

## **PROCESS ANALYSIS WITHOUT SAMPLE CONDITIONING**

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### **Abstract**

Recent advances in the design of optical probes and related hardware for spectroscopic sample interfacing have significantly improved the practicality of direct in-situ process analysis by molecular spectroscopy. By obviating the need for sample conditioning, in-situ analysis eliminates a major source of installation cost, maintenance requirements, and risk. At the same time, by making the measurement within the reaction vessel, under actual reaction conditions, it improves measurement speed, accuracy, and reliability. Long used for a few relatively benign types of measurements, in-situ molecular analysis is now being applied to a wide variety of challenging on-line applications, often involving high pressures, extreme and rapid temperature changes, and highly aggressive chemistries – applications for which sample conditioning may be highly undesirable, or perhaps, impossible.

### **EXTRACTIVE PROCESS ANALYSIS:**

Process analyzers come in many forms, usually referred to by acronyms such as GC, LC, NDIR, MS, FT-IR

(MIR), NIR, etc. However, traditionally they have had one thing in common; for most installations, they have required sample extraction and conditioning. For many processes – petroleum blending for example – sample conditioning is relatively easy and routine. However, if the process involves rapid changes, extreme pressures or temperatures, aggressive chemistry, or severe hazards, or, if the chemical properties are highly dependent on reaction conditions, sample conditioning may be problematic or, at worst, impossible.

A generalized diagram of a typical extractive sampling system for use in liquid analysis is shown in Figure 1. This includes two subsystems in addition to the analyzer itself. The “fast loop” must maintain a sufficient flow of sample past the entrance to the analysis system to insure that the sample reaching the analyzer at a given time is representative to the actual current conditions in the process stream or vessel. The “sample conditioning system” must maintain the condition of the sample as close as possible to that existing in the actual process while removing particulate matter or bubbles that might interfere with the analysis.

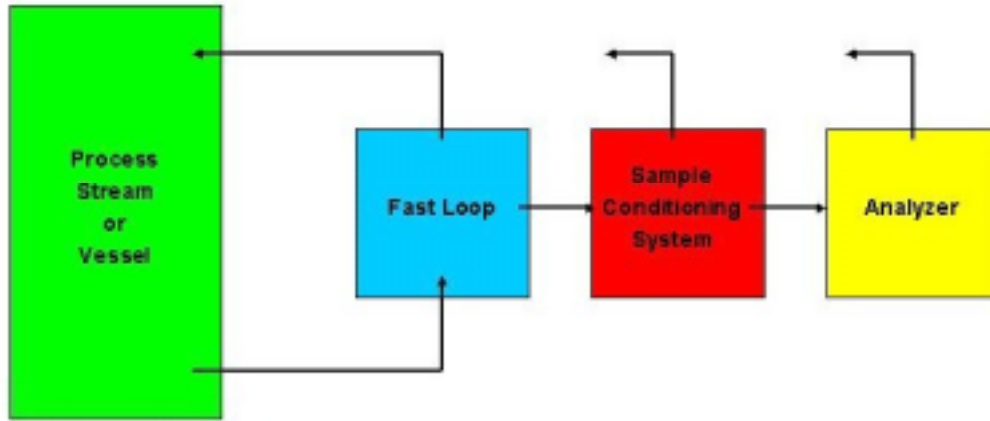


Figure 1: Generalized extractive liquid sampling system

The typical extractive sampling system includes a number of different components such as a sample extraction probe, valves, filters and separators, flow meters and controllers, pressure gauges and regulators, and usually a sample pump. Each of these must maintain the molecular characteristics of the sample stream while enduring any extreme chemical or physical conditions that may be present. And, of course, each must maintain the integrity of the overall system. Needless to say, every component in the system is a potential source of maintenance requirements and risk – a particular concern if the stream is at all hazardous.

#### THE ALTERNATIVE – IN-SITU ANALYSIS:

Fortunately, for many processes, there is an alternative to sample extraction. This is the use of molecular spectroscopy in conjunction with an optical sample interface integral to the reaction vessel. In its purest form this will be an optical immersion probe inserted into a batch reaction vessel, a continuous process line, or a recirculating loop on a reaction vessel as

illustrated in Figures 2 and 3. However, some processes are compatible with the use of a flow cell or a cross-line transmission sampling system in place of an immersion probe. This is the case if the process already involves small diameter flow lines or if a sample can be diverted to a side stream without changing its physical or chemical properties and without requiring sampling conditioning other than temperature control.

