

CRITICAL CONSIDERATIONS FOR SUCCESSFUL IN SITU LIQUID PROCESS SAMPLING FOR SPECTROSCOPY

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ABSTRACT

A sample interface that fouls or otherwise provides inconsistent or inaccurate measurements provides little benefit for process quality applications in oil refineries and downstream chemical manufacturing. The selection of the sampling interface needs careful attention to ensure the proper function of the analyzer. Considerations include material compatibility of wetted parts, temperature and pressure ratings, serviceability, flow requirements (Reynolds number and density), and direction of flow relative to the optical path. Discussion will focus on the fiber optic-based process spectroscopy of semitransparent liquids suitable for transmission measurements, with specific examples from a diesel fuel blending process, and from a synthetic fiber manufacturing facility. When considering a fit-for-purpose NIR or UV/VIS sample interface, care must be taken to ensure the vendor design constraints match your requirements.

INTRODUCTION

The sample interface is arguably the most critical decision any process engineer can make for a process analyzer. An analyzer regardless of any specified precision and accuracy will be rendered useless if the sample interface is inadequate for the application. A non-operating analyzer provides little benefit nor contributes to process quality or control. The selection of the sampling interface needs careful attention to ensure proper analyzer utilization for either optimization or ongoing process monitoring and control purposes.

The focus of this white paper will be limited to the fiber optic-based process spectroscopy instruments of semitransparent liquids suitable for transmission measurements with

UV/Vis or near-infrared (NIR). By moving light rather than process materials, the analyzer can be installed in a general-purpose environment, and an intrinsically safe sample interface can be installed in situ in a potentially hazardous (Class 1 Division 1 or zone 1) environment.

Careful planning is needed to select the analyzer type and location within the process. Process parameters (e.g., pressure, temperature, density, and flow rate) and the chemical compatibility of the sample streams with the analyzer hardware must be evaluated. Considering these parameters and their implications on the analyzer hardware ensures a fit-for-purpose measurement. Furthermore, the proper location for interfacing and monitoring the process must be identified to ensure it is consistent with the defined measurement goals. As an example, the location where a quality control “grab sample” is taken may be in a transfer line downstream from the reactor. This manual measurement is to be automated with a process spectrometer. If the analyzer is added after the reactor, the measurement will likely be limited to a post-reaction grab sample sent to the lab for inspection. Whereas, if an insertion probe is installed through the sidewall of the reactor, the chemical reactions can be monitored directly. The in-situ measurement allows process spectroscopy to provide real-time actionable information for process trim control. Depending on the desired measurement goal, either location may be ideal.

The following discussion provides selection considerations when working with process spectroscopy instrument providers.

GENERAL CONSIDERATIONS

Every analyzer vendor has an application worksheet that collects information necessary for a technical sales proposal. Vendors have their selection criteria based on the types of products they offer. In the case of process spectroscopy, the site engineer needs to work with the sales team to select the sample interface. For some applications, buying the analyzer and probes from different vendors may be better. When considering the sample interface, care must be taken to ensure the material compatibility of wetted parts, temperature and pressure ratings, serviceability, flow requirements (Reynolds number and density), direction of flow relative to the optical path, and other parameters. These considerations can be used to select the type of optical sample interface best suited to the process. The following sections get more granular regarding selecting the sample interface.

MATERIAL COMPATIBILITY

Selecting the proper metallurgies and elastomers for constructing the sample interface is vital for stable, long-term operation. A sample interface is only fit for purpose if it is compatible with the process to be monitored. If measuring trace water in an acid stream, a Teflon flowcell body may last longer than a 316 L stainless steel body. Durability also depends on how the optics are sealed in the sample interface. Typically, this is achieved

with Viton™, Kalrez™, or Markez™ O-rings. O-Ring seals require scheduled changeout. Alternatively, a thin metal braze such as GEORO™ can be used as a more permanent seal. Regardless of the seal type, process reactivity must be considered. For example some amines species may reactive with the braze material, but are perfectly compatible with Kalrez™ 6375.

