Benefits of Fiber Optic Probes for Mid-IR Analysis
Raman vs. Mid-IR vs. Near-IR

Voting results from Spectroscopy, July 19, 2011:

Which technique has been the most useful in your work?

Mid-IR 57%
Raman 32%
NIR 11%
Choice of Spectral Range

Optimal optical path length at the measurement depends on the absorption coefficient of the substance

**Example: Acetone Absorption Bands**

The most intensive fundamental vibrational absorption bands are mostly in so-called “finger-print range” which is the field of mid-IR spectroscopy. Near-infrared spectroscopy deals with weak overtones of the fundamental bands and needs, therefore, much more long optical path in medium to get informative spectrum – up to 20mm vs 5-50µm optical path in mid IR range. So different spectroscopy techniques are used both for sampling methods and for fiber optic spectroscopy: transmission and reflection techniques are for Near-IR and **Attenuated Total Reflection** - for mid-IR. We note also that ATR fiber probes are mostly immersible probes for liquids not for powders or solids.

Unfortunately, the most convenient and robust silica fibers are transparent only in visual and Near-IR range and can not transmit mid-IR radiation.

**Near IR** range – transmission and reflection probes, optical path 1-20mm

**Mid IR** range – ATR probes, optical path 1-10µm
There are two different types of special optical fibers which work in mid-IR range:
Chalcogenide glass fibers of As$_2$S$_3$ composition work in the range 7000-15500cm$^{-1}$. Polycrystalline fibers extruded from crystals of AgClBr solid solutions cover the spectral range approx. 3100-600cm$^{-1}$. Graphic example of transmission ranges is shown at the spectra.
Flexible fiber probes enable remote spectroscopy in-situ – to see all key spectral bands with no need of the sampling. Mid-IR measurements can nowadays be performed with advanced fiber optic probes as well. Example: no great difference is between liquid sample on ATR accessory in FTIR spectrometer and spectrum measured with fiber optic ATR probe coupled with the same spectrometer.
What are probe parts: ATR crystal tip at the end of immersible part (so-called shaft) and flexible fiber bifurcated to 2 legs with SMA connectors. Probes with metal shaft and reliable stainless steel protective conduit are suitable for reaction monitoring in the plant and in a lab reactor. Probes with polymer shaft and replaceable ATR tips are suitable for lab application.

**Standard Design for Process monitoring**

- Robust probe shaft made of Hastelloy C-22 with OD=12mm or 6,3mm
- Laser welding of distal part with ATR-tip
- Durable ATR-tip design to withstands high outer pressure

**Special Design for Lab application**

- Replaceable ATR tip based on ATR-cone or PIR-fiber loop
- Sealing with polymer o-ring
- Lower price
ATR Probe - Design of the Tip

Standard Design

- Two-bounce reflection ATR crystals
- (1+1) Input and output fiber
- ATR crystals of conical or pyramid shape are sealed with PEEK washer
- Special design of ATR crystal provides better sensitivity based on the refractive index
- Crown (optional) at the probe tip protects ATR crystal from impact

Ray-tracing is very simple – the radiation goes from the input fiber to the ATR crystal and reflects inside into the output fiber. The ATR crystal is reliably fixed inside metal or polymer parts of the tip, sealed with polymer o-ring and can not fall away.
# ATR Crystal Choice

The whole variety of ATR crystals is presented to your attention in this table including main parameters and properties.

<table>
<thead>
<tr>
<th>Material of the tip</th>
<th>Angle at the Top</th>
<th>Refractive Index</th>
<th>Number of Reflections</th>
<th>Spectral Range</th>
<th>Chemical Resistance</th>
<th>Mechanical Strength / Durability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>90°</td>
<td>2.4</td>
<td>2</td>
<td>600-1900 cm⁻¹</td>
<td>Highest - can be used in any liquid</td>
<td>Ultimate</td>
</tr>
<tr>
<td>ZnSe</td>
<td>90°</td>
<td>2.4</td>
<td>2</td>
<td>600-3100 cm⁻¹</td>
<td>pH range: 5-9 Complexing agents (ammonia and EDTA) will also erode surface</td>
<td>Low</td>
</tr>
<tr>
<td>Si &amp; Ge</td>
<td>120°</td>
<td>Si: 3.4 Ge: 4</td>
<td>2</td>
<td>600-3100 cm⁻¹</td>
<td>Si: pH range 0-10 Ge: pH range 1-12</td>
<td>Moderate</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>60°</td>
<td>1.9</td>
<td>3</td>
<td>1550-9000 cm⁻¹</td>
<td>pH range: 0-14 Do not use with strong acids and alkalis</td>
<td>High</td>
</tr>
<tr>
<td>Detachable Loops</td>
<td>Not defined</td>
<td>2.1</td>
<td>Multiple</td>
<td>600-2500 cm⁻¹ or 1550-6500 cm⁻¹ depending on fiber in probe</td>
<td>pH range: 5-9 Complexing agents and SO₄²⁻ ions will also erode surface</td>
<td>Low</td>
</tr>
</tbody>
</table>
An unusual ATR tip is a Polycrystalline fiber loop. It is attached to detachable loop probe and is replaceable or disposable. Kits of 5 or 10 fiber loop tips can be purchased separately to be used with the probe bought once. Loop tips can be made with several fiber turns to enhance sensitivity of such tip.