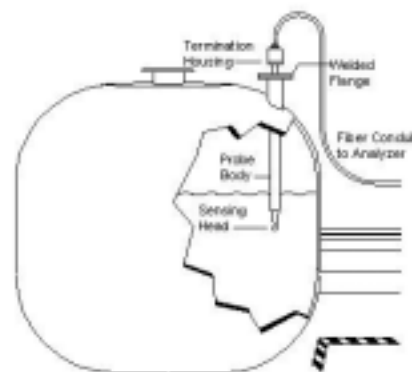


Figure 2: Fiber-optic coupled near-IR transmission probe in a batch reaction vessel.

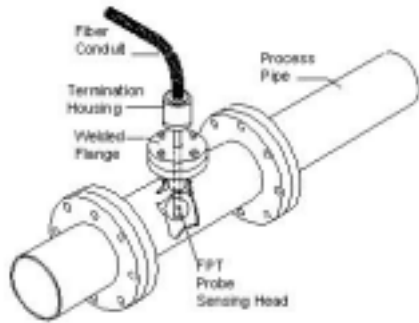


Figure 3: Near-IR probe in a process flow line

The potential advantages of in-situ sampling are readily apparent. They fall in two general areas; the elimination of the many components (and associated costs and risks) of the sample conditioning system and the location of the analysis right where the reaction is taking place – greatly improving speed, accuracy, and reliability. When combined with the ability of molecular spectroscopy to provide a direct view of chemical structure, the potential can be extremely attractive. Indeed, in-situ sampling has been used for some processes since the mid-1980's. However, for many years, its implementation was limited due to high hardware costs, labor-intensive calibrations, and the limited robustness and reliability of the sample interfacing equipment then available. This last factor was especially important in view of the harsh conditions characteristic of many process installations combined with the extreme consequences of failure.

Over the past few years, there has been a steadily increasing application of molecular structure analysis directly in-line. This is a direct result of a number of technical advances

including the advent of smaller and more robust instruments, the development of powerful chemometric software, the availability of fiber-optic signal transmission and multiplexing, the development of more robust probes and flow cells, and the implementation of new forms of analysis such as process diffuse reflectance and Raman spectroscopy. Some of these advances are quite recent. As their implications become more fully realized, we expect that in-situ spectral analysis will have major impact on the chemical processing industries.

## THE VARIED FACES OF MOLECULAR SPECTROSCOPY

Three different forms of molecular spectroscopy are currently in use for process analysis; mid-infrared, near-infrared, and Raman spectroscopy. Theoretically, mid-infrared would appear to be the most attractive of the three since each band of a mid-IR “fingerprint” spectrum corresponds to a specific molecular vibration (1). As a result, changes in molecular structure can often be tracked by simply monitoring the strength of a single band corresponding to a particular functional group (2). However, despite this attractive feature, the growth of mid-IR process analysis has been hampered by three factors: the extreme strengths of most mid-IR absorption bands, the sensitivity of mid-IR optical materials to chemical attack, and the lack of practical fiber-optic systems for use in the mid-IR. Although mid-IR has been used continuously on-line since the 1970's, its use has been largely restricted a very small number of large chemical companies with the sufficient in-house expertise to deal with its specialized

requirements. The recent advent of probes which use diamond as an ATR element offers the potential of more widespread use of process mid-IR, especially for short runs of complex high-value products (3,4).

Near-infrared spectroscopy has some distinct instrumental advantages over mid-IR due to its much weaker absorption bands and the availability of both practical fiber-optics for signal transmission and robust optical materials such as sapphire and fused silica for use in transmission probes and flow cells (5). However, spectral interpretation is much more difficult in the near-IR due to the fact that the useable absorptions are generally restricted to overtones and combination tones involving CH vibrations. Within the past few years, modern “chemometrics” has come to the rescue, providing a variety of mathematical tools for performing process calibrations even in the presence of highly complex dependencies (6). These calibrations do tend to be quite time consuming, requiring large data sets covering all possible process conditions. As a result, near-IR analysis is most generally used for products such as polymers and other commodity chemicals that are produced in sufficiently long production runs to justify the cost of calibration.

