

Raman vs Mid-IR ATR Fiber-Optic Immersion Probes for In-Line Reaction Monitoring

Mid-infrared (mid-IR) and Raman techniques are both based on vibrational spectroscopy: they use optical electromagnetic radiation to probe molecular vibrations through complementary effects. Mid-IR ATR detects absorption of mid-IR radiation, whereas Raman detects inelastic scattering of laser light, making both powerful tools for in-situ reaction monitoring and process analytical technology.

Mid-IR ATR with a fiber optic probe

- Measures fundamental molecular vibrations in the mid-infrared region through an ATR crystal.
- ✓ Strong molecular fingerprinting technique
- ✓ High analytical sensitivity; sub-percent LODs achievable
- ✓ High selectivity (sharp peaks)
- Interference from water absorbance



Raman with a fiber optic probe

- Measures inelastic scattering of visible/NIR laser light, producing a molecular fingerprint
- ✓ Low water interference
- ✓ High analytical sensitivity; sub-percent LODs achievable
- ✓ High selectivity (sharp peaks)
- Interference from fluorescence



Mid-IR ATR spectroscopy with fiber-optic probes

Mid-infrared radiation is absorbed when its frequency matches a fundamental vibration that changes the molecule's dipole moment. Polar bonds such as C=O, O–H, N–H and C–O therefore produce strong, sharp, well-resolved bands, giving mid-IR high analytical sensitivity and spectra rich in directly interpretable information. In a fiber-optic attenuated total reflection (ATR) probe, mid-IR radiation is transmitted through specialty optical fibers to an ATR crystal in contact with the medium. Internal reflection in the crystal creates an evanescent field that decays within the first few micrometers of the sample (typical penetration depth about 0.5 - 2 μm), so the measurement is dominated by this thin contact layer. This makes it robust in turbid, bubbly, or particle-laden media, but the liquid must maintain optical contact with the crystal. Strong water bands can mask some regions, though ATR's short pathlength keeps aqueous measurements practical. Sub-percent LODs are achievable in favorable matrices, but actual values are matrix- and method-dependent.

In process monitoring, mid-IR ATR probes follow functional-group chemistry in real time - esterification, hydrolysis, oxidation/reduction, amide/peptide formation and polymerization - providing direct progress markers and clean kinetic data without physical sampling. They are natural for organic/non-aqueous synthesis, pharmaceutical manufacturing, and highly turbid streams. The main practical limit is total fiber length, which must match source power and detector sensitivity: cable lengths are typically 2-3 m with FTIR, extending to around 10 m with quantum cascade laser (QCL) sources or dual-comb spectrometers. The smallest outer probe diameter is about 6 mm, and its length can be adapted to the application. Available mid-IR ATR configurations cover fingerprint (600 - 3100 cm^{-1}) and high-wavenumber regions (1550 - 9000 cm^{-1}); the exact range depends on the ATR crystal and fiber type.

Raman spectroscopy with fiber-optic probes

Raman probes the same vibrational levels by inelastic scattering rather than absorption. A monochromatic laser, commonly in the visible or near-infrared region (e.g. 532, 785 or 1064 nm), illuminates the sample, and a tiny fraction of the scattered photons is shifted in energy by a vibrational frequency - the Raman shift. A vibration is Raman-active when it changes the molecule's polarizability, so symmetric and non-polar bonds, such as C=C, S–S and aromatic ring modes, that are weak or silent in IR can give strong, sharp Raman peaks - high selectivity complementary to mid-IR.

In process monitoring, Raman's standout feature is weak water scattering, making it ideal for aqueous solutions. Conventional Raman can reach sub-percent LODs in favorable cases. Main constraints are fluorescence from colored/impure samples and scattering losses from bubbles or particles. Raman signal scales as $\sim 1/\lambda^4$: 532 nm gives stronger signal and better spatial selectivity but more fluorescence, whereas 785/1064 nm suppress fluorescence at the cost of weaker signal. Since Raman uses a focused laser, there is a risk of photodegradation/burning of dark or absorbing samples that can be an additional constraint. The probe length is limited by free-space beam divergence; for a 12 mm outer probe diameter, lengths above 200-300 cm are challenging. From probe to spectrometer, low-loss silica fibers allow cable lengths of tens of meters. Common probes cover about 130–4000 cm^{-1} and can extend to 25 cm^{-1} or lower (THz Raman) – wavenumbers that mid-IR fiber systems cannot reach.

Bottom line: Raman and mid-IR ATR fiber-optic spectroscopies are complementary, not competing techniques. Running ATR and Raman in parallel captures polar/non-polar, aqueous and solid-phase information that either technique alone would miss.