Sealing technology can be of critical importance. The following questions should be considered: What is your occupational health and safety risk if the primary seal fails? Does the probe have a secondary backup seal in case the primary fails? Is the proposed seal compatible with the process chemistry?

TEMPERATURE, PRESSURE, AND FLUID DENSITY FLOW CHARACTERISTICS

Likely, the most straightforward parameters to consider when selecting a sample interface are the design temperature and pressure of the process stream and if parameters are within the design limits of the sample interface. Some additional considerations include: If the pressure is over 500 psi, should a hydrostatic test be performed to verify the workmanship of the sample interface and reduce the risk of a leak? Will the probe hold up to the thermal cycling of the process, or will the optics or seal fail due to incompatibility with a material coefficient of expansion?

Figure 1 depicts a probe body that yielded to process conditions. In this real-world example, a the probe was exposed to process pressure that exceeded the strength of the schedule 40 stainless pipe used for the body. As shown in the photo, the insertion tube collapsed around the internal fiber optic cables, but the seal on the optical path and at the welded flange was intact. Despite the mechanical deformation of the tube, the probe still optically functioned, and the failure did not cause a process leak.

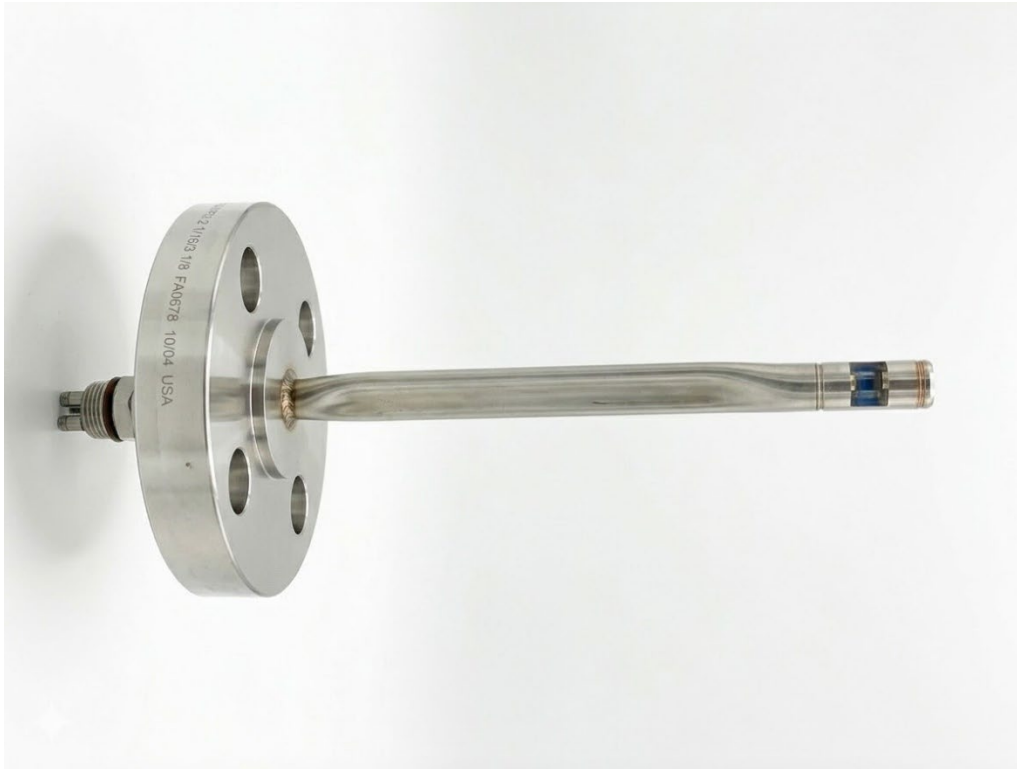


FIGURE 1. FAILED PROBE DUE TO PROCESS PRESSURE EXCEEDING DESIGN SPECIFICATIONS

Process fluid density is often an overlooked process parameter in sample interface selection. All materials have leak rates. This is why balloons filled with helium are usually deflated after a few days. For a metal braze seal on an insertion probe, the vendor will typically conduct a helium leak test and then rate the probe as water-tight, fuel-tight, or virus-tight [1]. Leak rate tests