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DESIGNING ROBUST SAMPLE INTERFACING EQUIPMENT FOR INFRARED PROCESS ANALYSIS

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To the process engineer, the appropriate parameters for use in the design of equipment to be employed in a process plant may seem axiomatic. However, most analytical instruments are not designed by process engineers. This fact has historically been a major factor impeding the widespread application of infrared spectroscopy to process analysis. This paper outlines the guidelines that we have used in our efforts to remedy this situation for both near and mid-infrared analysis, and surveys a number of practical designs for robust sample interfacing systems. The designs covered include near-IR cross-line transmission systems, near- IR probes, mid-IR ATR flow cells and probes, and long path gas cells.

1. INTRODUCTION

The rules underlying the optical design of sampling equipment for use in the process environment necessarily encompass those which apply to any other equipment to be used in this environment. This is a fact that is often not appreciated by optical designers approaching such tasks. However, additional requirements are also imposed by the nature of the optical equipment itself. These fall into two broad categories: (A) the need to achieve a required level of optical performance under a wide range of process and environmental conditions, and (B) the need to deal with limitations imposed by the nature of the optical materials required for specific applications.

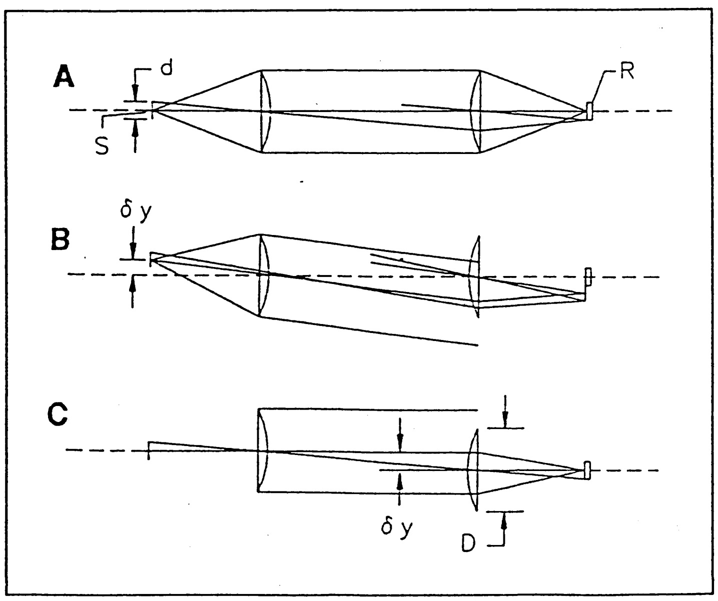

Figure 1: A generalized optical system model. A: Properly aligned optics. B: Effect of lateral displacement in the focussed region. C: Effect of lateral displacement in the collimated region.

Much of what follows will be concerned with the first of the above categories. In particular, we will focus on two topics: the use of optical designs, wherever possible, which are inherently insensitive to environmental effects and, when this is not possible, the removal of sensitive optics from areas involving significant thermal or mechanical stress. Later, we will review some specific sample interface designs from the viewpoint of both optical and mechanical integrity.

2. SAMPLE INTERFACE DESIGN CONSIDERATIONS

2.1 Optical Mechanical Interactions:

The potential for optical performance degradation due to structural movement is a major concern in designing sample interfacing equipment for process applications. Movement will be caused by factors such as temperature, pressure, vibration, or differential forces associated with sample flow. Slow changes will lead simply to a loss of optical signal or, in some cases, a change in absorbance calibration and/or a shift in frequency scale. Rapid changes - eg: due to vibration - can have even more serious effects, leading to excess noise or, in some cases, spectral artifacts. In any case, it is essential to design an optical sampling system so as to minimize the effect of movement on performance.

