

under the experimental conditions. Typical chromatograms indicating the separation of several penicillins are shown in Figures 2 to 5. Relative retention times, as well as response factors and their relative precision, are shown in Tables I and II. Precision was determined for each compound by calculating the relative standard deviation of response factors obtained from six separate preparations of reference standard. Response factors were calculated from peak areas of internal standards and reference standards, measured by the peak-height times half-width method.

An LBK 9000 gas chromatograph-mass spectrometer was used to confirm the identity of the silyl derivatives of each penicillin. Chromatographic peaks were shown to be the trimethylsilyl esters of the intact penicillins by observation of their molecular ions.

CONCLUSIONS

Good precision of response factors of reference standards indicates the direct applicability of the procedure to penicillin prime bulk material. Combined with suitable sample preparation the method could be extended to include bulk blends, tablets, syrups, and other commercial preparations.

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CORRESPONDENCE

The Internal Reflection Probe

SIR: Double-pass internal reflection plates for Internal Reflection Spectrometry (IRS) (1) permit a light beam to enter and exit through one and the same end of the plate. These plates can then be used as "Internal Reflection Probes" for recording spectra of liquids and powders and for reaction monitoring since the free end can be immersed into the sample material (Figure 1a), thus eliminating the need for special cells (2).

The double-pass geometry was conceived to overcome the difficulty of building vacuum chambers, dewars, and ovens having two optical windows, such as used in IRS surface studies with single-pass plates. The double-pass geometry requires only one optical window. This geometry also simplifies the design of the transfer optics for their use in spectrometers and, furthermore, permits use of reflection plates of any length without altering the optics.

Studies were made for NASA on the potential use of such a probe for dipping into the surface of the moon to record spectra of moon dust. The advantage that IRS offers is that particulate matter, regardless of size, does not scatter light in its interaction with the evanescent wave (3), and, therefore, spectra of powders can be recorded without elaborate sample preparation.

The prisms (or equivalent mirrors) in Figure 1a rotate the slit image from the usual vertical orientation to a horizontal orientation, and the mirrors direct the light beam at the required angle so that light will travel *via* multiple reflection, vertically along the length of the reflection plate. A more sophisticated structure, the vertical double-pass plate, was developed (4) to minimize the number of optical components required to achieve the same result. The VDP plate, shown in

- (1) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, Division of J. Wiley & Sons, New York, N. Y., 1967.
- (2) N. J. Harrick, *ANAL. CHEM.*, **36**, 188 (1964). Flexible optical fibers may also be used for this purpose as demonstrated by W. N. Hansen, *ibid.*, **35**, 765 (1963).
- (3) N. J. Harrick and N. H. Riederman, *Spectrochim. Acta*, **21**, 2135 (1965).
- (4) N. J. Harrick, *Appl. Opt.*, **5**, 1 (1966).

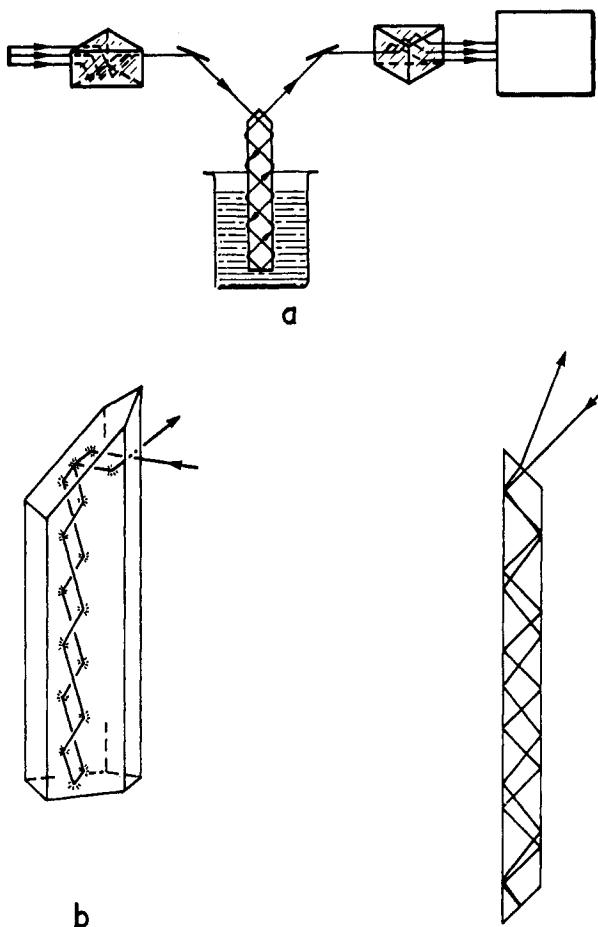


Figure 1. Internal reflection probes

a. Double-pass plate; b. Vertical double-pass plate; c. Double-pass, double-sampling plates. The free end can be dipped into liquids, powders, etc. for recording spectra