are typically performed at room temperature. If the process stream has low density, high temperature, and high pressure, it is more likely that the process may find a pinhole defect in the seal, creating a leak. Many vendors offer dual seals to reduce the risk of the process escaping into the environment. It is essential to understand if the leak rate of the probe is sufficient to avoid an unexpected leak for your process conditions.

Figure 2 shows a real world example where a GEORO™ brazed insertion probe was installed in a process location that underwent a thermal event exceeding the specifications of the probe design. The thermal event caused discoloration of the steel and likely exceeded the reflow temperature of the braze. This resulted in the delamination of the bottom optical window and allowed the inside of the probe to fill with process. Fortunately, the probe was designed a secondary seal that prevented a process leak. Without a functional probe, the analyzer malfunctioned and therefore the control room was blind. The site was forced to increase the frequency of grab samples being run in the lab and ramp down production to avoid bad batches.



FIGURE 2. FAILED PROBE DUE TO THERMAL EVENT EXCEEDING SPECIFICATIONS

FLOW CHARACTERISTICS

Most sample interfaces require consistent and fully developed process flow through the light beam or optical path. Either laminar and/or turbulent flow is typically recommended. Bubbles or other types of two-phase sample flow disturbances (separation of solvent and solutes) can occur with Reynolds numbers between 2000 and 4000 and are not ideal for most sample interfaces. Figure 3 demonstrates the flow-induced noise vs. Reynolds number. When the flow transitions between laminar and turbulent flow, measurement noise increases. If these types of flow induced noise occur, the process stream may violate the assumptions of Beer–Lamberts law and cause erroneous readings to be reported by the analyzer.