Figure 1A is a simplified illustration of conditions which occur in a great variety of optical systems. The source "S" might correspond to a hot radiation source, the output slit of a monochromator, or the output end

Liquid Transmission

The fundamental absorbances corresponding to the functional groups of organic chemicals fall in the mid infrared "fingerprint" region of the spectrum. These absorbances are generally very strong. The use of a transmission cell for such a system would require a window spacing of typically 25 *jxm* or less. This requirement gives rise to a number of problems including poor flow characteristics, marked interference fringes due to the high refractive indices of most appropriate window materials, and the nonlinear response which occurs if the sample gap is wedged enough to overcome the interference effects (ref. 2). As a result, transmission cells are seldom used in this spectral region.

As one moves to the first overtone region, the optimum pathlength increases by more than an order of magnitude to typically 0.5 mm. At this thickness, it becomes practical to wedge the gap enough to overcome interference effects. However, two problems remain: the difficulty of fabricating appropriate wedged spacers for the still relatively small gaps and the need to minimize dead volume. At higher frequencies yet - where the observed bands are typically due to second and third overtones and combination tones - optimum sample gaps are usually 5 mm or greater. At this point, interference fringes no longer pose a problem and dead volume is generally quite low relative to cell volume. The sample interfacing task has become rather easy, albeit at the expense of considerably more difficult spectral analysis.

Attenuated Total Reflectance:

Attenuated total reflectance (ATR) makes the analysis of fundamental bands practical by providing the equivalent of a very thin transmission cell - typically 1 *fim* to 25 /xm depending on ATR element material and number of reflections employed. However, ATR has its own set of concerns. In particular, a potential for performance variation results from the fact that the effective pathlength depends on the angle of incidence of the IR radiation at the interface between the ATR element and the analyte. Any mechanical hange which affects the distribution of optical ray angles will result in a change in measured absorbance.

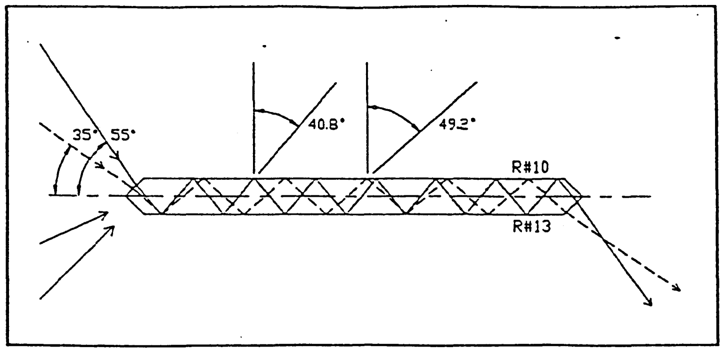

Figure 3: Generalized attenuated total reflectance (ATR) geometry using a circular cross section reflectance element.

Figure 3 illustrates a generalized ATR geometry using a circular cross section reflectance element. This type of element is generally preferred for process applications due to its compatibility with the use of "O" ring seals. For this figure, we are assuming that the IR radiation is focussed into the end of the rod so as to maximize the optical throughput for a given rod diameter. The range of ray angles incident on the entrance aperture will depend on the numerical aperture of the optics, typically ranging from 35° to 55°. As the light enters the element, the range of angles will be reduced in proportion to the inverse of the element's refractive index. However, there will typically still be enough variation to give rise to a significant variation in effective path length if the distribution of ray angles changes. For the focussed case shown, this distribution will be altered by any movement of the element, such as might occur during element replacement or removal for cleaning. This is due to the nonuniform distribution of ray angles as a function of position across the aperture surface. Once again, we see the importance of using collimated radiation in the critical portions of the optical system whenever possible.