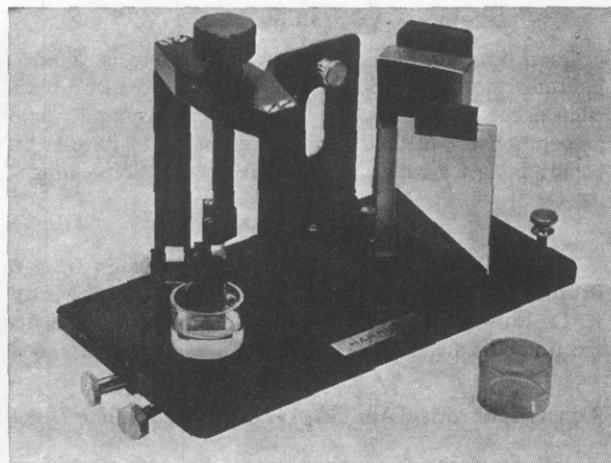


Figure 2. Vertical double-sampling internal reflection plate with versatile reflection attachment can be adapted to most commercially available spectrometers

Figure 1b, is the equivalent of the double-pass plate, the mirrors, and the two prisms of Figure 1a. These more sophisticated internal reflection plates require precision in fabrication but with careful fabrication high performance is achieved.

Double-pass plates are not limited to a roof-top bevel at one end. The light may, for example, be introduced through the sampling surface and deflected internally *via* the bevel (1). Because of sensitivity and aperture size considerations, double-pass, double-sampling plates were developed. In

this case the light enters and exits *via* the same aperture and the light beam strikes each point on the surface twice. In order to separate the entrance and exit beams, the opposite bevel is cocked slightly and metallized so that the light beam is reflected back down the length of the plate at a slightly different angle of incidence. A horizontal double-sampling plate is shown in Figure 1c.

Vertical double-sampling plates can also be made by providing a single bevel (rather than a roof-top bevel) along one edge of the plate and cocking and metallizing the bevel at the end of the plate. Such an internal reflection probe (IRP) with transfer optics that can be adapted to most spectrometers is shown in Figure 2. [This accessory, the Versatile Reflection Attachment (VRA), is a multi-purpose attachment that in addition to its use with the IRP, can be used for internal reflection spectrometry with double-sampling reflection plates of any length or with double-sampling plates having the sampling surface in a horizontal position. It can also be employed for specular reflection (low angle of incidence, $\theta = 12^\circ$, as required in epitaxial film thickness measurements) and with the addition of a retro-mirror accessory (5), such measurements can be made over a wide range of angles of incidence. This is useful for studying thin films on metals and measuring both refractive index and film thickness (6).] In this reflection plate the average angle of incidence is 45° , there are approximately 15 reflections

(5) N. J. Harrick, ANAL. CHEM., 37, 1445 (1965).

(6) N. J. Harrick, *Appl. Opt.*, in press.

