

# Insertion Probes vs. Slip-Streams for Reaction and Process Monitoring by FTIR Spectroscopy

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## Abstract

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 immersion probes or via flow through cells installed in slip streams. FTIR spectroscopy 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 methods is presented and real examples of both techniques are discussed.

## Introduction

FTIR spectroscopy enables real time in situ monitoring of the chemical composition of process liquids. This monitoring can be achieved in two ways: in situ via immersion probes or via flow through cells installed in slip streams. 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 techniques and the concentration of each component can be calculated. In addition, the high specificity of IR spectroscopy enables detection, identification, and, sometimes, quantification of 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.

When using an insertion probe, the process fluid is analyzed as *is* in the vessel. In many cases the reaction conditions are such that the processed fluid is corrosive, or at a high pressure, or at a temperature far from ambient, or any combination of these conditions. It is advantageous not having to extract the sample out of the process line or reactor.

On the other hand, slip streams offer much greater flexibility. For instance, if something with the sensing element goes bad during the process, it would not be easy 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 slip stream 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 used in IR spectroscopy, the choice of sensing elements is limited to those based on the ATR spectroscopic technique. However, the flow of processed fluid through a slip stream interrupts the process conditions. These conditions have to be maintained in the slip stream so that product degradation does not occur prior and during the measurement.

## Insertion Probes

An insertion probe is introduced into the process liquid through a port in the vessel wall. Light is guided down the probe to a sensor at the probe 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.

