

Getting to grips with the process: extractive and remote “sampling”

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Having identified an opportunity for process spectroscopic analysis (the application) and decided what type of measurement/output is required, the next step is to identify and engage the sample—sampling.

It would be highly desirable to proceed in a systematic manner to determine the optimum type of sampling given the state of the sample and the information required from it. The problem, however, is that the “decision tree” begins to look more like a “decision shrub”, i.e. multi-stemmed, highly branched, interconnected, overlapping and complex.

If we are following the decision making process outlined in the previous “Process Column”,¹ the technique to be used is yet to be determined, and this will obviously have a huge bearing on the type of sampling to be employed. However, in most cases the process (and therefore the sample) is a higher-weighted determining factor, as it will normally already physically exist and therefore will regulate where the process (sample) may be accessed by whatever technique. The plant is already in place and reactors are often glass lined and pressure certified. Major plant alterations can be extremely costly (often exceeding the capital cost of any process spectrometers) and, more importantly, would require unacceptable downtime. Remember that one of the drivers for process spectroscopy (analysis) is to de-bottleneck a process that may already be running at full capacity.

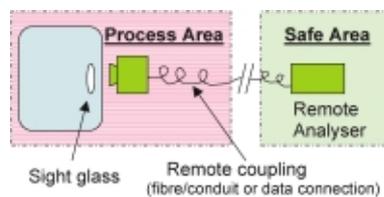
A general guiding principle might be “to perturb the sample as little as possible”.

The more a sample is perturbed by the measuring system, the more artefacts are introduced into the measurement. These artefacts then have to be compensated for in any models produced to relate the spectroscopic data to sample parameters. An example of this might be the on-line determination of hydroxyl number using NIR spectroscopy. This measurement is highly temperature dependent, and if the sam-

ple is removed from the bulk of the reaction mixture, and the sample temperature not properly controlled, then the predicted hydroxyl value can vary wildly. If sample temperature control is not possible, temperature variation has to be built into the quantitative model.

The main types of sampling may be grouped under the following four categories (listed in order of decreasing desirability): Non-Contact Sampling, Remote Sampling, Extractive Loop Sampling and Grab Sampling.

Non-contact sampling



The “ideal” sampling regime for any analytical technique requires no interaction between the sample and the measurement process. As this is theoretically impossible, the minimum interaction between the measurement device and the sample is the optimum practical situation. The interface with the sample is normally an existing sight glass, therefore the techniques most suited to this form of “sampling” are those which can analyse through a significant (3–6 cm) thickness of silica glass. Raman is an ideal technique for such situations as the Raman scattering is proportional to the power density of the illuminating laser beam. Practically this means that spectral information is almost exclusively obtained from the laser focus (inside the reactor) and yields little or no contribution from the unfocussed beam passing through the sight glass. This property also allows Raman to be successfully utilised in the analysis of the highly corrosive, toxic and/or moving process samples.² Even when using non-contact sampling, it can be of great benefit to site the analyser remotely from the non-



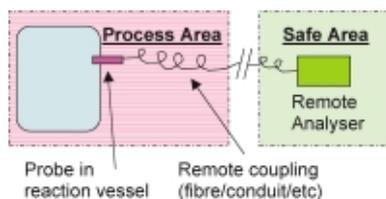
Figure 1. Reflectance near infrared analyser monitoring a fluid bed dryer.

contact probe head. This removes the necessity for expensive purged enclosures either to protect the spectrometer from the process or the process from the electricity in the spectrometer.

This type of sampling also allows the analysis of solid and even powdered samples, e.g. the use of reflectance NIR to monitor product drying either in a fluidised bed (Figure 1) or in a cake passing on a conveyor beneath the measurement head. Because of the small amount of incident light returned in a diffuse reflectance measurement, one approach has been to increase the amount of energy at the sample by bringing the source and analyser close to the sample, to collect the maximum amount of reflected light. The resultant analyser can be encased in an explosion-proof cabinet. Other techniques allow sampling without physical contact. Mid-infrared can be used to monitor gases over a long pathlength (many metres). Mid-IR is used extensively to monitor emission gas output from scrubber systems using multi-pass gas cells, however, it can be used “open beam” to monitor gas evolving from an area or production line, e.g. emissions from landfill sites. In these cases, the monitoring is of by-products rather than of product itself. Non-contact visible spectroscopy has been used for many years to monitor fast moving products, e.g. on-line monitoring of specialised coatings applied to fast moving glass. Non-contact sampling is also possible with some other laser-based techniques, e.g. laser frequency modulated spectroscopy (FMS), or laser induced fluorescence spectroscopy.