Raman spectroscopy has only recently started coming into its own. Although it does have some practical limitations, related to both hardware and sample characteristics, it also has some very attractive features. In particular, the Raman spectrum exhibits similar fingerprint region detail and functional group specificity as the mid-infrared spectrum but without the limitations of

mid-IR optical materials. This is due to the fact that the Raman spectrum is shifted to higher frequencies (in either the visible or the near-IR region) where common optical glasses and fused silica fiber-optics can be employed (8).

Of the three basic forms of molecular spectroscopy, near-IR is to date the most widely used for process analysis. By the late 1990's, sufficiently robust instruments and capable software were available so that near-IR was finding routine use in a number of applications. The most successful have been those, such as refinery analysis, which are particularly amenable to extractive sampling. In addition in-situ near-IR has been successfully used in some applications in which the sample conditions are relatively benign. However, until recently, attempts to apply near-IR to many other processes not well suited to extractive sampling have had, at best, mixed success. In fact, the number of unsuccessful installations has been sufficient to dampen enthusiasm for this form of analysis. The reasons for the difficulties are clear. The same factors that make extractive sampling impractical (such as aggressive chemistry and rapid temperature changes) often present significant challenges to in-situ sampling. At the same time, the consequences of a failure in a process application can be substantial. This places great demands on the reliability and performance of in-situ probes and other sample interfacing devices. This major problem has finally been solved within the past two years by the development of an approach to sample interface design capable of withstanding many of the harshest process conditions (9).

## SAMPLE INTERFACING EQUIPMENT FOR IN-SITU SPECTROSCOPIC ANALYSIS

In principle, In-situ analysis is much simpler to implement than extractive sampling. And, for many process, it will provide information, which is considerably more representative of the actual chemical state of the process. On the other hand, by subjecting the sample interfacing probe or cell to the full brunt of the process stream, it places more stringent demands on the performance of this device. Specifically, the sample interface must provide accurate and precise data over long periods of time while being subjected to such adverse conditions as extreme and rapidly varying temperatures, high pressures, side loads, vibration, and a wide range of aggressive chemical conditions. In addition, it must be immune to external damage due to rain, hose-down by high-pressure water, or human error. And it must adequately isolate the external human environment from hazards due to

the chemical nature of the process.

Figure 4 illustrates some of the provisions taken to meet the stringent requirements of in-situ sampling. This is a cross-sectional view of an Axiom Analytical FPT-850 near-IR transmission probe. First, the portion of the probe within the vessel is fabricated from thick-walled Hastelloy C-276 to provide a high degree of chemical resistance and mechanical strength. In addition, all external parts are electron-beam welded together. Even, the Hastelloy window seals are captured within a welded Hastelloy structure (patent pending) (see [Technical Note AN-919](#))(9). There are no elastomeric seals or brazes to serve as weak points for degradation due to high or varying temperatures or chemical attack. The metal seals themselves are rated for use at pressures to 6000 bar and temperatures to 1000 °C.

The optical design of the FPT-850 employs collimated radiation throughout the immersed portion of the probe thus eliminating any optically