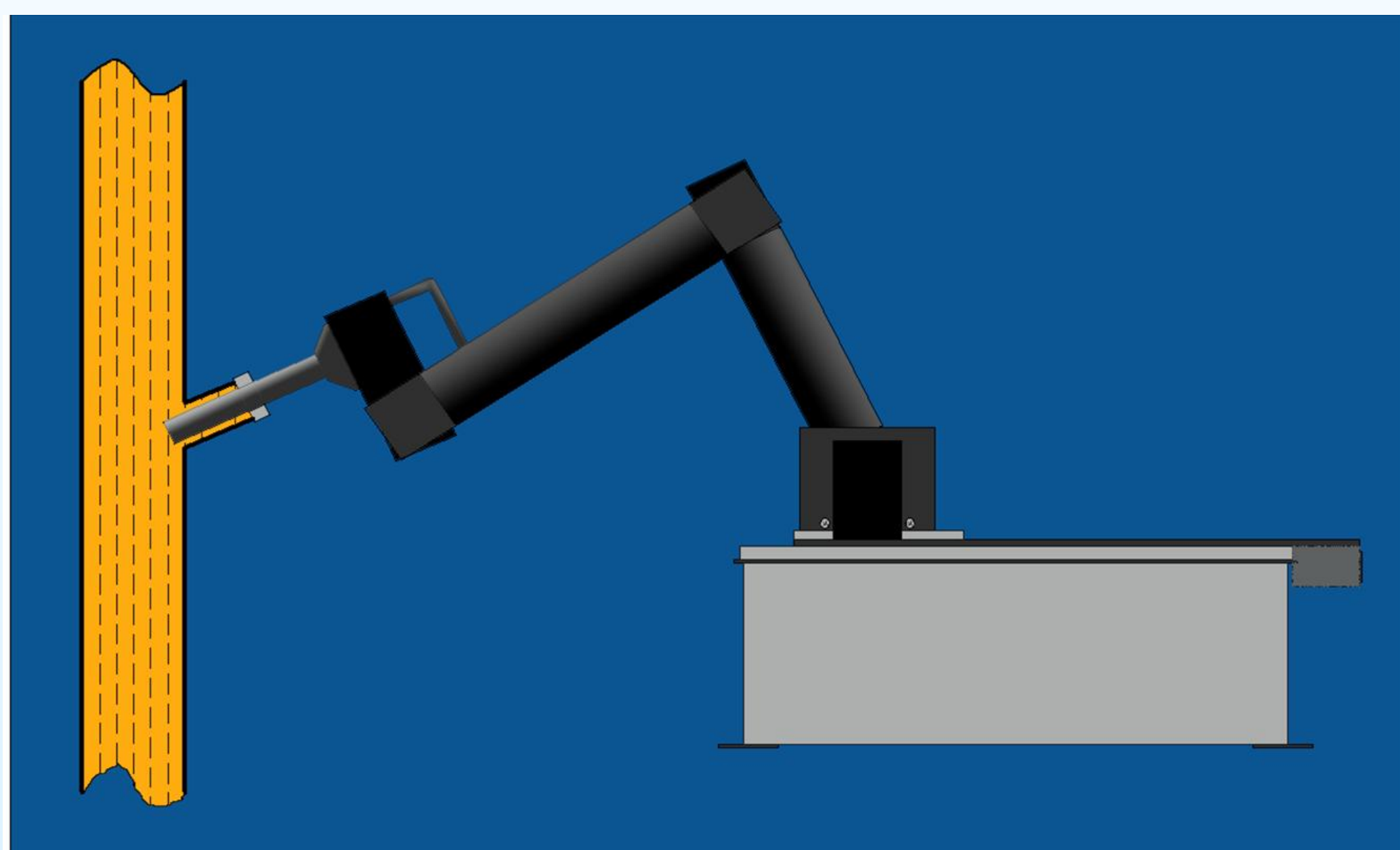


Figure 1 Schematic representation of the use of the DuraProbe™ with the Duralyzer™ for *in situ* real time process stream monitoring

### Advantages:

- Sample analyzed as *is* in the vessel

### Disadvantages:

- Only ATR sensors are possible, limiting the range of the effective pathlengths
- Generally low signal requiring highly sensitive liquid nitrogen cooled detectors
- Probes cannot be serviced without shutting down the process

Insertion probes use two ways to guide light to the sensor and back to the spectrometer. One way is to use fiber optics; the other way is to guide light with the use of mirrors. Fiber optics are simple to setup and are maneuverable, but limit the available spectral range and have low energy throughput. On the other hand when using mirrors to guide light, the full spectral range is available and much higher signal levels are achievable, in some cases allowing the use of room temperature detectors. However, probes with mirrors are less maneuverable.

Insertion probes in the IR spectral region are almost exclusively based on ATR sensors. These ATR sensors typically use either 1 or 2 reflections thus having relatively short effective pathlengths. Multiple reflection ATR probes are also possible<sup>1</sup>, but no ATR sensor can achieve the sensitivity of a 0.25 mm pathlength transmission cell.

## Slip Streams

A continuous stream of the reacting fluid is extracted from the vessel and piped to a spectrometer where it is analyzed in a liquid or gas flow cell and then either discarded or returned back into the process. Fig. 2 illustrates this approach.