Another limitation of ATR results from the fact that it is inherently a surface effect. Any condition which involves a nonuniform distribution of chemical composition in the analyte - such as adhesion of material to the rod - can lead to faulty measurements. However, experience has shown that this effect is less often a problem than one might expect. Of greater concern is the fact that the materials which have suitable IR transmittance and sufficiently high refractive index to be used as ATR elements in the fingerprint

^.1 Cross-Line Optical Transmission Systems:

The design of a cross-line system for IR liquid analysis provides a good vehicle for illustrating the use of the design principles discussed in Section 2.1. Figure 4 illustrates three possible approaches. Each of these assumes the use of a pair of diametrically opposed, single ended optical probes inserted into a cell body. This is a common approach in situations in which the sample interfacing device is mounted in line with the process flow. One of its most promising applications is the analysis of hot polymer melts during extrusion.

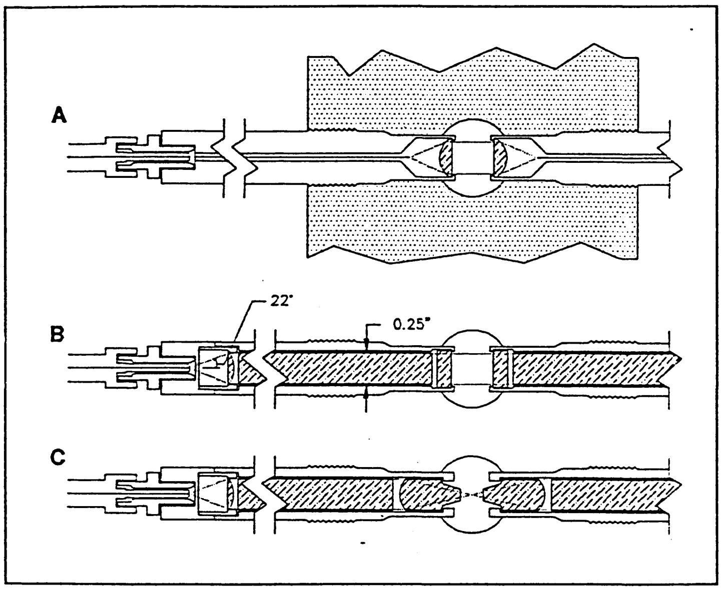

Figure 4: Cross line sampling system concepts. A: Use of fiber optics within the probe. B: Use of macroscopic light guide. C: Focussing windows for minimized gap cross section.

In the design illustrated by Figure 4A, a length of optical fiber is used to conduct the optical signal through the length of the probe. A combination lens/window is then used to form a collimated beam for transmission across the sample gap to the opposing probe.

This design has a number of drawbacks. First, it violates the rules laid down in section 2.1 by placing the most optically sensitive part of the system in contact with the sample, which will often be quite hot. To make matters worse, the optical fiber will have a much lower coefficient of expansion than the stainless steel probe body. If we assume that the fiber is anchored at the connector end to minimize changes in fringing, then the substantial temperature change which takes place when the probe is brought up to process temperature will necessarily lead to defocussing of the collimating optics. Finally, there is the fringing problem itself. (See Section 2.4.) This will occur whenever a conventional connector is used to interface between the fiber internal to the probe and an external fiber-optic transmission system. Although measures are available to minimize this problem, each of these has its own drawbacks.

From the viewpoint of the optical design purist, the design of Figure 4A has the additional defect of placing the convex side of the collimating lens toward the point source, thereby maximizing spherical aberration. However, reversing the lens would result in nonuniform pathlength, a factor that could be significant for small sample gaps. The relative importance of these two effects would have to be assessed on a case by case basis.

Figure 4B illustrates a design which obviates the problems evident in Figure 4A by placing the collimating lens at the end of the probe farthest from the hot process. This accomplishes two major objectives. First, it eliminates the thermal problems inherent in the use of an internal optical fiber and the placement of the sensitive optics in contact with the process. In fact, it allows the temperature of the collimating optics to be stabilized to any required degree by the use of an appropriate heat sink. Second, it eliminates the fiber-to-fiber connection and hence the problem of temperature dependent interference fringes. As a bonus, it also allows the collimating lens to be designed so as to minimize spherical aberration.