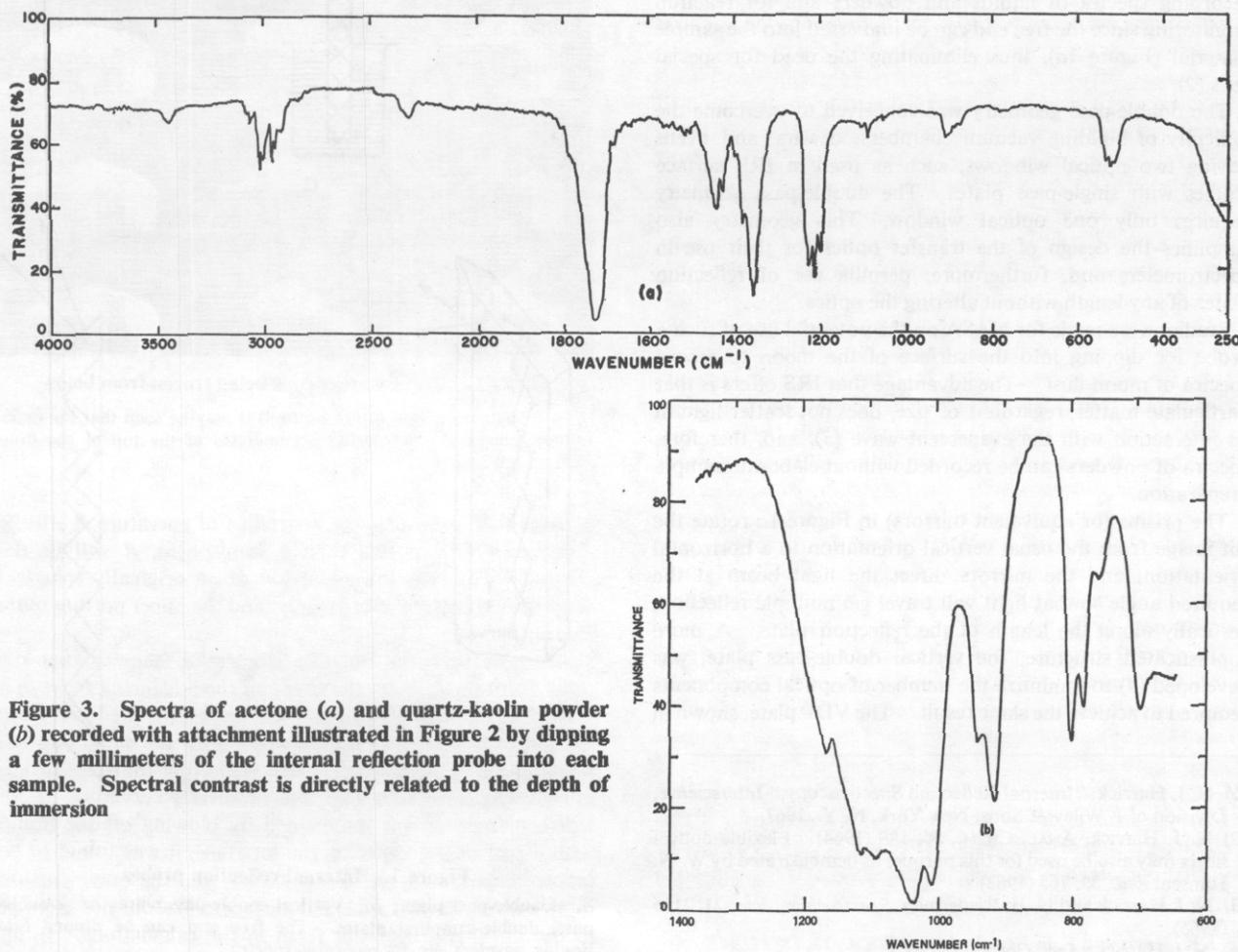


Figure 3. Spectra of acetone (a) and quartz-kaolin powder (b) recorded with attachment illustrated in Figure 2 by dipping a few millimeters of the internal reflection probe into each sample. Spectral contrast is directly related to the depth of immersion

per cm length of the plate and about 3 cm (45 reflections) can be employed if necessary.

There are many applications of the Internal Reflection Probe. As originally illustrated, it eliminates the need of special cells for studying liquids and powders. It is also useful for viscous media and turbid solutions where suitable cells cannot be made. The spectra of acetone and quartz-kaolin powder were recorded by dipping a few millimeters of the end of the IRP into the sample and are shown in Figure 3. Spectral contrast can be controlled by adjusting the depth to which the IRP is immersed into the sample. Of particular interest is the use of the IRP for reaction monitoring as re-

quired in process control. The Internal Reflection Probe can readily be combined with a low cost commercially available instrument for this purpose. Although the use of the internal reflection probe has been demonstrated only for the IR, it can be adapted to any spectral region from the UV to the far IR.

