

A beginner's guide to industrial spectroscopic analysis

W. Michael Doyle

This guide is intended to serve as a brief introduction to the diverse forms of vibrational spectroscopy. The goal is to provide the beginning user with the general information needed to make an initial selection among the various possible approaches to a given application. However, it should be kept in the mind that the choices are not always clear and that more than one approach may be applicable to a given task. It is for this reason that we encourage the reader to consult with the experts at Axiom Analytical when questions arise or when the application appears to be outside the scope of this general guide.

1. Introduction

The application of molecular spectroscopy to industrial tasks was jump started during World War II, fueled by the requirements of the synthetic rubber program.¹ These efforts led eventually to the introduction, in 1950, of the Perkin Elmer 21, the first commercially successful mid-infrared spectrometer. Since that time, the field of molecular spectroscopy has expanded and diversified steadily. Some of the significant developments have been the introduction of commercial Fourier transform infrared (FTIR) spectrometers in the late 1960's², the development of practical near-IR instruments (also in the 60's)³, and the development of sensitive Raman spectrometers in the 1980's.⁴ These developments, along with the application of UV-visible spectroscopy to chromophore analysis, have brought us to the point where we now have four well established forms of molecular spectroscopy to consider when tackling a new application. But, if you are a beginner, where do you start? This paper will guide you through the various options available and lead the way to answering the question: What is the optimum approach for my application, or at least what might be possible.

2. The Varieties of Molecular Spectroscopy

TABLE 1 provides a summary of some of the pertinent characteristics of the four major forms of molecular spectroscopy. Each of these forms is discussed briefly in this section and

The author is with Axiom Analytical, Inc., 17751-B Sky Park Circle, Irvine, California 92614. W. M. Doyle's e-mail address is mdoyle@goaxiom.com.

expanded upon in Appendix I. In addition, a list of several other technical notes published by Axiom Analytical is given in Appendix II. These technical notes offer a much more detailed discussion of certain topics introduced in this paper and are provided as further reading if a more comprehensive understanding is desired.

A. Mid-IR

The attractiveness of mid-IR spectroscopy stems from the fact that it directly monitors the fundamental vibrations corresponding to the functional groups that govern the chemical properties of interest. This greatly eases the task of data interpretation and calibration. However, mid-IR has two drawbacks. First, most of the optical materials used for mid-IR sampling tend to be subject to chemical attack. The one impervious material, diamond, is extremely expensive and limited to small sizes. Second, no suitable fiber optics are available for communicating between the measurement point and a remote instrument.

B. Near-IR

Near-IR overcomes the two major drawbacks of mid-IR since it is compatible with highly robust optical materials (fused silica and sapphire) and with fused silica fiber optics. However, it has its own drawbacks resulting from the fact that near-IR bands are dominated by overtones of CH stretch vibrations. As a result, the bands are often overlapping and difficult to interpret. Near-IR calibrations thus tend to be quite time consuming and tedious.

Molecular Spectroscopy Characteristics				
	Mid-IR	Near-IR	Raman	UV-Visible
Sampling Methods	ATR Transmission Specular Reflectance Sparging-IR	Transmission Diffuse Reflectance	Raman Backscatter	Transmission ATR
Band Types	Fundamentals	Overtones	Fundamentals	Chromophore
Calibrations	Easy	Tedious	Generally easy	Easy
Optics	Chemically sensitive	Resilient	Resilient	Resilient
Fiber-Optic Coupling	Marginal	OK	OK	OK
Sample Fluorescence	OK	OK	Can be a problem	OK
Background Radiation	OK	OK	Can be a problem	OK
Referencing	OK	OK	Can be a problem	OK
Cost of Ownership	Moderate to high	OK	Moderate to high	OK
General Applicability	OK	OK	OK	Low

C. Raman

Raman combines the best features of mid-IR and near-IR in that it views fundamental vibrations but operates in a spectra region where robust optics and fused silica fiber optics are applicable. However, Raman has its own drawbacks for some types of sample systems due to interference from sample fluorescence and background radiation and lack of a universal referencing capability. In addition, the cost of ownership can be relatively high due to the lack of maturity of some of the available hardware and the need for periodic maintenance.

D. UV-Visible

We have included UV-visible spectroscopy in the above table for sake of completeness. However, most organic molecules

are transparent in this region of the spectrum. The major exception is the category of substances called chromophores, i.e. substances in which molecular structure has a measurable effect on the electronic transitions. The resulting absorbances can be extremely strong. As a result, they are often analyzed by means of attenuated total reflectance (ATR) spectroscopy. Since chromophore analysis is limited to a few classes of molecules, we will not include it in the discussions below. However, a much more detailed analysis is provided in Axiom Technical Note AN-915.