With these techniques it is the ability to focus the laser light through space, into the sample volume that allows remote sampling. These techniques allow the monitoring of headspace gases above product (e.g. in sealed vials). Microwave and acoustic spectroscopies also offer minimal interference with the sample, although normally require a physical contact between the sensor and the process vessel.

Remote sampling



This class of sampling utilises probes that enter the process and are immersed in the product, usually a liquid. There are four main types of optical probe used to sample process streams: Transmittance (double probes and single sided probes), Transflectance, Reflectance and Attenuated Total Reflection (ATR) (see Figure 2).

Transmittance probes are some of the simplest probes, allowing light to pass through a small gap filled with sample. In the simplest arrangement light is carried to one probe via a fibre optic, passes through a narrow gap and is collected by another probe on the other. The advantages of this type of probe arrangement are high throughput and allowing the sampling of a relatively wide pipe. However, access is needed to both sides of the process stream and so sampling inside reactors is better achieved using a one-sided transmission probe. Light is carried down the probe body and passes through a window and then a narrow sample-filled gap and re-enters the probe through a second window. The light is then transferred to a return fibre via a retroreflector. Typical path lengths for both of these probes are of the order of 1–2 mm for the NIR to 10–20 mm for the UV/visible. The small path lengths required for mid-IR (sub millimetre) would normally be too small to allow sample flow and (unless special measures are taken, e.g. an ATR probe) would result in the sample channelling around the probe and bypassing the sample gap entirely.

Transflectance probes are very similar to transmission probes, except that the light beam is reflected by a mirror after its first pass through the sample and is collected by a lens arrangement on the same side of the sample gap as the initial illuminating fibre. The collected light is then returned to the analyser via a fibre

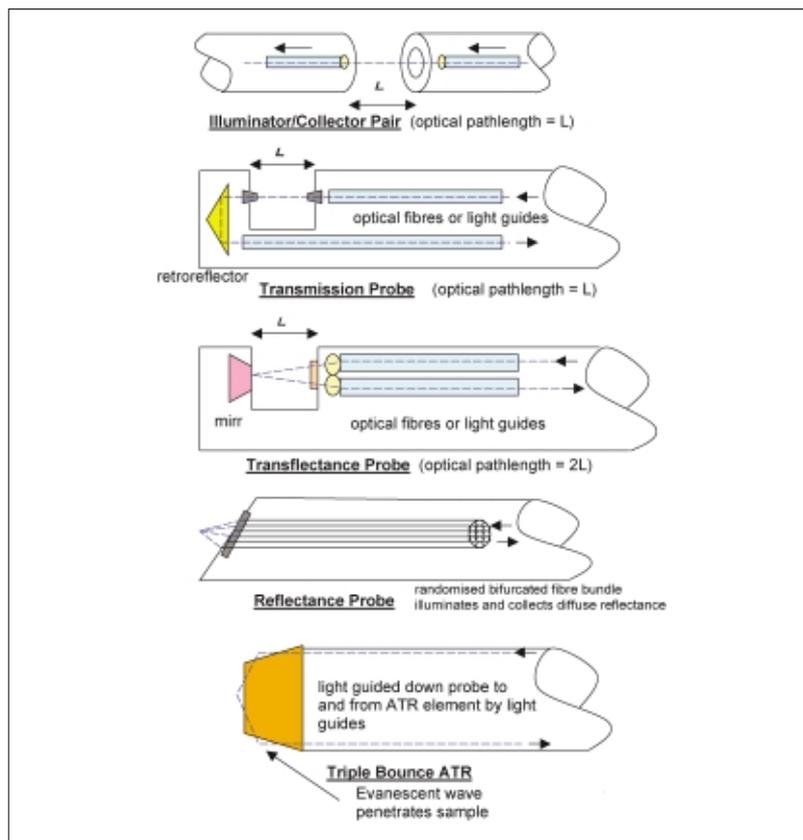


Figure 2. Probes for optical process spectroscopy.

optic or light guide system, having traversed the sample gap twice. This means that the physical gap in the probe through which the sample is required to flow is half that of a one-sided transmission probe for the same optical path-length. This means that a transflectance probe, whilst being a simpler design, is less suitable for higher viscosity samples or samples containing particulates than a single sided transmission probe. The simple design, however, does make adjusting the optical path length simpler than for a transmission probe and this makes it more suitable for applications where the path length may be varied from time to time.