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Changes of Drop-Shapes on Freezing

SIR: Davis and Bartell (1) determined the surface tension of molten materials by measurement of the shapes of solidified pendent drops, obtaining reasonable results for a variety of substances, including metals. Their method requires that the shape of the drop not change during "cooling." This is at least a two-stage process, except for glasses—namely freezing, followed by cooling of the solid to room temperature. They suggest that for isotropic substances the second stage should cause no trouble, but they do not comment on the first stage.

Unless customary precautions are taken, metal castings, on solidification, commonly form depressions at the free surface, or even deep pipes into the body of the casting, owing to shrinkage on freezing. The reverse phenomenon occurs with water and materials such as type-metal, which expand on freezing. The effect of this on drop-shape can invalidate the method unless solidification occurs superficially first, and the interior is frozen in such a way that the volume change is in some way vented. Cheng (2) has reported the ejection of microdroplets during freezing of a supercooled water drop. An experimental arrangement to allow this venting in a more controlled way can be imagined but it is difficult to see that this was achieved in the method as originally described.

A clear example of the distortion that can occur may be seen in the photographs, Figure 1. Three drops of water are shown, each resting in a shallow depression on top of an aluminum rod, the bottom of which dips into freezing mixture. As each drop is frozen from below, a change of shape occurs, leading ultimately to the formation of a cusp. In other experiments, when water drops were placed directly in depressions in pieces of Dry Ice, the form of the frozen drop resembled (in cross section) a Gothic arch. These more Byzantine forms were always obtained when the aluminum rod was used.

The general features of the distortion of a drop on freezing in this way may be understood by assuming that the original shape of the unfrozen drop is spherical, and that the solid advances in a front of some particular form. If the advance creates a volume dv of solid, the amount of liquid removed will not be dv , but $dv' = dv \rho_s/\rho_1$. For water $dv' < dv$, so a small extra volume $dv'' = dv(1 - \rho_s/\rho_1)$ is generated. If this is accommodated in the liquid, its volume is slightly increased over that contained in the original envelope. If this envelope

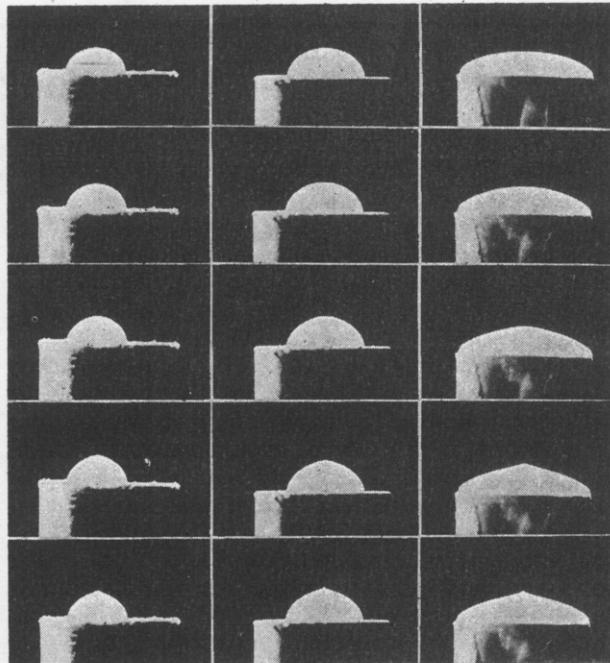


Figure 1. Three water drops being frozen from below

In each sequence (from top to bottom) it may be seen that the extra volume generated on freezing accumulates at the top of the drop (scale in millimeters)

is more than a hemisphere, its radius of curvature R will be increased. If it is less than a hemisphere, R will be decreased. Thus the lower portion of an originally spherical drop should become more gently, and the upper portion more sharply curved.

Attempts to carry out this calculation showed that the outer form depends on the shape of the advancing front in a critical way. When it was taken to be flat, the predicted form for the frozen drop was egg-shaped, with the small end up. Assumption of a spherical interface meeting the free surface at right angles led to a cusp, but no reverse curvature.

When freezing was interrupted by blowing off the liquid with a puff of air, exposing the interface, it was found to be saucer-shaped, with the center flatter, and the outer portion more curved, than a spherical surface. We did not attempt to use an interface of this form in the calculations. In all versions, the assumption was made that the free surface of the

(1) J. K. Davis and F. E. Bartell, *ANAL. CHEM.*, **20**, 1182 (1948).
(2) R. J. Cheng, *Science*, **170**, 1395 (1970).