These attachments directed the beam to and from the internal reflection elements (IREs). The internal reflection plates were typically parallelepipeds or trapezoids with apertures slightly larger than the slit image of the spectrometer. This configuration produced highly efficient internal reflection attachments such as the TMP[4] and Skin Analyzer[5] (Harrick Scientific, Ossining, New York). When FTIR spectrometers began to replace dispersive instruments, many attachments designed for dispersive spectrometers continued to be used. The FTIR spectrometers have beams with round cross sections that do not match the rectangular aperture of the standard IRE. This mismatch results in energy losses, which reduce the throughput of the attachments and therefore reduce the signal-to-noise ratio (S/N) in the resulting spectrum. Consider, for instance, the Skin Analyzer,[5] an attachment that was one of the earliest designs, similar to the Horizon™ (Harrick Scientific), which was used for solid and liquid samples. No modifications were introduced either to alter the profile of the light beam to match the entrance aperture of the IRE or to restrict the path of the light beam so that the radiation did not interact with the edge of the plate and thereby avoid spurious spectral bands from the adhesive that bonded the IRE to its holder. Other attachments that used internal reflection plates located the IREs at the bottom of a trough. To avoid the spurious bands, the edges of the plates were sometimes metallized. However, metallizing is a costly procedure and contributes to large energy (light) losses.

Two general approaches have been taken to improve the performance of internal reflection plates with FTIR instruments: redesigning the IRE to match its aperture to the FTIR beam, or reshaping the FTIR beam to match the IRE. In the former category, IREs with square and round apertures have been fabricated in an attempt to reduce energy losses. Both configurations have their limitations. The IREs with square cross sections are designed with apertures slightly larger than the focused FTIR beam. Like the standard rectangular IREs, they have flat sampling surfaces that are easily polished. These flat sampling surfaces are also suitable for mounting the sample and for applying pressure to obtain optimum contact between solid samples and the IRE. However, square cross-sectioned IREs have fewer reflections and hence lower S/Ns than the traditionally shaped IREs of the same width and length. Use of a longer IRE can increase the S/N, but there is a practical limit to its length. This limit is based on the width of the sample compartment, the fragility of the IRE, the ability to achieve good contact between the IRE and the sample, and the high cost of the IRE.

Alternatively, rod-shaped IREs require expensive transfer optics to direct the entering and exiting beams. These transfer optics are typically difficult to align and result in low throughput. Typically, the throughput is even lower than that of attachments that use rectangular IREs. Furthermore, rods do not produce a well-defined angle of incidence due to their curved sampling surfaces.[1] These curved surfaces are difficult to polish to a high-quality optical finish, resulting in higher scattering losses than the standard rectangular IREs. The curved sampling surfaces also limit the types of samples that can be examined. Since solids and powders cannot easily be clamped to the crystal, rod IREs are normally used only for liquid sampling.

Internal reflectance beam condensers represent still another approach to solving the FTIR beam–IRE aperture incompatibility problem. Beam condensers focus and condense the round FTIR beam into the IRE aperture. This produces a beam that is smaller than the entrance aperture of the IRE, but it expands within the IRE and completely fills the exit aperture. The beam exiting the IRE has a rectangular cross section with a width comparable to the diameter of the condensed FTIR beam and a height several times larger. This elon-

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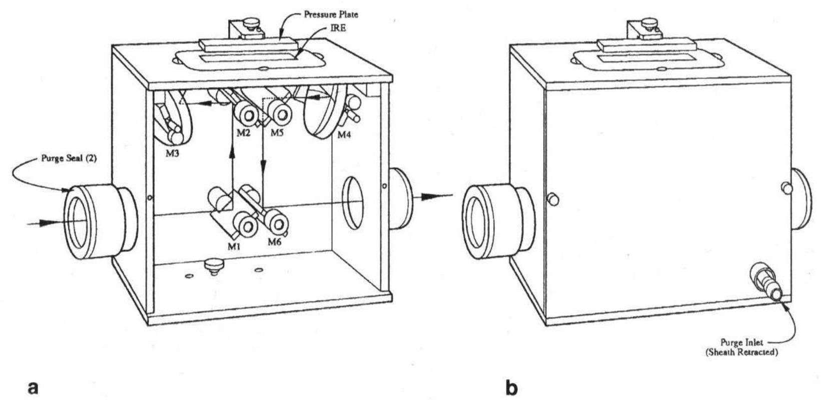

Figure 1 *Horizon: a) optics and optical path, and b) enclosed in its purgeable box. (Enclosing the attachment permits rapid sample exchange with minimal interruption of the purge of the spectrometer.)*