In the design of Figure 4B, the collimated optical beam is conducted through the length of the probe by a transparent macroscopic light guide. This will typically be fabricated from either fused silica or sapphire depending on the wavelength range being employed. The window in contact with the process is usually sapphire for maximum durability. Depending on the requirements of a particular application, this is either of a retroreflector to reverse the direction of the beam, allowing both the transmitting and receiving optics to be contained within the same probe. Since this folded path design can be inserted into a process through a single port, it is appropriate for large diameter lines, batch processes, and situations - such as in the screw region of an extruder - where access from both sides is not possible.

3.3 ATR Flow Cells

Figure 7 illustrates an optimized design for a liquid flow cell based on the ATR (attenuated total reflectance) principle, (ref. 5, 6). The figure shows a cross section through a plane containing the axis of the cell and corresponding to the plane of incidence for the rays shown (ie: an axial plane). The key element of this design is the use of a pair of 22.5° half angle reflecting cones adjacent to either end of a cylindrical ATR rod with 45° half angle conical ends. With collimated input radiation, the input reflecting cone reflects each ray through the same angle so that it enters the conical end of the ATR element at normal incidence. Thus, in this idealized case, every ray will strike the interface between the ATR rod and the analyte at the same angle (45°). Obviously, this design meets the requirement outlined in Section 2.1 above.

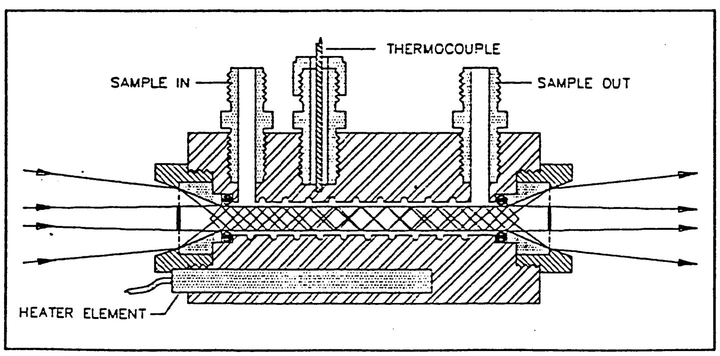

Figure 7: Optimized cylindrical ATR design.

In practical applications, flow cells using the above nonfocussing optical design - commercially called Tunnel Cells - are often used in the sample compartments of FTIR spectrometers. These typically employ focussed optics with a numerical aperture of something like 0.1 corresponding to a maximum divergence angle of typically 6° (as shown in Figure 7). In addition, the inherent interferometer field of view will result in a divergence of typically one degree. Adding these two factors, we see that the ray angles entering the Tunnel Cell can be inclined as much as 7° to the axis. On entering the ATR element, the divergence angle of a given ray will be reduced by a factor approximately equal to the element's refractive index (typically 2.4). Thus for this example, the maximum divergence from the nominal 45° at the analyte interface will be 2.9°. If conventional focussing optics - rather than the reflecting cone - were used to condense the IR beam to the diameter of the ATR rod, the divergence angle would be approximately 2.4 times greater.

By eliminating focussing in axial directions, ie: from all planes of incidence of the optical rays, the Tunnel optics design eliminates any significant effects on calibration due to mechanical displacements in these planes. Of course, given the unitary design of the optics, the only displacement that could take place would be movement of the ATR element along the axis of the cell. This would result in selective vignetting of rays. However, since all rays make approximately the same angle with the axis, no significant change in average penetration depth will take place.

It should be noted that, with the Tunnel design, beam condensing is accomplished by focussing in directions which can be projected in a radial plane. While this type of focussing does have some effect on angles of incidence for skew rays, the effect is far less than would occur if focussing were used in the axial planes. Furthermore, the mechanical design eliminates the possibility of relative movement in a radial direction within the cell.