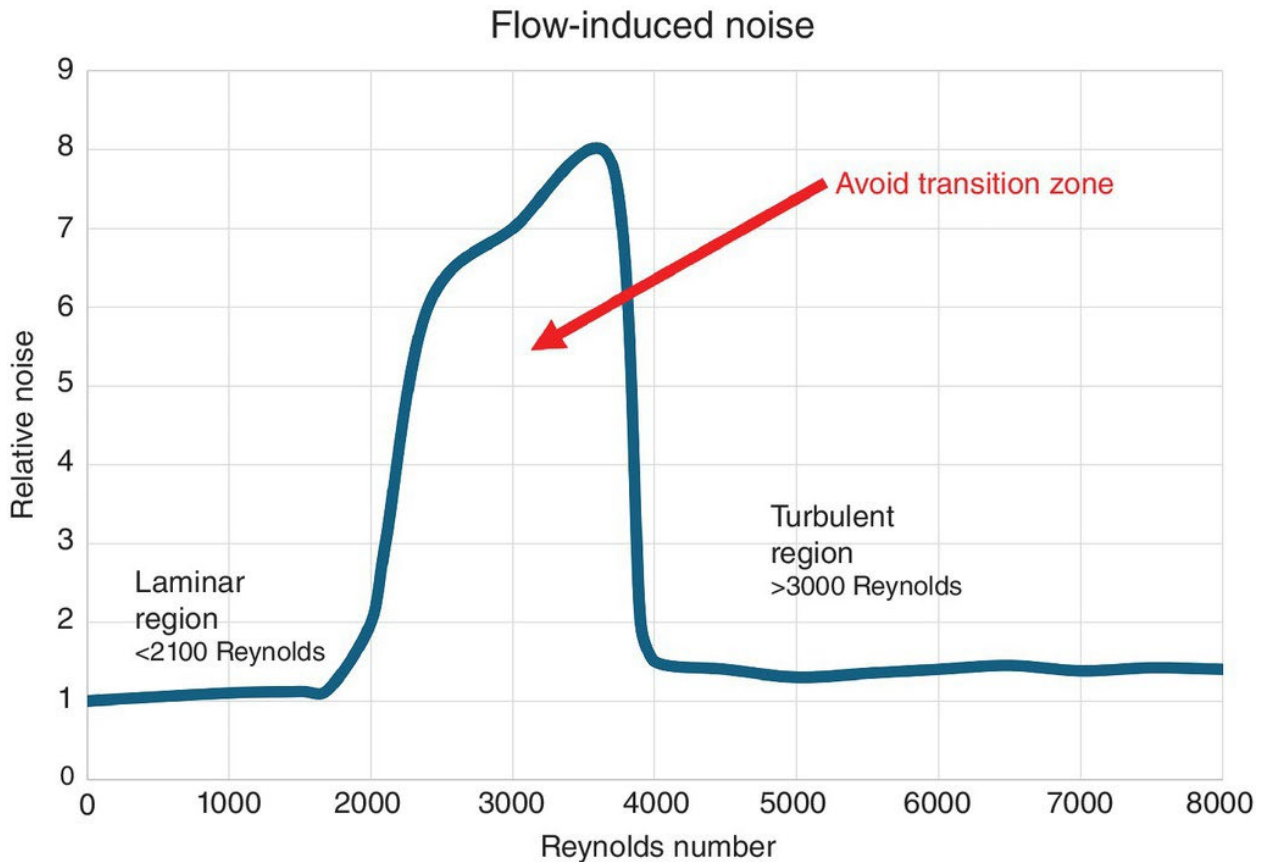


FIGURE 3. EXAMPLE CHART OF RELATIVE NOISE VS REYNOLDS NUMBER

In fluid dynamics, there is a concept of an “entrance limit,” which refers to the distance required for the flow to be fully developed[2]. The requirement of fully developed flow is not limited to spectroscopic measurements; many types of flow instrumentation, such as flow meters, require a fully developed flow to function properly[3]. This implies that many of the same rules for where to place a flowmeter in a process pipe apply to an inline optical flowcell. In the author's experience, the general rule is to select a sample installation point 10 times the pipe diameter downstream from pipe elbows and avoid pre-pump suction zones. In practice, if you have a 90° bend in a ½ inch pipe, there must be at least 5in. of straight pipe before and after the flowcell to ensure a fully developed flow maintained in the optical path.

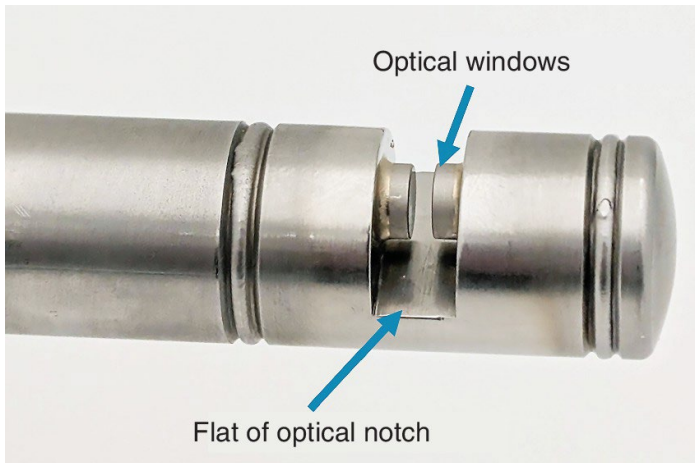


FIGURE 4. ANATOMY OF A TRANSMISSION PROBE. OPTICAL WINDOWS CONTROL THE SPOT SIZE. THE DISTANCE BETWEEN THE WINDOWS IS THE OPTICAL PATHLENGTH. THE FLAT OF THE OPTICAL NOTCH IS A SLOT.