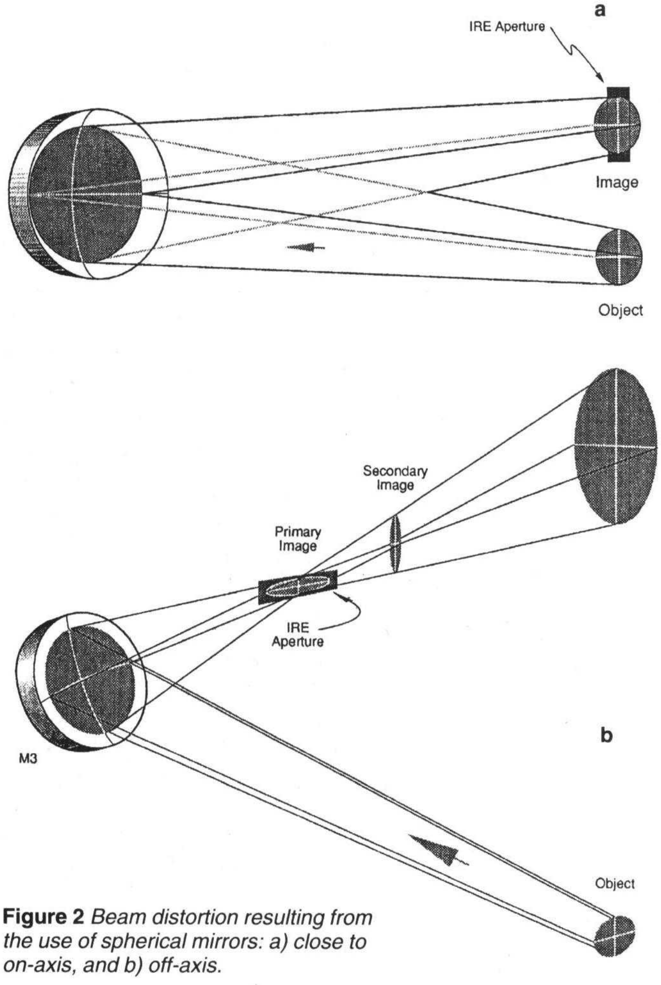

Figure 2 *Beam distortion resulting from the use of spherical mirrors: a) close to on-axis, and b) off-axis.*

gated beam is directed to the detector of the spectrometer. Since the detector is matched to the round beam of the spectrometer, some fraction of the elongated beam does not strike the detector. This results in energy losses, low throughput, and a less than optimal S/N.

The Horizon is a multiple internal reflection attachment in which the internal reflection plate is oriented horizontally (see *Figure 1*). It can be used for liquid or solid sampling. Its design takes advantage of the astigmatism that occurs when spherical mirrors are operated in an off-axis mode. This increases the light throughput by at least 30% and, since the light path does not come near the edges of the IRE, adhesives or O-rings may be used to seal the IRE to the plate holder without introducing spurious spectral bands.

The mirrors used to direct the beam to and from an IRE are normally designed to produce well-defined images of the light source. This can be achieved using spherical mirrors in an on-axis or near on-axis mode, as shown in *Figure 2a.* Although the resulting image is well-defined, this configuration provides inadequate space for accessories between the incident and reflected beam. Hence, ellipsoid segments, paraboloids, toroids, and off-axis spherical mirrors are typically used to provide the necessary working space.

Attachments that generate well-defined images have the disadvantage that the image of the round source overfills the rectangular aperture of the commonly used internal reflection plates. This results in severe light losses. Figure 2*b* shows the use of spherical mirrors in an off-axis mode where severe astigmatism* occurs. This distortion can be used to advantage by carefully selecting the off-axis angle for the spherical mirrors such that:

1. The oval-shaped primary image matches the rectangular aperture of the IRE; this produces approximately 50% higher energy throughput.

2. The infrared beam converges to the secondary image and is focused at the center of the internal reflection plate. In this configuration, the height of the beam is constrained by the reflection from the top and bottom surfaces of the IRE. Furthermore, the infrared beam does not strike the edges of the IRE, i.e., the edges of the IRE are insensitive.[6] Thus, spurious absorption bands from the adhesive or O-rings in contact with the edges of the internal reflection plate do not appear.

3. A second spherical mirror, also off-axis, recombines the images from the exit aperture and the secondary image and focuses the recombined infrared beam onto the detector (*Figure 3*).

The ATR (attenuated total reflectance) attachment, shown in Figure 1, takes advantage of the astigmatism that occurs for spherical mirrors used off-axis, as de-

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*The focal lengths for the primary and secondary images are, respectively, $fp=f\cos\theta$, and $fs=f/\cos\theta$, where f is the on-axis focal length of the spherical mirror, and θ is the angle incidence on the mirror for off-axis imaging.

