

Insertion Probes vs. Slipstreams for Real Time Reaction and Process Monitoring

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ABSTRACT

The chemical composition of a fluid in a reaction vessel or process line can be monitored in real time by using spectroscopic sensors. FTIR spectroscopy is particularly useful as it provides very specific chemical information on both the chemical identity of the components in the mixture and on their concentrations. This information can be used for real time reaction/process control. To achieve spectroscopic monitoring electromagnetic radiation has to be brought into spectroscopic interaction with the processed material. There are two possibilities; either light is brought to the sample or the sample is brought to the light. A general discussion of the advantages and disadvantages of the two approaches will be presented and real examples of both techniques are discussed.

INTRODUCTION

FTIR spectroscopy provides a powerful means for real time in situ reaction or process monitoring. This monitoring can be achieved in two ways: in situ via insertion probe or via flow through cells installed in slipstreams. In the first case an insertion probe is inserted into the process material through a port in the vessel wall and light is guided down the probe to a sensor at the probe's tip and then guided back to be analyzed. A spectrometer, attached to the probe, analyzes returned light and extracts the desired analytical information. Fig.1 illustrates this approach. In the second case a continuous stream of the reacting liquid is extracted from the vessel and piped to a spectrometer where it is analyzed in a liquid flow cell and then either discarded or returned back into the process. Fig. 2 illustrates this approach. Each of the two methods has its advantages and disadvantages.

Whichever way it is obtained, the information extracted from the measurement is complex and multifaceted. Spectra of complex mixtures containing many individual components can be analyzed using standard chemometric software and the concentration of each component can be calculated. In addition, the high specificity of IR spectroscopy enables detection, identification, and, sometimes, quantification of the unknown and often unanticipated contaminants. The information thus obtained can be used to provide real

time monitoring and documenting of process reactions. Once the necessary confidence in the spectroscopic measurement is reached, the outcomes of the measurements can be fed back into the process control room and used to automatically pull the levers, open or close valves, etc.

There is a great deal of comfort with not having to extract sample out of the process line or reactor. The sample is analyzed *as is* in the vessel. In many cases the reaction conditions are such that the processed material is corrosive, or at a high pressure, or at a temperature far from ambient, or any combination of these conditions. The flow of processed fluid through a slipstream interrupts the process conditions. These conditions have to be maintained in the slipstream so that product degradation does not occur during the measurement.

On the other hand, slipstreams offer much greater flexibility. For instance, if something with the sensing element goes bad during the process, it would not be easy at all to withdraw the probe and investigate the problem, especially if the vessel is pressurized. With slip streams it is easy to close the valve on the line that brings the sample to the cell, disconnect the cell from the stream, replace it, open the valve, and continue monitoring. The slipstream option also offers a much broader selection of flow cells. One can use either transmission or ATR flow cells and utilize virtually any level of sensitivity that is needed to optimize the S/N of the measurement. With insertion probes the choice of sensing elements is limited. For all practical purposes all that IR insertion probes can really use are sensing elements based on the ATR spectroscopic technique.

INSERTION PROBES

Insertion probes use two ways to guide light to the sensor and back. One way is to use fiber optics; the other way is to guide light through an open tube. Both ways are fairly delicate and both require sophisticated optical designs to optimize performance. Also, both approaches result in significantly reduced optical signal levels and hence are generally used in conjunction with liquid nitrogen cooled detectors. Since the dewars of liquid nitrogen cooled detectors need to be refilled at least daily, they are not very convenient to use in process environments.