In the case of optical transmission insertion probes, the angle of the flow relative to the flat of the optical path or optical notch is also an important consideration, see Figures 4 and 5. If the flat is parallel to the flow, then cavitation, due to flow over a sharp edge, can occur, causing bubbles or fouling. If the flat is perpendicular to the flow, process fluid flow between the optical windows will be sporadic and may lead to stagnation. The flow angle recommended by vendors is typically between 5° and 45° . It is the author's experience that 3° – 7° of “bite” relative to the process flow, provides for best measurement practice. This technique provides a “micro-zone compression” that helps push the sample through the optical notch and, therefore, fully developed flow (no stagnation, recirculation) between the optical windows.

Single sided optical transmission probe

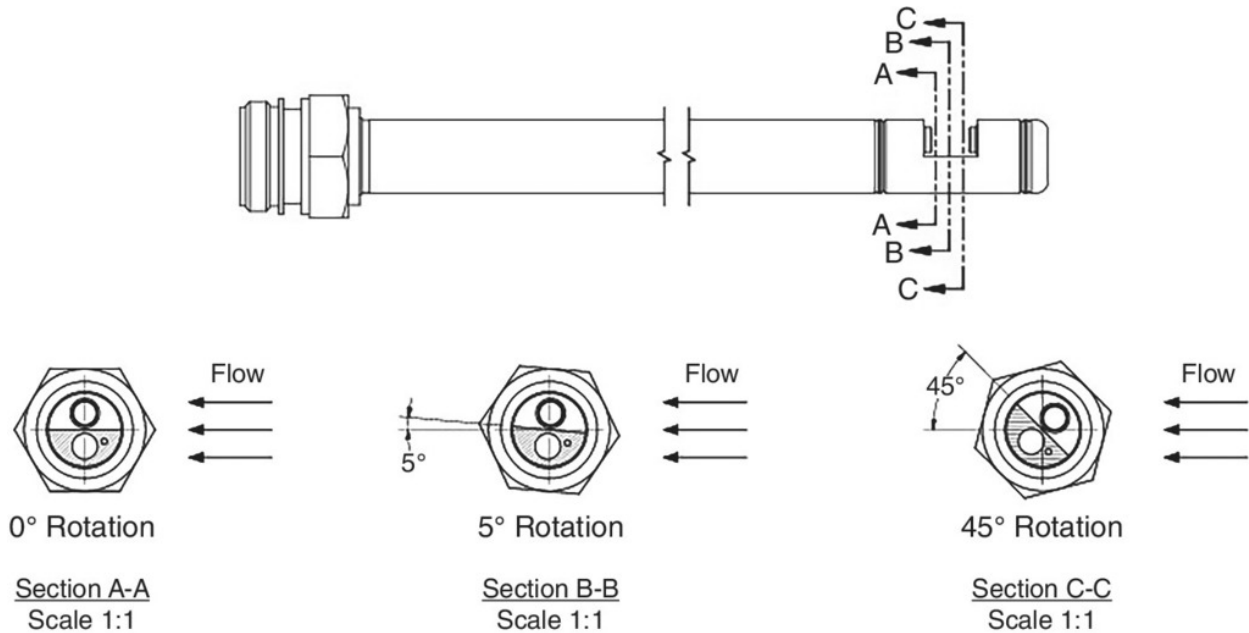


FIGURE 5. SECTIONS LINES A, B, AND C ILLUSTRATE FLUID FLOW THROUGH THE FLAT IN THE OPTICAL PATH OF A TRANSMISSION PROBE AT VARIOUS ANGLES.