How to replace loop tip

How to enhance sensitivity
Single beam spectra of fiber probes with different ATR crystals are shown here to demonstrate different working spectral ranges.
Detection limit of FTIR-fiber system depends on:

1. Sensitivity of ATR tip defined by:
   - number of reflections
   - reflection angle
   - refractive index

2. SNR in the system spectrometer-coupler-probe defined by:
   - Spectrometer detector - DTGS or MCT
   - Coupling efficiency to the fiber
   - Probe signal performance

Average signal of the IR-fiber probe is about 1-1.5% of the open beam intensity

Effect of number and angle of reflections

Calculated effective optical path in acetone
- 10.5 µm
- 7.3 µm

Example:
- diamond ATR crystals of different shape

Refractive index influence

Calculated effective optical path in acetone
- 10.5 µm
- 5.1 µm

Example:
- ATR crystals of the same shape, different materials = different refractive index

Real advantage of 2 * 45°-bounce cone

Real advantage of diamond cone vs calculation

art photonics developed a special design of Ge and Si cones of perfect sensitivity – see slide 14
• Detection limit of FTIR-fiber system is often the first question from the customer. Let’s consider what it depends on: Sensitivity of ATR tip (1) and SNR of the whole system spectrometer-coupler-probe (2) are most important.

• Look at a couple of illustrative examples how the sensitivity of ATR crystal varies with different factors:
  • First picture: number of reflections does not always increase the sensitivity. Reflection angle (which is an angle between the beam and perpendicular to the surface) is also important and two reflections in a diamond cone with 45 degrees are really more advantageous than 3 reflections 60 degrees each.
  • Second picture: different materials have different refractive index. For example, the same crystal shape for a material with high refractive index which is 4.0 for Germanium, results in a low sensitivity. That is why art photonics developed special shape for each type of ATR crystal to reach the best contrast – see slide 14.

• SNR in the system depends on many parameters as shown at the slide 11. Some examples of the factors are shown at the next slide. To your knowlegde, average signal of fiber probe system is only about 1-1.5% of the open beam intensity. But the advantages of non-sampling technology are determinant for a whole number of applications.

• first column – 2 pictures illustrate the detector choice effect: the same Diamond ATR probe at the same spectrometer Nicolet 6700 using either MCT or DTGS detector. The detection limit with MCT detector is 5 times better.

• Second column – 2 pictures illustrate the probe choice. Silicon ATR probe shows usually 2 times lower intensity as compared to Diamond ATR. Then a double advantage of detection limit can be reached with a diamond probe. Why we offer Silicon ATR probe? Broader spectral working range of Si-ATR is determinant for some customers.
Sensitivity Depends on Detector Choice/Probe Choice

Example:
Spectrometer - Nicolet 6700 **DTGS vs MCT** detector
Fiber coupler - FPC-6M
Probe - Diamond ATR, 1.5m long

Zero line is much more smooth with MCT detector. Detection limit with DTGS is approx. 0.5% ethanol in water vs 0.1% with MCT detector.

Example:
Spectrometer – iS5 Fiber coupler - FPC-2M
**Diamond ATR probe vs Si ATR probe**

Zero line is more smooth for Diamond probe. The detection limit advantage of Diamond probe is approx, 2 times vs Si-ATR probe.
The special design of ATR crystals results in their more or less comparable sensitivity (contrast) in art photonics ATR-probes. It is shown at this picture at the example of acetone absorption peaks.
Special probes

High Temperature Probe’s working range \(-150^\circ C +250^\circ C\) vs standard range \(150^\circ C +140^\circ C\)

The air flow cools delicate polycrystalline fibers inside the probe shaft. A thermocouple is only for the monitoring of fiber temperature to avoid their over-heating.

High Temperature probe is available only with 12mm diameter shaft.

Probes for laboratory applications do not contain metal parts in the tip and can be used for the monitoring of electrochemical reactions, potentiometric cells, measurements in high-frequency fields. PTFE tip is available on request.
art photonics Probe Overview

How to orientate yourself in this table? Left column shows different ATR tips with their spectral working range. The line “Design” contains different probe designs such as standard, Lab, HT, Sterilizable. Short description of each design is in the table heading and main parameters of each probe are in cells. Empty cell= no option.