Reflectance probes are used for powders, fluidised beds and highly loaded slurries, or any other samples that have a significant diffuse reflectance. The amount of light returned by diffuse reflectance is much less than for transmission arrangements. It is usual to employ larger (core) diameter fibres (600–1000 μm) to collect the maximum amount of diffusely reflected light.

Raman immersion probes are similar in design to reflectance probes. Most Raman probes are designed to collect the 180° Raman backscatter. The laser beam is normally carried to the top of the probe via silica fibre(s). The beam is transferred to the tip of the probe as a collimated beam and then focused on to

the sample by a lens mounted behind a protective window (often sapphire). The Raman 180° back-scattered light is then returned back up the probe as a collimated beam and then focused into a collection fibre.

For all types of immersion probe, the main probe bodies are usually constructed of some inert metal. Popular choices are high-grade stainless steel, Hastelloy®, titanium or even tantalum, which provide the physical strength required, combined with sufficient chemical resistance to withstand the process stream. Ceramic probes are available which offer high chemical resistance at a lower cost. However, in all process applications the probes need to be very physically tough and “process hardened”. This means that even though it is possible to produce transflectance/ATR probes with a diameter of only a few millimetres, the most common diameter for a process probe is 1† (25 mm). Small diameter probes are often not physically rugged enough to withstand the shear forces present in a process stream. If necessary, smaller probes can be protected from the exacting process forces by installing them inside existing reactor baffles (often already present to aid product mixing).

The window material will depend upon the technique being used. For

NIR, visible, Raman and other visible laser spectroscopies, industrial sapphire is a commonly used material. This material combines physical toughness and high chemical resistance with the ability to transmit a wide range of optical frequencies. Other materials often used are quartz (NIR/visible/UV) and silica glass (Raman).

The seal between the probe window and the probe body is critical and is generally made up of some form of fluoropolymer "O"-ringed compression fitting or a mixed-metal brazed joint. Both fittings allow probes to be constructed that can tolerate extremely high pressures and temperature (e.g. 300°C, 15,000 psi depending upon materials and probe diameter).

The ATR (attenuated total reflection) probe is the most unusual type of probe, as the light does not physically leave the probe, but interacts with the sample via an evanescent wave at the sample/ATR crystal interface.^{3,4} The effective path length experienced by the light in an ATR probe depends upon the probe geometry, the relative refractive indices of the ATR element and the sample, the number of internal reflections and the wavelength of light being considered. ATR path lengths are orders of magnitude shorter than those used for the transmission arrangements. Therefore ATR is generally only used for techniques which would require an unfeasibly short pathlength if sampling were attempted by the more conventional type probes. ATR has been successfully employed in process measurements for UV/visible and mid-IR applications. Sapphire can be used as the optical element for visible wavelengths and would lead to pathlengths of the order of 100 nm. In mid-IR using a ZnSe element, pathlengths of a few microns (1–10 µm) are common. A more robust ATR material for process applications in the mid-IR is diamond. This has a similar refractive index to ZnSe, but is physically stronger and much more resistant to chemical attack. Unfortunately diamond attenuates mid-IR radiation to a larger extent than some of the other ATR materials and so more sensitive detectors, such as cooled MCT (mercury cadmium telluride), are needed to obtain good signal-to-noise ratios. The cooled detectors require cooling to liquid nitrogen temperatures and therefore the installation becomes much more complex as coolant needs to be supplied to the system or complicated refrigeration systems need to be installed. ATR pathlengths are generally too small for operation in the NIR (~0.1 µm per reflection), as it would require many hundreds of bounces to achieve a useful pathlength due to the

low extinction coefficients of absorbances in the NIR region. Measurements in the visible region of the spectrum can be made on samples with very high optical densities using ATR probes. The small ATR pathlength (~0.1 µm per bounce) in this region, allow spectra to be recorded from materials with extremely high optical densities, e.g. inks and pigments, without significantly impeding the flow of the process stream.