A particular schematic representation of the use of an insertion probe for *in situ* analysis of process streams specifically the Durasens DP-R Series Diamond ATR Fiberless Probe is shown in Fig.1

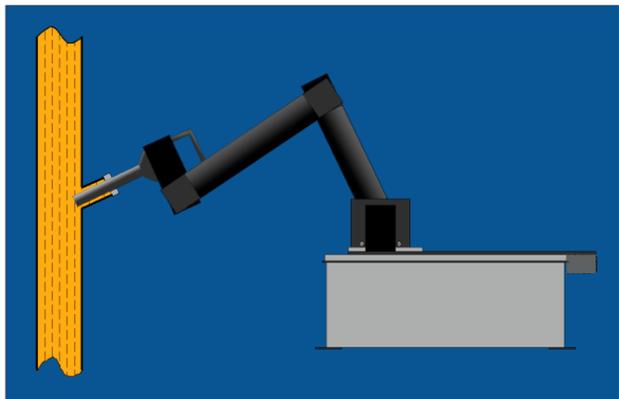


Figure 1 Schematic representation of the use of the Durasens DP-R Series Diamond ATR Fiberless Probe for *in situ* real time stream monitoring

This probe does not use fiber optics to communicate light between the spectrometer and the sensor. The probe connects to the spectrometer by means of a flexible articulated optical arm that uses only metal mirrors to direct light from the spectrometer to the sensing element at the end of the probe and back to the spectrometer for analysis. The light path within the arm is enclosed in a purged environment to remove atmospheric interferences in the collected spectra. The Arm can reach up, down, and forward, and the probe can be oriented at any angle to match the port configuration on the line or vessel.

This approach to guiding light between a spectrometer and a probe does not suffer from the spectral range restrictions typically encountered with optical fibers. The entire spectral range is accessible. Spectral range restrictions, if any, come from the spectrometric sensor. This approach also provides higher optical efficiency in many cases enabling the use of room temperature detectors.

As mentioned above, most IR probes utilize ATR spectrometric sensors. However, the use of transmission spectrometric sensors is fairly common for NIR probes. The reason why transmission sensors are not used with IR probes has to do with the shortness of pathlengths needed in IR. For instance the pathlength of 100 μ m is commonly used in IR transmission cells. If such a short pathlength was used in a transmission IR probe, the process liquid surrounding the probe element would have to somehow penetrate into this narrow space from the outside without the benefit of the fluid being forced

in, as it is in transmission flow cells. Even if sample penetration occurred spontaneously, the liquid that penetrated between the two windows would likely become stagnant and hence would not reflect the changes occurring in the process, thus rendering the probe ineffective. If the space between the two windows somehow got clogged, the probe would have to be fully disassembled for cleaning and then reassembled for the next run. Such a delicate operation is not realistic in process environments. Thus, despite the great allure of transmission sensors, ATR remains the only viable approach for IR probes.

Most insertion ATR probes use ATR elements that provide either one or two reflections. These sensors provide a sensitivity that is adequate for applications where only the major components in the process stream are monitored. There are a few probes that use multiple reflection ATR elements¹. These probes provide a significant step-up in sensitivity. In the majority of cases diamond is used as the ATR material. Diamond lattice absorptions partially obscure a portion of the spectral range roughly between 1800 cm^{-1} and 2600 cm^{-1} and, especially with the multi-reflection probes, the lattice absorptions may interfere with the measurements of some compounds that have absorption bands in the affected spectral region.

While the use of multiple reflection ATR probes may significantly increase the sensitivity with respect to one or two reflection probes, even these multiple reflection probes cannot provide the enormous sensitivity that is offered by i.e. a transmission cell with a 200 μ m pathlength.

SLIP STREAMS

Slipstreams require the process fluid to be brought from a vessel to a cell inside the spectrometer for analysis. A schematic illustrating this approach is shown in Fig.2. Arrows next to the fluid lines indicate the flow of the liquid. A pump can be used to divert a stream of sample through the flow cell and return it back. In some cases the existing flow, or pressure of the process fluid can be used and eliminate the need for a pump. The slipstream can be set up using the same type of access port that is used for insertion probes. In other words, the slipstream setup does not require any additional installations.