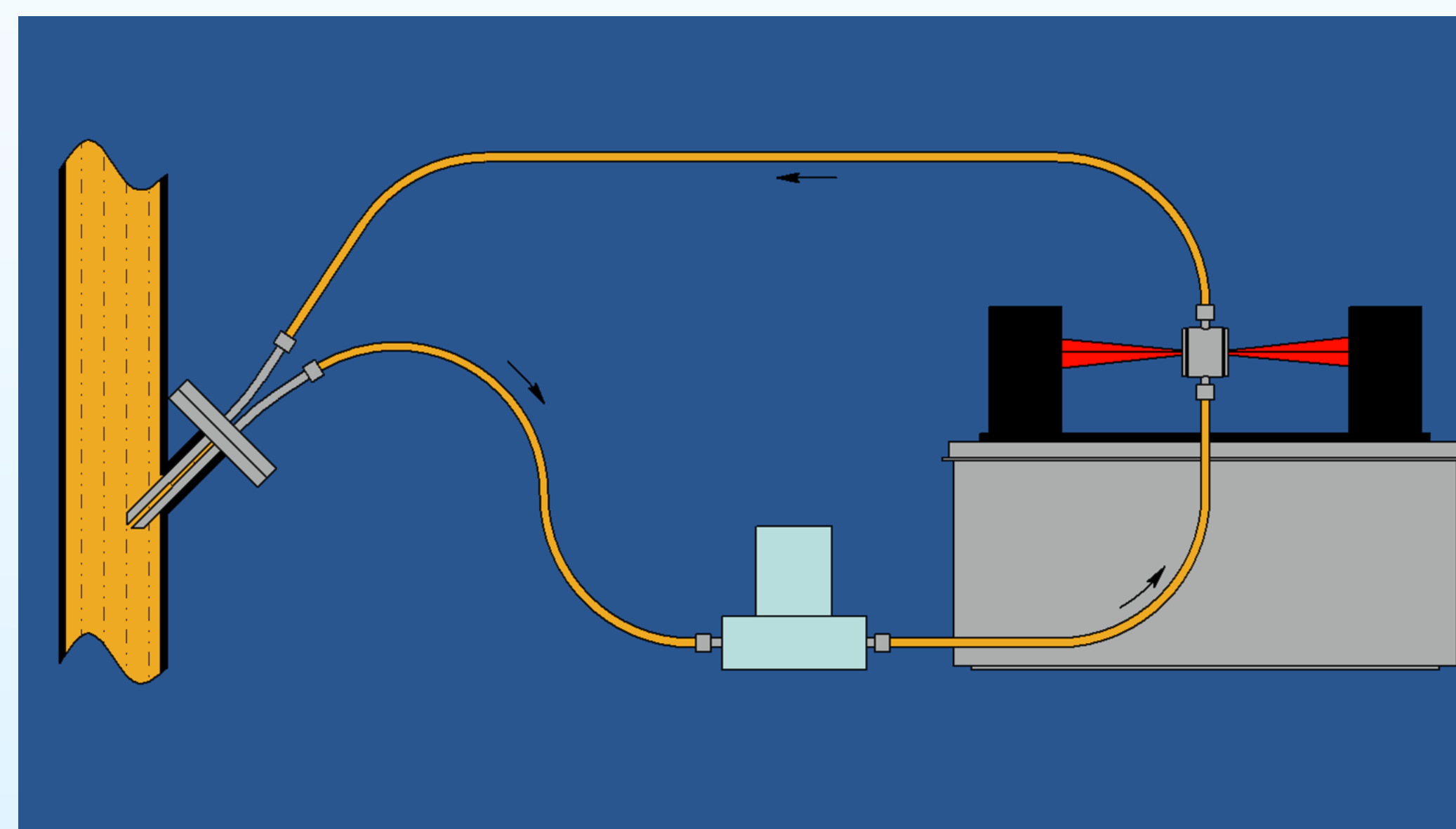


Figure 2 Schematic representation of the use of the Rapid Flow Cell™ in the Duralyzer™, attached to a slip stream for real time process stream monitoring

### Advantages:

- Can be used with both transmission and ATR cells
- Can analyze both liquids and gases
- No restrictions on spectral range
- No restrictions on spectrometer signal level
- Slip stream can be shut down for cell maintenance

### Disadvantages:

- Setup is more involved than inserting a probe
- The sample needs to be taken out of the process

Transmission flow cells present virtually no resistance to flowing liquids for pathlengths above 1mm. Below 1 mm the narrow pathlength may become an impediment to the flow, especially for viscous liquids. For pathlengths below 0.1 mm ATR flow cells are more appropriate. ATR cells with effective pathlengths longer than 0.1 mm are not available. For pathlengths between 0.1 mm and 1 mm ATR cells are not available and transmission cells may not be appropriate for viscous samples. A more effective solution is offered by the Rapid Flow Cell™ (Durasens, Pleasantville, NY) which is constructed in 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

It is relatively straightforward to set up and use sensors for spectroscopic monitoring of reactions/processes. Figs. 1 and 2 illustrate two principal approaches that are available – insertion probes and slip streams. As the figures illustrate the interface to the process is almost identical in the two cases.

We reviewed the pros and cons of using insertion probes vs. using slip streams for reaction and process monitoring by FTIR 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 insertion probes currently being in vogue, in some applications slip streams<sup>2</sup> may have significant advantages.

## References

1. M.Milosevic, D.Sting, and A.Rein, Diamond-Composite Sensor for ATR Spectroscopy, Spectroscopy 10(4), p. 44, (1995)
2. Paul Wilks, Process Monitoring: In-line, At-line, or Slip-Stream, Spectroscopy 21(3), p.2, (2006)

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