Fibre optics

The optical connection between the analyser is most often provided by optical fibres.⁵ For any technique using visible/NIR/Raman these fibres are fabricated from silica or quartz. The optical fibres used for spectroscopy differ from those used for optical data communication networks frequently found in plants. Data optical fibres are normally only required to transmit digital data (ones and zeros). In comparison spectroscopic fibre optics must have a high transmittance for polychromatic radiation and not interact (scatter or absorb) with the radiation that they carry. To minimise interactions between the light (spectral information) and the fibre, spectroscopic fibres generally have larger core diameters (50–1000 µm). As the core diameter increases the fibre starts to behave less like a flexible fibre and more like a glass rod. Care needs to be taken not to physically shock thicker fibres or to bend them over sharp edges or through tight bends. As a general rule the minimum fibre bend radius should be greater than 600 times the diameter of the fibre core. This means a multimode Raman illumination fibre (50 µm diameter) can be bent round curve of radius 3 cm, whilst a 1000 µm collection fibre for NIR reflectance spectroscopy needs a minimum bend radius of the order of 60 cm. Damage to fibres due to long-term over stressing (tight bending) or physical shocks is not always immediately apparent. However, over time, micro-fractures can start propagating through the fibre matrix, leading to an increasing and irreversible loss in transmission and possible eventual complete fracture. To protect from physical damage fibres can be coated in a number of different materials from PVC, polyimide, direct metal coats, external stainless steel braid etc. Inside the coating, tough metal or polymer strengthening fibres can also be run parallel to the optical fibres to increase the physical protection. Care must always be taken when installing these fibres in a plant that they are not over stressed whilst being pulled

through ducting, or fractured by over tightening of cable ties.

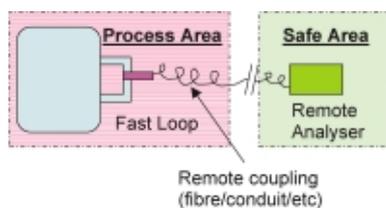
The maximum operational temperature of a silica fibre is usually constrained by the coating material (e.g. acrylate coated fibre can be used up to about 85°C, polyimide coated fibre to 350°C, whilst gold coated fibres can be used up to 750°C). NIR fibres are drawn from high quality "low OH" silica formers, which have a low hydroxyl content. This is necessary as any OH groups within the fibre will absorb NIR radiation. The fibre pathlength in a process NIR installation could be as much as 1000 m. If the fibre OH content exceeds more than a few ppm, the absorbance due to even this small amount of OH in the fibre becomes significant. The attenuation reduces the signal-to-noise in the spectral regions associated with hydroxyl absorbances (especially around 7300 cm⁻¹). Typical attenuation outside this region might be 3 dB km⁻¹ at 1300 nm.

UV/visible fibres can have higher OH contents and visible region applications have utilised fibre lengths of in excess of 100 m. Typical attenuations might be 0.3 dB m⁻¹ at 300 nm. Silica/quartz fibres begin to attenuate the light below 400 nm, but in the short wavelength region of the UV spectrum (below 220 nm) actual damage to fibres can occur due to the "solarisation" of colour centres in the fibre matrix. This leads to a progressive decrease in the transmission of the fibre. Sometimes a certain amount of this damage is reversible after a recovery period (seconds to hours) and some manufacturers are now able to supply "solarisation-resistant" fibres.