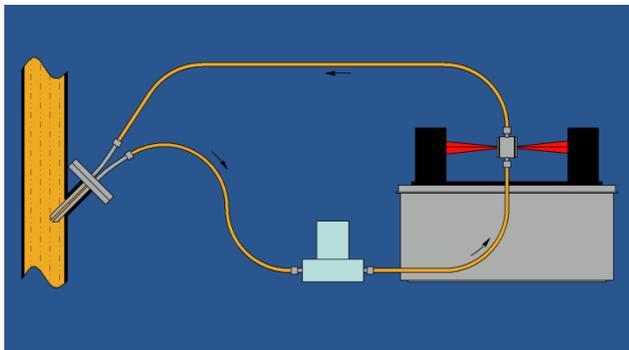


Figure 2 Schematic representation of the use of the Durasens Rapid Flow Cell attached to a slipstream via a Durasens probe like slipstream feeder for real time stream monitoring.

The main advantage of slipstreams is that they allow many different types of flow cells to be employed, from single reflection ATR cells to 20 m pathlength gas cells. This enables cell pathlengths to be selected virtually without limitation.

One can adjust the pathlength of a transmission cell almost at will, but at very short pathlengths (typically under 25 μm and generally dependent on the viscosity of the sample) the flow of liquid through the cell becomes difficult, tiny particulates in the stream may accumulate and clog, which will impede the flow. The flow through the cell may become uneven, or the resistance to the flow may generate a too high backpressure in the input line. Fortunately, for shorter pathlengths one can use ATR flow cells, which can employ either single reflection or multiple reflections. The clear benefit of using ATR cells in these cases is that these cells do not present a restriction to the flow of liquid through the cell. The space above the ATR element in the cell is not restricted and can be as large as necessary to facilitate good flow conditions.

Note that the monitoring strategy illustrated in Fig.2 is not limited to liquids. It can be just as well used for gas analysis. In the case of gas streams, the flow cells would be gas cells. Gases are generally a thousand times less dense than liquids so the pathlengths of gas cells are typically a thousand times longer. In many cases single pass 10 cm pathlength cells are adequate, but other situations may require pathlengths in tens of meters. The cells in those cases are multiple pass cells. Mirrors are used to fold the beam path through the cell 10 to 100 times so such cells, despite the huge pathlengths, fit easily in the same place in the spectrometer as the liquid cell does in Fig.2.

The use of transmission liquid cells in slipstreams sometimes brings the problem of how current is the information obtained. As indicated in Fig.2, the liquid is

picked up from the process line or vessel and carried through the slipstream to the flow cell. If the cell is using a short pathlength, say 100 μm , the resistance to the liquid flow could be significant. That reduces the rate of flow through the slipstream and can cause the sample travel time between the port and the cell to be long. For instance, if the speed of flow of liquid in a 1 m long slipstream is 5 mm/s, the time of travel between the port and the flow cell is 200 s (over three minutes!). In those cases where the level of sensitivity required for the measurement is such that ATR insertion probes just cannot be used and a slip stream fed transmission cell is the only realistic solution, bypass loops around the cell are sometimes constructed to speed up the flow of liquid through the slip stream by shortening the length of the portion of slip stream input line within which the sample flow rate is restricted. This does solve the initial problem, but can have as an unintended consequence that all the flow then could go through the bypass loop. Regulating the split of the flow between the bypass loop and the cell is difficult to start with, but it could be further complicated by the change of the viscosity of the sample as the reaction proceeds.

A more effective solution is offered by the Rapid Flow Cell (Durasens, Pleasantville, NY), which is constructed in such a way that provides rapid unrestricted flow through the cell at any pathlength. This cell uses the siphoning effect generated by the rapidly flowing sample to help flow fluid through the space between the windows.

CONCLUSION

We reviewed the pros and cons of using insertion probes vs. using slipstreams for reaction and process monitoring by IR spectrometric techniques. Not unexpectedly, we conclude that each approach has its upsides and its downsides. Those who plan on utilizing spectroscopic reaction or process monitoring should carefully review all the requirements their process imposes and explore all the available options. Despite the insertion probes currently being in vogue, in some applications slip streams² may have significant advantages.

REFERENCES

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