3. Applicability to Various Sample Types

Table II summarizes the applicability of the three major forms of molecular spectroscopy to specific sample types. Below are a few general comments.

Applicability of Spectroscopic Techniques to Various Sample Types					
Sample Type	Mid-IR Transmission	Mid-IR ATR	Near-IR Transmission	Near-IR Diffuse Reflectance	Raman
Clear fluids	Some cases	Yes	Yes	No	Yes
Scattering fluids	No	Liquid phase only	Some cases	Some cases	Yes
Powders	No	No	Some cases	Yes	Yes
Clear bulk solids	No	No	Some cases	No	Yes
Scattering bulk solids	No	No	Some cases	Yes	Yes
Gases	Yes	No	Some cases	No	Some cases

TABLE III			
Considerations for the Analysis of Clear Fluids			
Consideration	Applicability of Spectroscopic Technique		
	Mid-IR ATR	Near-IR Transmission	Raman
Need for remote sampling	Poor	Good	Good
Multiplexing of widely separated sample points	Poor	Good	Fair
Very high temperature or pressure	Poor	Good	Good
Need for in-situ sampling	Fair	Good	Good
Corrosive samples	Fair	Good	Good
Harsh ambient conditions	Fair	Good	Good
Need for functional group specificity	Good	Poor	Good
Rapid survey of chemicals or reactions	Good	Poor	Good
Short production runs	Good	Poor	Good
Strongly fluorescent samples	Good	Good	Poor
High thermal background	Good	Good	Poor
Lack of an internal reference	Good	Good	Poor
Low cost of ownership	Fair	Good	Fair

A. Considerations for Clear Fluids

All three forms of spectroscopy are generally applicable to clear liquids. The choice will usually be determined by the nature of the spectroscopy, the application requirements, and the physical conditions at the sampling point. However, we can generalize to some extent, as illustrated by Table III.

Near-IR transmission will often be the method of choice for on-line or in-line monitoring as long as the economics of the application can justify the calibration requirement. Typically, this will be the case when monitoring long production runs of commodity chemicals.

Mid-IR ATR is generally the choice for survey and reaction development applications and for on-line monitoring situations requiring high functional group specificity or frequent calibration changes.

Raman combines the most attractive features of both near-IR and mid-IR. However, it can be more difficult to implement and maintain due to presence of fluorescence and background interference, referencing issues, and equipment maturity.

B. Scattering Fluids

Most of the considerations outlined above for clear fluid will also apply to scattering fluids. However, there are some differences, as follows:

Mid-IR ATR is generally insensitive to particulate matter and hence will only monitor the liquid phase.

Near-IR Transmission may only be applicable for short pathlengths due to signal loss.

Near-IR Diffuse Reflectance is applicable in cases where the backscatter from the particulate matter is sufficient.

Raman will often monitor both the liquid and solid phase. It is particularly useful for monitoring particulate matter in water since the Raman scattering of water is quite weak.

C. Scattering Solids (powders and bulk)

Both near-IR diffuse reflectance and Raman are generally applicable to this case. The choice may typically require a detailed analysis of the particular sample and ambient conditions as well as the calibration requirements of each approach. (For a more detailed comparison of near-IR and Raman, see Technical Note AN-922.)

D. Clear Bulk Solids

This is the one case where Raman is the clear choice for most situations. Another method that might be considered for some applications is mid-IR specular reflectance (see Technical Note AN-908).

E. Gases

Until recently mid-IR has been the method of choice for most gas analysis since the dilute nature of the samples made it necessary to monitor the fundamental bands which fall in this region. This situation has started to change with the introduction of highly sensitive near-IR spectrometers such as those based on tunable lasers. The sensitivity and potentially

high resolution of these instruments now makes it practical to monitor the overtone CH and OH bands of many species.

4. Extractive Vs. In-situ Sampling

In addition to the choice of spectroscopic technique and sampling method, one will often be faced with the choice of extracting a sample from the process or performing the measurement in-situ using an immersion probe or, in some cases, a large cross-section flow cell. Extractive sampling has a long history and is the approach used with techniques such as gas and liquid chromatography which are not compatible with in-situ analysis. More recently, the advent of extremely robust spectroscopic immersion probes has made in-situ sampling a practical reality. Some of the trade-offs are discussed in Axiom Analytical Technical Note AN-918. A few generalizations are provided in this section.

A. General Considerations

Conditions compatible with extractive sampling

- Slowly varying samples whose properties are not effected by the extraction process
- Moderate temperatures and pressures
- Non-aggressive chemistries

Factors favoring in-situ sampling

- High sample temperature or pressure
- Rapid changes in sample characteristics
- Corrosive chemicals
- Need for multiple point measurement
- Safety considerations

B. Considerations for Individual Spectroscopic Methods

Mid-IR

Extractive sampling is the method of choice for many gas analysis applications. A couple of exceptions are long path ambient air monitoring and situations in which the gas stream of interest can be passed through a large cross-section infrared transmission cell.