Fibres that can efficiently transmit mid-IR radiation have to be constructed of more exotic materials, e.g. heavy metal fluorides, chalcogenide, mixed silver halides. Whilst it is possible to construct fibres of these materials they have very poor physical and transmission (in excess of 1 dB m⁻¹) characteristics compared to those available for the NIR and visible regions. Therefore these fibres tend to be used in short lengths (1–5 m) and have to be heavily armoured and protected from physical strain. In addition some of the materials have strong absorptions (e.g. chalcogenide glasses around 2000 cm⁻¹) which mask certain regions of the spectrum. Light guiding conduits can be used to take mid-IR radiation over much longer distances. The light guides are made of metal tubing with coated internal surfaces (usually gold or nickel). The tubes themselves are straight, but multiple surface-coated mirror corner-units can be used to divert the light round corners and obstacles. The transmission

characteristics of this type of light guide (absorbance in the region of 0.03 absorbance units m^{-1}) allow the use of 20–30 m lengths. The light guides are mainly of metal construction and are therefore physically robust, can tolerate high temperatures ($>350^{\circ}C$) and can be purged with nitrogen to combat harsh process conditions. At the end of the light guides, beam condensers or short lengths of mid-IR fibres can be used to focus the light into ATR probes.

Extractive loop sampling



This type of sampling is very similar to remote sampling, except a fast-loop or by-pass loop is inserted in the stream to be analysed, which continually snatches and returns sample from the process (Figure 3). Probes of all types described previously can be inserted in these fast loops. This has the advantage of allowing the isolation of the probe from the process to facilitate maintenance, without disruption to the main process. Also the inclusion of a by-pass loop allows the use of fibre-coupled flow cells, which would otherwise cause an unacceptable constriction if they were installed in the main process stream. Flow cells and flow cell windows are made of similar materials to the probes (stainless steel, nickel alloy, sapphire, quartz etc), and can be made to withstand extremely challenging temperatures and pressures (e.g. 3000 psi and $250^{\circ}C$). The extraction loops can also remove the measurement point from some of the extremes of the process area. This can reduce the specification needed for the fibres and flow cells, however, the further the sample is transported, the more likely it is to be altered from that found in the bulk reactor/process line. This can lead to spectral artefacts and hence require more complex data modelling. In addition there is the danger that changes in temperature, pressure, shear etc. in the by-pass loop may cause the sample to change form catastrophically, e.g. crystallise or solidify in or around the extraction loop. From a safety perspective, it is often not desirable to extract a portion of a toxic or corrosive process sample from safe containment within a reactor and to pump it around a plant. However, many processes already con-

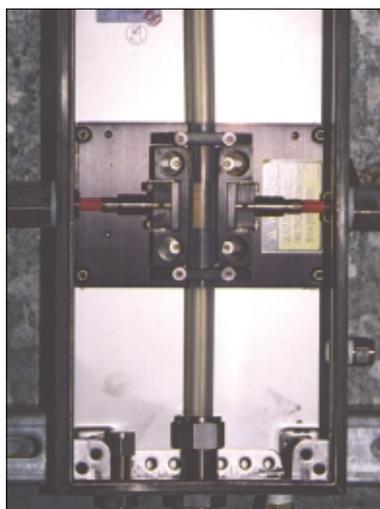


Figure 3. Near infrared flow cell (cover removed to show detail). Product side loop flows through fluoropolymer tube 10 mm o.d. (vertical). NIR beam brought to cell via two optical fibres (horizontal). Lens assemblies collimate light from and focus transmitted light back into fibres. Photograph courtesy of Morris Partnership.

tain legacy fast-loop or extraction ports and therefore this means that installation engineering costs are rapidly reduced by using existing plant.

Grab sampling



Traditional “grab sampling” is something to be avoided as it usually means entering a process, capturing a quantity of the process stream, removing the “sub-sample” from the process environment, exposing it to some form of analysis and then discarding the analysed product. None of these steps is particularly desirable in its own right and one of the drivers for process spectroscopy is often to remove one or more of these steps. Once the sample has been removed from the process environment it can rapidly cease to be representative of the bulk of the process mixture. The power of process spectroscopy lies in the ability to take the measurement to the sample, rather than extracting, conditioning and moving the sample to the measurement device. However, a “near line” spectroscopic analytical solution may still provide many advantages (usually a massive decrease in analysis time) compared to traditional wet chemical analysis (Figure 4).



Figure 4. Raman analysis of process grab sample inside sealed sample container.

Conclusions

There are many elegant and imaginative sampling solutions available for process spectroscopic applications. All have strengths and weaknesses and the determination of the most suitable solution for a particular application is dependent upon many considerations: cost, ease of engineering, existing plant, but most importantly upon the type and properties of the sample. It is crucial to consider the requirements and constraints of the sample to yield a successful process spectroscopic application.

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