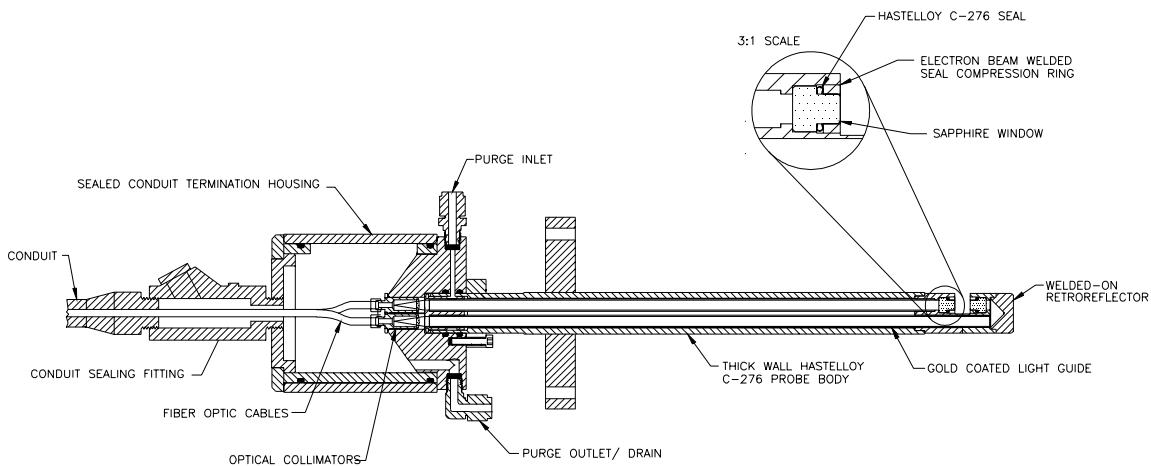


Figure 4: A robust near-IR transmission probe for in-situ process analysis

critical components within this region that could result in performance changes with varying temperature or mechanical deflection (See Technical Note AN-912)(8).

The parts of the probe assembly external to the vessel are just as important as those within since these must protect it and the critical fiber-optic terminations from threats such as rain, high pressure hose-down, or mechanical maltreatment. To provide the needed protection, the external portion of the probe is enclosed in a robust, O-ring sealed conduit termination housing. This can be opened to provide access to the fiber-optic terminations while allowing the fiber cables to remain sealed within a protective conduit. When properly installed, both the conduit and the termination housing will be tightly sealed. However, the housing is still provided with both purge and drain fittings, and the internal structure is designed to insure that any moisture that inadvertently gets into the housing will drain away from the fiber-optic connections.

For many applications, near-IR transmission probes are permanently installed through a suitable flange into a process pipe or the wall of a reaction vessel. However, for other applications, it is necessary to withdraw the probe for cleaning or referencing. This can be accomplished by means an insertion mechanism similar to those used for many years in the oil and gas pipe-line industry. An example is shown in Figure 5. In this case, the length of the probe has been extended to 150 cm, allowing the probe to be extracted through a ball valve into flush chamber.

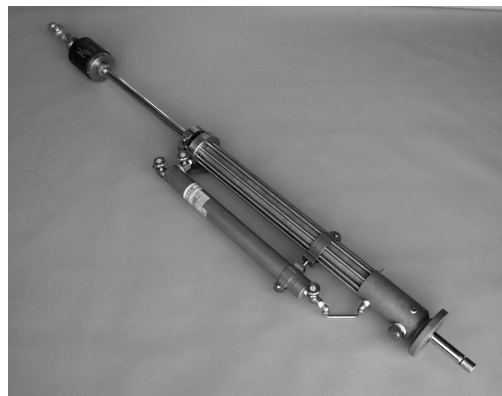


Figure 5: A near-IR in-situ sampling system incorporating hydraulic probe insertion

Near infrared transmission probes of the type described above are now performing in-situ analysis tasks in numerous installations world-wide. Based on this success, the welded Hastelloy seals as well as other elements of the probe design have now been incorporated into several additional products, including large scale probes for top entry into process batch reaction vessels, process diffuse reflectance probes, transmission cells, and probes for process Raman spectroscopy. Each of these addresses a distinct set of potential applications for in-situ analysis. Together with other products now in development they promise to go a long way toward removing the last obstacles to wide spread application of in-situ process analysis.

## SUMMARY AND CONCLUSION

Three different forms of molecular spectroscopy are currently being used for the in-situ analysis of a variety of chemical processes. Of these, near-infrared spectroscopy is by far the most advanced with numerous successful installations around the world. Recent advances in robust

sample interfacing promise to aid in the expansion of near-IR applications to cover an even greater range of processes – including those that utilize diffuse reflectance rather than transmission analysis. In-situ mid-IR has a long history but has been restricted to a fairly narrow range of applications, largely due to the limitations of mid-IR optical materials. However, even in this field, recent probe developments combined with mid-IR's ease of calibration promise to expand the use of in-situ mid-IR, especially for expensive products involving short run batch processes. The use of Raman spectroscopy for industrial process analysis is still quite new. However, given ongoing hardware improvements and instrument cost reduction, along with the inherent advantages of Raman for many applications, this branch of molecular spectroscopy is also likely to find widespread application. Together, all of these forms of analysis provide a varied set of tools that can be used to tailor in-situ analysis to meet the needs of many different process applications.

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