3.4 ATR Immersion Probes

Figure 8 illustrates an immersion probe using the same optical design principles as the Tunnel Cell (ref. 7, 8, 9). In this case, metallic light guides are used to transmit a nominally collimated IR beam to and from the sampling optics. This establishes the optimum conditions for stability and linearity.

Probes based on the design illustrated in Figure 8 are widely used both in laboratories and for process monitoring. Laboratory probes are one inch in

3.5 Mid-IR Optical Conduit Systems

As noted in Section 2.4 above, the use of fiber optics for optical transmission over any useful distance is generally limited to wavelengths of 2.5 /zm or less. Not only are suitable materials not available for practical mid-IR fibers but also the relatively low emittance of radiation sources in the mid-IR combined with relatively low detector sensitivities results in a need for the highest possible throughput in the optical transmission system.

The need for high throughput can be met by the use of large diameter hollow metallic lightguides. As a practical compromise, we use nickel or gold plated brass tubing with a 32 mm inner diameter. This is a reasonable match to the diameter of the IR beam of process FTIR spectrometers. Given a uniform distribution of ray angles across the input aperture, the distribution at the output will be the same, (ie: throughput is conserved.) Of course there will be some signal loss due to reflection at the walls of the tubing. In practice, this is roughly equivalent to absorptions of p.07 AU/meter and 0.035 AU/meter for nickel and gold coatings, respectively, for short to moderate pathlengths (eg: up to 10 meters).

The large scale lightguides have been incorporated into a system of optical modules which we call the Axiot system (ref. 11). This includes stationary and switching mirror assemblies and a variety of adapters enabling the system to be used with virtually any combination of spectrometer and sample interfacing system. Most of the modules do not include adjustment provisions. In others, adjustment is possible. But this is usually only done once on initial installation. The adjustments are then epoxied so that no further movement can take place. The performance of this system is highly stable and predictable, and its large size and all metal construction renders it inherently robust.

The Axiot system was developed with the goal of making mid-IR remote analysis practical. However, it has also proved advantageous for use in the near-IR in situations where high throughput and/or stability are more important than long distance transmission.

3,6 Process Compatible Long Path Gas Cells

We've applied the same general principles to the design of long path gas cells as were used for the various liquid sampling systems discussed above. The most fundamental rule is the elimination of focussing optics from any region which will be subjected to temperature variations or other sources of strain. The result is a series of gas cells (the LFG Series) based on the same principles as the Axiot system of light guides (ref. 12). This basic design is illustrated by Figure 10.

In the LFG design, the optical path is contained within a tubular structure which is folded into a. convenient form factor by means of rooftop mirror modules. The gas to be analyzed is introduced into the cell at one end and exhausted at the other. As a result, there is complete overlap at all times between the IR beam and the analyte. Since the gas flows in a "plug"