Mid-IR liquid analysis also favors extractive sampling. There are at least three reasons for this. First the instrument will already be located close to the process, removing any arguments related to remote sampling. Second the vulnerability of ATR sampling devices to chemical attack, thermal shock, fouling, and physical breakage mitigates in favor of locating the sampling system external to the chemical process where it can be valved off for service. Finally, the performance of a mid-infrared liquid analysis system will be maximized by closely coupling the instrument to a relatively high-transmission sampling device such as an ATR flow cell. High transmission diamond-tipped ATR probes are available for dealing

with highly corrosive samples. However, even when using one of these it is advisable to employ extractive sampling with the probe mounted in a suitable flow fixture.

Near-IR and Raman

In-situ sampling has proven to be the approach of choice for the great majority of near-IR and Raman applications. This is made possible by the availability of extremely robust near-IR and Raman probes. Mounting a probe directly on a process vessel or recirculating loop is generally both more reliable and less costly than outfitting the process with an extractive sample conditioning system. In situations where probe fouling is a concern, the probe can be equipped with a spray nozzle to allow periodic flushing. Probe extraction mechanisms are also available. These allow a probe to be withdrawn into a flush chamber for cleaning or referencing, or to be removed completely from the process.

In some situations, in-situ sampling can also be accomplished by using a large cross-section flow cell (FCT Series) in an existing recirculating line or in a rheometer loop on a polymer extruder.

The use of extractive sampling with near-IR and Raman is typically limited to clear liquid samples at moderate temperatures and pressures. In such cases, it is sometimes possible to minimize system cost by employing stream switching or by optically multiplexing a number of relatively inexpensive flow cells.

References

1. P. A. Wilks, Jr., "The Evolution of Commercial IR Spectrometers and the People Who Made It Happen", *Anal. Chem.* **64**, 833A-838A (1992).
2. P. R. Griffiths, "Chemical Infrared Fourier Transform Spectroscopy", John Wiley & Sons, Inc., New York (1975).
3. K. H. Norris and J. R. Hart, "Proceedings of the 1963 International Symposium on Humidity and Moisture," **4**, 19-25.
4. R. L. McCreery, "Raman Spectroscopy for Chemical Analysis", John Wiley & Sons, Inc., New York (2000).

Appendix I: Further Discussions Of Individual Spectroscopic Techniques

A. Mid-infrared (Mid-IR)

Mid-IR spectroscopy is the old-timer of molecular spectroscopy, having been in-use for industrial process analysis since the early 1940's. It is also the most fundamental of the various methods since it directly views the spectral absorbances corresponding to the fundamental vibrations of molecules. These absorbances have two basic characteristics. First most of them lie in the spectral region between 2.5 and 25 μm (4000 – 400 cm^{-1}). Second they have very high absorptivities. As a result of the second characteristic, transmission analysis is generally only practical for very dilute (e.g. gas phase) samples or thin films. The required pathlength for liquid samples would be prohibitively short.

The solution to the need for a short pathlength is to use the attenuated total reflectance (ATR) technique. In this technique, absorption takes place at the interface between the sample and an IR-transparent sensing element. The essential requirements for this element are that it be transparent to the analytical wavelengths and that have a refractive index which is high compared to that of the sample liquid. For further information about ATR sampling, see Axiom Analytical Technical Note AN-906.

The major advantage of mid-IR spectroscopy results from the fact that each IR absorption corresponds to a unique, unambiguous molecular vibration. It is thus relatively easy to relate specific absorbances to the chemical changes that are of interest to a given application. As a result, mid-IR calibrations are often quite easy and fast. This makes mid-IR highly attractive for batch processing and short production runs where it is difficult to justify the more tedious calibration procedures often required for near-IR analysis.

The disadvantages of mid-IR stem from two factors, the lack of practical fiber-optics for the mid-IR spectral range and nature of the optical materials necessary for the ATR elements used in liquid analysis. Although mid-IR fibers are available in short lengths (1 – 2 meters), these do not meet the need for a means to communicate between the measurement point and an instrument located in a control room or instrument shack.

The material issues have to do with strength and, most importantly, chemical resistance. Only a few materials offer the combination of high refractive index and transparency throughout a significant part of the mid-IR spectrum. From the spectral viewpoint the most attractive of these is zinc selenide (ZnSe). However, ZnSe is attacked by acids and oxidizing agents. An alternative for use with acids is AMTIR-2, a glassy blend of semiconductor materials. However, this material has a more limited spectral response and is attacked by bases. The other available materials have similar trade-offs.