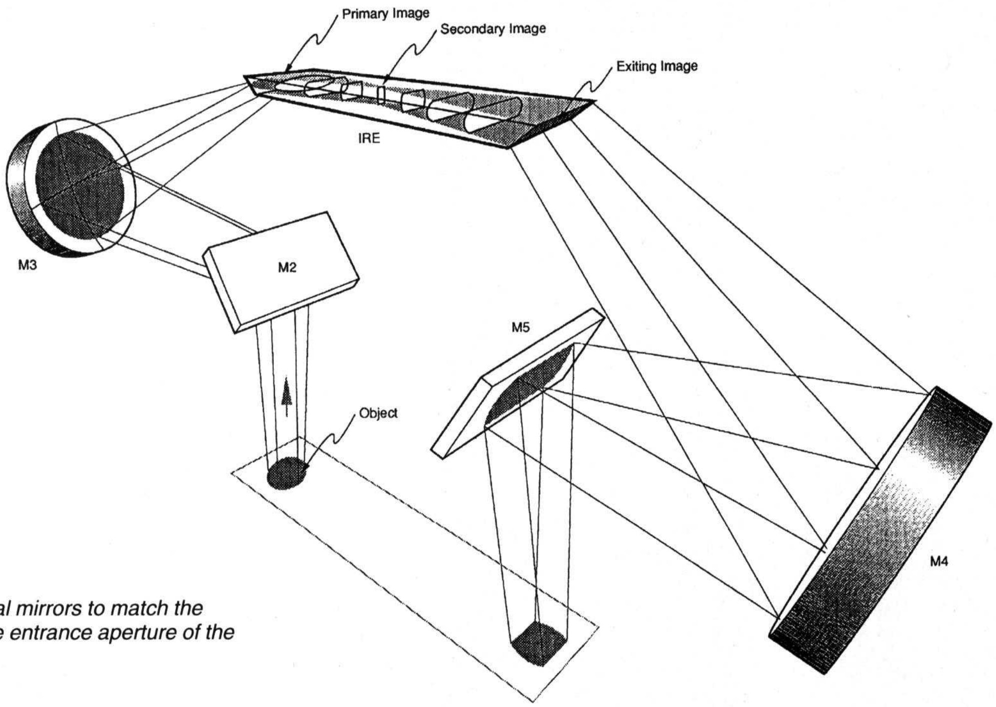


Figure 3 *Use of spherical mirrors to match the beam to the shape of the entrance aperture of the IRE.*

scribed above. Mirrors M1 and M2 direct the incident beam to spherical mirror M3. This spherical mirror is used off-axis and focuses the beam on the IRE aperture. The radiation propagates down the length of the crystal, where it interacts with the sample, and is then collected by the second spherical mirror, M4, which is also oriented off-axis. Mirror M4 reflects the beam from mirror M5 to mirror M6 and onto the detector of the spectrometer.

The Horizon uses standard trapezoidal internal reflection plates that are 50-mm long, 10- or 20-mm wide, and 1-, 2-, or 3-mm thick. This provides 8, 13, or 25 reflections from the sampling surface for 3-, 2-, or 1-mm-thick IREs, respectively. The attachment features PermaPurge™, which permits rapid sample exchange with no interruption of the purge of the system and crystal exchange with minimal disruption of the purge.

Applications

Several samples were examined to illustrate the applications of the Horizon used in conjunction with a Nicolet 740 FTIR spectrophotometer (Madison, Wisconsin). The attachment generates high-quality spectra of a variety of materials, as demonstrated in *Figures 4, 5,* and *6.* Figure 4 shows the internal reflectance of a piece of black foam packing material, recorded using a 2-mm-thick ZnSe internal reflection element.

Figure 5 illustrates the difference between new and used Castrol® GTX Super Multi-Grade 10W/30 motor oil (Castrol Inc., Wayne, New Jersey). In particular, note the disappearance of the transition slightly below 1000 cm^{-1} and the spectral changes around 1700 cm^{-1}. Both spectra in Figure 5 were obtained using a 2-mm-thick KRS-5 crystal.