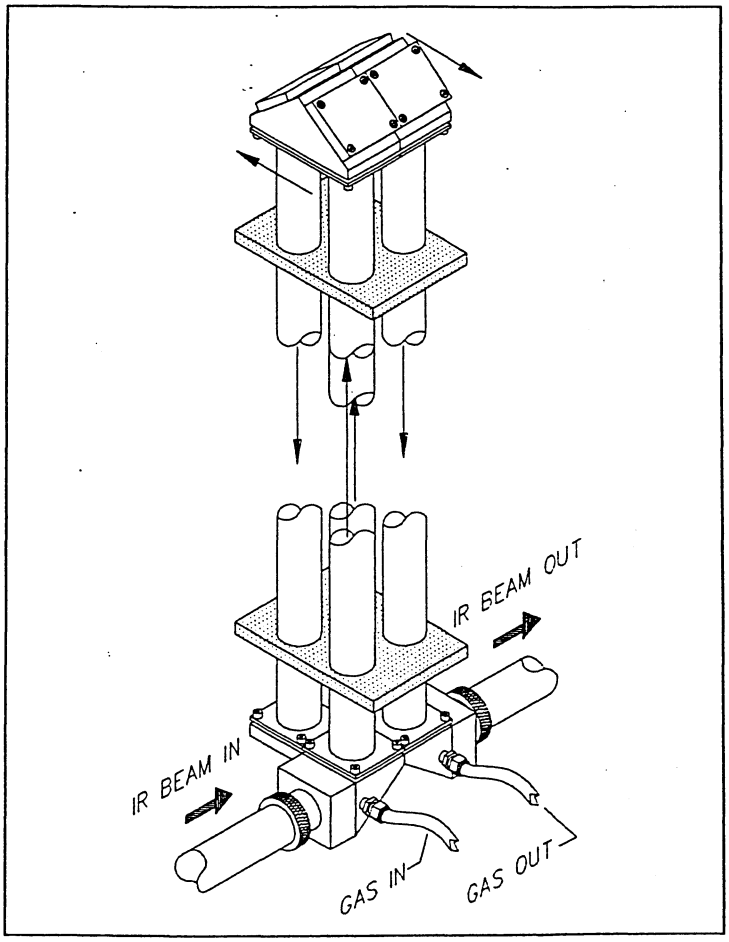

Figure 10: Linear flow gas cell using metallic light guides.

\. PERFORMANCE EXAMPLES

To test the stability of the optical designs used in our various probes, we simply immerse the probes in silicone oil and record spectra as the temperature of the oil is cycled between room temperature to 300°C. The end points of such an experiment with the FPT-720 NIR transmission probe (see Figure 6) are given in Figure 12. In each case, the spectrum is ratioed against an air background. Since the presence of the oil reduces the reflection loss at the surfaces of the sapphire windows, we would expect the measured absorbance in the absorption free regions of the spectrum to be below 0, as observed. The difference between the measured absorbances at the two temperatures is within the uncertainties encountered with slight movements of the optical fibers. The changes in the shapes of the silicone oil bands are an inherent characteristic of the oil.

Figure 13 is the result of a similar test of a model DPR-206E ATR probe. Here we do observe an increase in baseline absorbance at elevated temperature - especially at low frequencies. This is probably a result of the fairly high refractive index of the silicone oil combined with the temperature dependence of the ATR element's refractive index. If this decreases sufficiently at elevated temperature, a portion of the IR radiation will be incident on the interface at less than the critical angle and thus will be lost. We found this effect to be highly repeatable with successive temperature cycles.

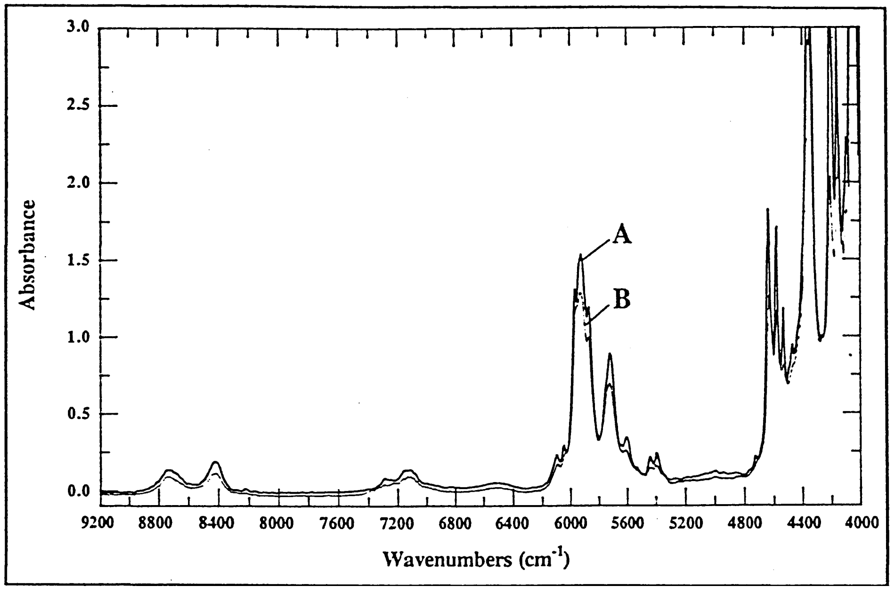

Figure 12: Near IR spectra obtained with a folded path transmission probe immersed in silicone oil at A: 25°C and B: 300°C.