One IR transparent material that has both a refractive index and very high chemical resistance is diamond. Indeed diamond tipped ATR probes are available with suitable characteristics for both lab and process applications. However, the

cost of diamond increases very rapidly with size. As a result, diamond-tipped probes are quite expensive. In addition, the small size of practical diamond elements is not consistent with the extremely high seal reliability available with near-IR and Raman probes.

In summary, mid-IR spectroscopy offers some extremely attractive characteristics. However, it is generally only practical when the instrument can be located quite close to the measurement point. Furthermore, in view of the relative vulnerability of mid-IR sample interfacing devices, it is desirable to employ mid-IR with an extractive sampling system so that the ATR device can be valved off for cleaning and service.

B. Near-infrared (Near-IR)

Near-IR spectroscopy analyzes the overtones of the fundamental vibrations that fall in the region between 4500 and 12000 cm^{-1} , a region characterized by robust optical materials and practical fiber optics. Since the overtone absorption bands are orders of magnitude weaker than their mid-IR counterparts, optical transmission can be used for the analysis of clear liquids.

The problem with Near-IR is not, as is often stated, that the overtone and combination tone bands are broad. It is rather a result of the overlap of the various orders of overtones. Only vibrations involving very light atoms (e.g. CH and OH) have first overtones in the near-IR region. And these usually swamp the much weaker second, third, and fourth overtones of the fingerprint spectra falling in the same spectral region. Thus near-IR calibrations tend to be quite tedious and often require continuous maintenance.

Near-IR has found broad acceptance for the analysis of commodity fluids such as gasoline, polymer intermediates, and polymer melts – products for which long production runs, multiple sample points, and economic return can easily justify the cost of developing and maintaining the required calibrations. Even more fruitful has been the use of near-IR diffuse reflectance for the analysis of agricultural products such as grains and meats. And most recently, this technique has started find acceptance for pharmaceutical measurements such as drying and blend uniformity.

Axiom Analytical, Inc. manufactures a full range of probes and flow cells for near-IR fluid analysis and probes for diffuse reflectance analysis. To decide on the optimum device for a given application, please consult our various Product Selection Guides and Data Sheets or contact Axiom directly.

C. Raman

Raman is the most recent of the three primary forms of molecular spectroscopy to be applied to industrial analysis. Indeed, Raman has already been quite successful in dealing with a number of tasks for which near-IR did not provide adequate sensitivity or specificity.

In planning for an industrial application of Raman, the first consideration is often the choice of laser excitation wavelength. Shorter wavelengths increase the strength of the Raman scattering but can also result in significant fluorescence for many samples. On the other hand, systems employing longer wavelength excitation can be troubled by thermal radiation from a hot sample. Excitation at the long wave end of the visible spectrum (e.g. 785 nm) has proven to be a good compromise for many applications.

The second issue to be dealt with is the need for some form of reference for normalizing the raw data. In many cases, normalization can be accomplished by ratioing the bands of interest to some spectral feature that is not effected by the reaction being studied. Another approach is closure normalization of the measured concentrations. See Axiom Technical Note AN-922 for a discussion of closure normalization as well for a comparison of near-IR and Raman for specific types of measurements.

Appendix II: Further Reading

The following Technical Notes provide more detailed discussions of some of the topics treated above.

AN-906 “Principals and Applications of FTIR Process Analysis” – Includes a general discussion of mid-IR.

AN-908 “Non-Invasive Chemical Analysis by Isotropic Specular Reflectance Spectroscopy” – A comprehensive treatment of mid-IR specular reflectance.

AN-910 “Modular FTIR Sample Interfacing with the Axiot System” – Examples of system configurations.

AN-911 “Near and Mid-IR Process Analysis – a Critical Comparison”.

AN-913 “High Performance ATR Probes for the Mid-infrared Analysis of Highly Corrosive Liquids” – A discussion of diamond-tipped probes.

AN-915 “Analysis of Strongly Absorbing Chromophores by UV-visible ATR Spectroscopy”.

AN-916 “Signal Level Considerations for Remote Diffuse Reflectance Analysis”.

AN-917 “Hollow Optical Conduits for Vibrational Spectroscopy” – Further treatment of mid-IR sample interfacing.

AN-918 “Process Analysis Without Sample Conditioning” – A comparison of extractive and in-situ sampling.

AN-922 “Comparison of Near-IR and Raman Analysis for Potential Process Analysis”.

Several of these technical notes are available as downloads on the Axiom Analytical, Inc. website (www.goaxiom.com). Copies of the others can be obtained in paper form directly from the company.