Larger angles such as 45°, increase the blockage effect of the insertion probe in the pipe. In order to maintain continuity of volumetric flow, the fluid velocity through the optical notch in the probe must increase. Therefore the process fluid will accelerate as it transit the optical path. However, faster transit time is not always better for representative sampling. In the case of liquid polymers, care must be taken to ensure shear-induced gelation and thermal trigger due to adiabatic heating are avoided. A simple fluid flow computational model can be used to optimize the angle of an insertion probe for any specific process stream.

PATHLENGTH REPRODUCIBILITY

When designing an optical sampling system, be certain to ask the vendor for information regarding the reproducibility of the optical pathlength. Some vendors offer adjustable optical pathlength sample interfaces. These are suitable only for proof-of-concept benchtop studies or R&D at the beaker level. However, a fixed pathlength is essential for process applications to achieve precision needed for “trim control” process adjustments. Routine maintenance such as disassembly for O-ring replacement should not alter the optical path. To overcome variability, some analyzer vendors include a pathlength correction within the chemometric preprocessing tools used for calibration model development. Reducing errors at the point where the actual measurement occurs, will improve precision and accuracy compared to mathematical correction for measurement

variances such as pathlength deviations. In transmission optical spectroscopy, a pathlength variance of no more than $\pm 0.2\%$ allows sample interfaces to be interchangeable without impacting calibration performance. The change in absorbance due to small pathlength variance is typically less than the diurnal thermal noise in the fiber optic cables connecting the sample interface to the analyzer.

SERVICEABILITY

A sample interface that is fit for purpose will also be designed to allow easy routine service and consider other occupational health and safety risks. For example, a cleanout port in a flowcell can be immensely useful, but if the process is pyrophoric, the cleanout port may become a risk that should be avoided. The frequency of how often you have to clean the probe, change the O-rings, or take a new reference (background correction) is a critical factor for determining the user's serviceability requirements. These considerations will be process-specific. A flowcell installed in a sample conditioning system for measuring the cetane value of diesel fuel will require less frequent maintenance than a probe installed in a transfer line measuring the polyol content of a polymer or paint. Some questions when considering serviceability requirements: Is the process likely to plug the sample interface? What will the procedure be for removing the sample interface from service for cleanout maintenance? How often will the O-rings need to be replaced? Should a bypass line for a flowcell, an insertion probe on a gear-driven extractor, or a flanged probe that can only be removed when the whole line is depressurized? If the sample interface needs to be factory serviced, how far away is the factory, and what is their typical turnaround time for an O-ring service?

Figure 6 is another real world example; an insertion probe and mechanical extractor are installed in a pipe under an I-beam. Care was not taken by the integrator to ensure that the vertical clearance was sufficient to allow the probe to be fully extracted from the process pipe. The top of the probe contacts the bottom I-beam, while the bottom of the probe is still in the top third of the process pipe. The vertical clearance issue prevents the isolation valve from closing and therefore the extractable probe cannot be serviced.



FIGURE 6. INADEQUATE INSTALLATION DESIGN PREVENTING PROPER MAINTENANCE

In Figure 7, A Teflon flowcell was installed with the with the removeable cleanout plug facing the back of wall of a junction box. This installation decision prevents the cleanout port from being access and requiring the probe to be completely removed from service for basic maintenance. Best practice is to have a flowcell on a block and bleed setup and the cleanout port accessible.