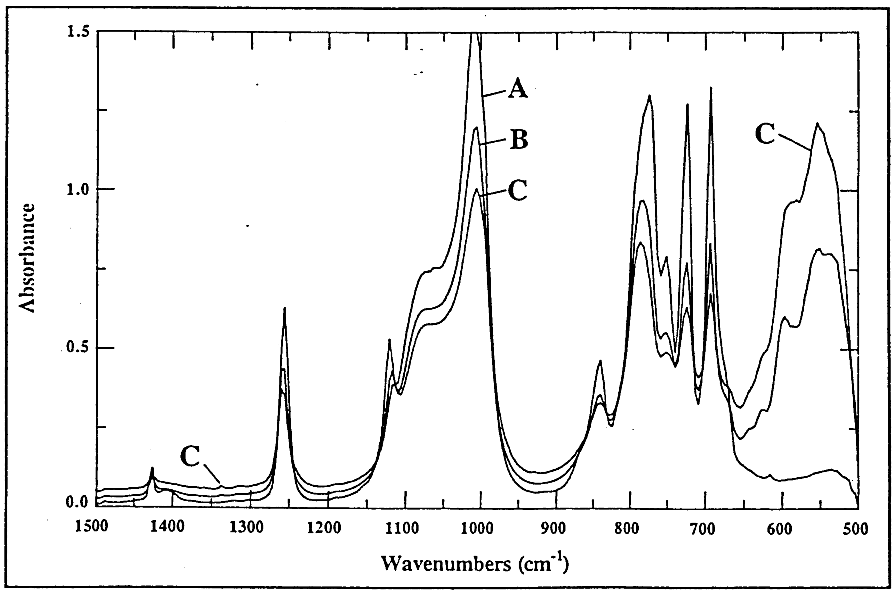

Figure 13: Mid IR spectra obtained with a two reflection ATR probe immersed in silicone oil at A: 25°C, B: 200°C, and C: 300°C.

f. CONCLUSIONS AND CAUTIONARY VOTES

This paper has reviewed the various guidelines that we use in designing spectroscopic sample interfacing equipment. One of the most important of these is the use of collimated radiation in any portion of the sampling system where differential movement might take place. As a further refinement, we should require that this radiation should be characterized by a uniform distribution of propagation angles at any point of the wavefront. The reason for this additional requirement is that the frequency scale of an interferometer depends on angle of propagation. Given an inhomogeneous wavefront, a change in vignetting due to movement of an aperture in the sampling system could give rise to a shift in frequency scale and hence a change in calibration.

We have omitted any discussion of optical aberrations since these are far less important in a spectroscopic sampling system than, for example, in an imaging system. Their primary effect in our case is pimply an overall reduction in signal.

We have also omitted any discussion of polarization effects. However, these can sometimes be significant since optical systems employing off axis mirrors tend to act as partial polarizers. The main area of concern here is the location of windows or other optical elements having significant birefringence between such partial polarizers. In such cases, the temperature dependence of the birefringence can lead to significant wavelength dependent transmission changes.

In addition to eliminating focussing optics from mechanically sensitive areas of an optical system, our guidelines call for eliminating adjustments whenever possible and for designing sampling devices as solid unitary structures with little or no allowance for relative movement of optical elements. These precautions have resulted in the development of a number of sample interfacing devices which exhibit a high degree of stability over a wide range of operating conditions.

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