Figure 6 shows the internal reflectance spectra of several varieties of soda, recorded using a 1-mm-thick

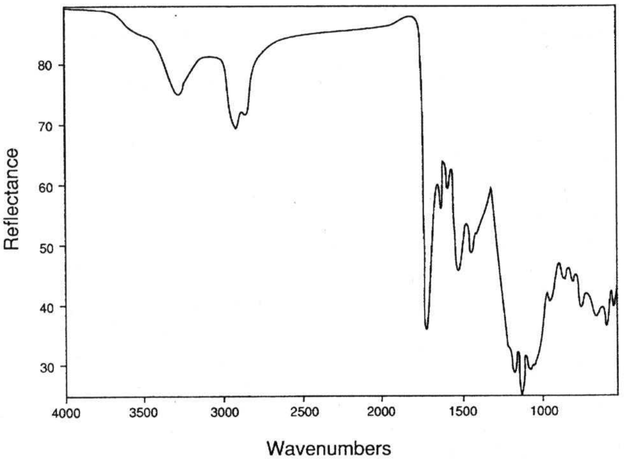


Figure 4 *Internal reflection spectrum of black foam packing material recorded with the attachment.*

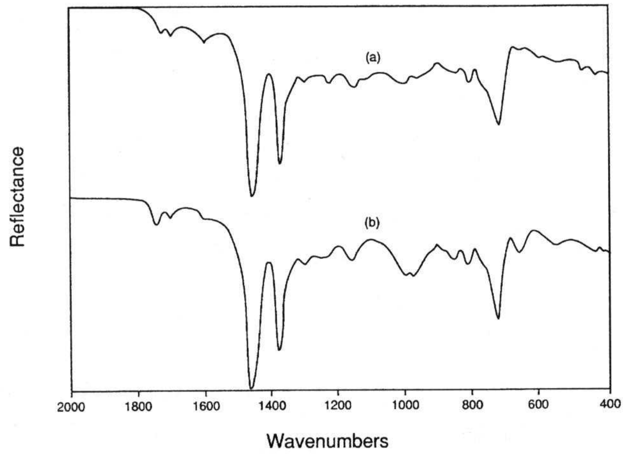
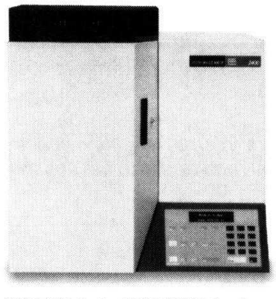


Figure 5 *Internal reflection spectra of a) used and b) new GTX 10W/30 Castrol motor oil.*



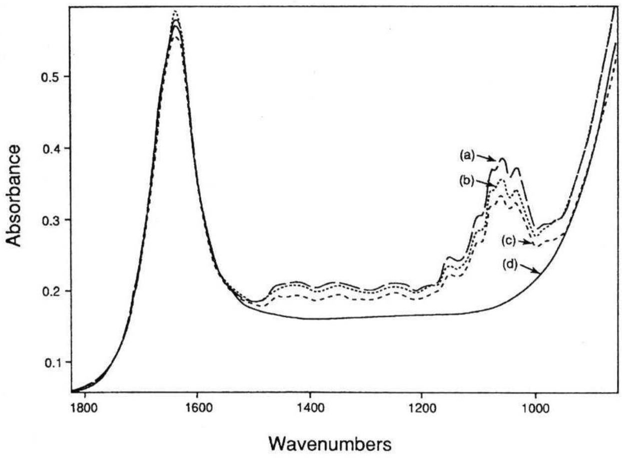


Figure 6 *Internal reflection spectra of a) Sunkist orange soda, b) Pepsi, c) Coca-Cola Classic, and d) Diet Coke.*

Ge IRE. Sunkist® orange soda (Coca-Cola Co., Atlanta, Georgia), Pepsi® (Pepsico, Inc., Purchase, New York), and Coca-Cola® Classic (Coca-Cola Co.) all have absorptions due to sugar in the 1000 cm^{-1} to 1500 cm^{-1} region. These peaks are easily distinguished from the underlying broad water absorption. Diet Coke (Coca-Cola Co.) has no sugar and hence lacks these absorptions. From the intensities of the peaks in this region, it is clear that Sunkist contains more sugar than Pepsi, and Pepsi is sweeter than Coca-Cola Classic. From these spectra, the sugar content of various sodas can be easily and precisely quantified, given a calibration curve.

Conclusion

The Horizon is a purgeable, horizontal sampling internal reflection attachment that uses standard trapezoidal internal reflection plates. This attachment is specifically designed to match the round FTIR beam to the rectangular aperture of the internal reflection plates and incorporates the PermaPurge feature, which permits the rapid acquisition of high-quality spectra.

Work is currently in progress to improve the Horizon's performance. In order to further reduce the spurious bands due to the adhesives or O-rings used to seal the ends of the IRE, the ends can either be shielded by metal foil, or small prisms can be optically contacted near the ends of the IRE to inject and extract the infrared radiation.

References

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6. U.S. Patent #4, 886, 387 (12/12/89).