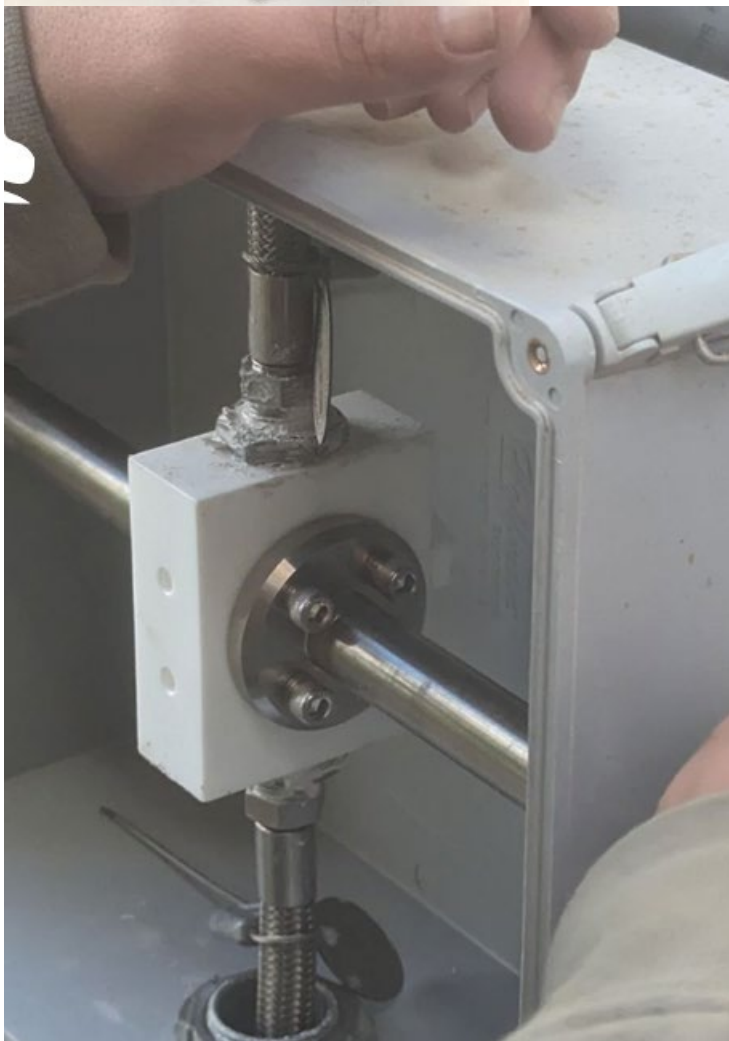
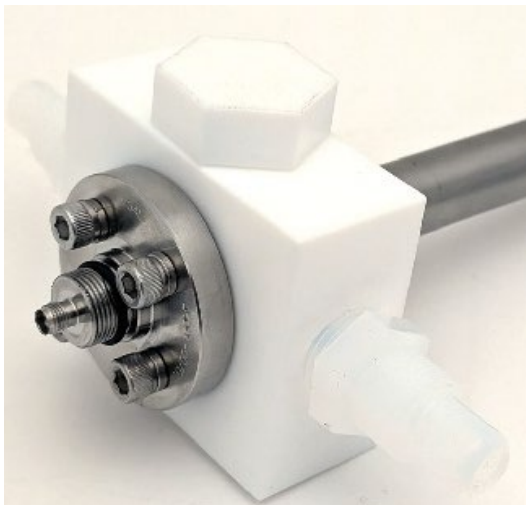


FIGURE 7. FLOWCELL INSTALLED PREVENTING ROUTINE MAINTENATNACE VIA CLEANOUT PORT

CONCLUSION

When considering adding process spectroscopy for process monitoring, it is important to ask the right questions and ensure that the complete analytical solution (spectrometer and sample interface) is fit for purpose. This requires considering that the analyzer and probe are correctly designed for making the measurement and that the physical installation in the analyzer shed or process pipe does not add noise sources or negatively impact serviceability. If the implementation of process spectroscopy is poorly thought through, then the value added by the technology cannot be realized.

REFERENCES

1. US Code of Federal Regulations (e-CFR), 40 CFR Part 98, Subpart RR, Section 98.443
2. US Code of Federal Regulations (e-CFR), 21 CFR Part 184.1240
3. ASTM standard E1747-95 (Reapproved 2005) Standard Guide for Purity of Carbon Dioxide Used in Supercritical Fluid Applications (ASTM International, 100 Barr Harbor Drive, P.O. Box CB700, West Conshohocken, Pennsylvania 19428-B2959, (800) 262-1373