<table>
<thead>
<tr>
<th>ATR crystal</th>
<th>Design</th>
<th>Shaft Ø</th>
<th>PIR fiber 900/1000, 30cm shaft Hastelloy C22, 150cm total, LTP conduit with SMA 905 connectors</th>
<th>PIR fiber 900/1000, 15cm shaft PEEK, 150cm total, PEEK protective tubing with SMA 905 connectors</th>
<th>PIR fiber 900/1000, 30cm shaft Hastelloy C22, 150cm total, LTP conduit with SMA 905 connectors, air flow cooling</th>
<th>PIR fiber 900/1000, 30cm shaft, 150cm total, LTP conduit with SMA 905 connectors, detachable fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
<td>PEEK Lab</td>
<td>High Temperature</td>
<td>Sterilizable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATR crystal</td>
<td>Shaft Ø</td>
<td>PEEK</td>
<td>Lab</td>
<td>High Temperature</td>
<td>Sterilizable</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond, 600-1900cm⁻¹</td>
<td>6,3mm dia</td>
<td>12mm dia</td>
<td>6,3mm dia</td>
<td>12mm dia</td>
<td>6,3mm dia</td>
<td>12mm dia</td>
</tr>
<tr>
<td>Si 600-3100cm⁻¹</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>7Bar, -100°C+140°C</td>
<td>100Bar, -150°C+250°C</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
</tr>
<tr>
<td>Ge, 600-3100cm⁻¹</td>
<td>10Bar, -150°C+80°C</td>
<td>10Bar, -150°C+80°C</td>
<td>7Bar, -100°C+80°C</td>
<td>10Bar, -150°C+80°C</td>
<td>10Bar, -150°C+140°C</td>
<td>10Bar, -150°C+80°C</td>
</tr>
<tr>
<td>ZnSe, 600-3100cm⁻¹</td>
<td>10Bar, -150°C+140°C</td>
<td>7Bar, -100°C+140°C</td>
<td>10Bar, -150°C+250°C</td>
<td>10Bar, -150°C+140°C</td>
<td>10Bar, -150°C+140°C</td>
<td>10Bar, -150°C+140°C</td>
</tr>
<tr>
<td>ZrO₂ with CIR 500/550 fiber, 1550-9000cm⁻¹</td>
<td>100Bar, -150°C+90°C</td>
<td>100Bar, -150°C+90°C</td>
<td>7Bar, -100°C+90°C</td>
<td>100Bar, -150°C+200°C</td>
<td>100Bar, -150°C+90°C</td>
<td>100Bar, -150°C+90°C</td>
</tr>
<tr>
<td>PIR-Loop</td>
<td>PIR fiber 900/1000, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 600-2500cm⁻¹, ≤ 100°C</td>
<td>CIR fiber 500/550, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 1550-6500cm⁻¹, ≤ 90°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Application: On-Line Reaction Monitoring

High or low temperature, high pressure or vacuum, harmful or poisonous mixture in the reactor or simply fast change of the mixture composition at the sampling and measurement at the room conditions – all these conditions push the customer to choose and use fiber optic for the remote reaction monitoring:

- Chemical synthesis
- Extraction, dissolution, crystallization
- Degradation and contamination of oils
- Cryo reactions
- Sludge measurements
- Determination of hydroxyl number of polyols
- Monitoring of anti-solvent crystallization
- Analysis of solvent mixtures

Conical design of ATR crystal makes it easy to retract the tip out of the cured epoxy. The transmission in the range 1600-1900cm\(^{-1}\) is enough to see absorption bands of C=O groups even using FTIR spectrometer iS5 from Thermo with DTGS detector.
Application: Polymerization Monitoring

Monitoring of PVA polymerization reaction showed abrupt not gradual concentration change.
Application: Synthesis Monitoring

08:49-09:01
10:00-10:59
11:00-11:59
12:01-12:59
13:00-13:35
13:36-15:06
art photonics probes can be fit into different process interfaces. Process interface is a special unit for automatic cleaning and calibration of the probe tip. For example, Ceramat and Sensogate units from Knick are shown here. Spectra demonstrate the stages of the ATR crystal cleaning with three different detergents. The matching of the probe to the unit should be checked in each case.
A reliable methodology utilizing an ATR-IR fiber probe for in-line monitoring of low temperature reactions is presented. Hence, in situ monitoring of lithiation reactions is realized and the potential to investigate sensitive intermediates is being demonstrated.

The progress in chemometrics and spectroscopic equipment provide possibility to study fast chemical reactions.
Application: In Situ Characterization of Waste Sludge

Double-Shell Tank

IR-attenuation of Heavy Water solutions in Water

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.23</td>
</tr>
<tr>
<td>Na$_3$PO$_4$</td>
<td>0.27</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>1.5</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>4.5</td>
</tr>
<tr>
<td>CsNO$_3$</td>
<td>0.00013</td>
</tr>
</tbody>
</table>

Calibration contents: 0.02%; 12.20%; 39.21%; 53.51%; 60.61%; 71.04%; 78.96%; 90.61%; 95.38%; 99.75%.

Note: No radionuclides
Application: Process Control On-Line in Fermenter

ATR-fiber probe immersed in biomass with process-interface and coupled with FTIR-spectrometer enables to control fermentation process on-line for a better yield in biogas production and to prevent expensive process failures.
Future Trends

<table>
<thead>
<tr>
<th>Probes for ATEX areas</th>
<th>Tiny probes of 3mm outer diameter for micro-reactors. Patented design.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATR flat crystals for touch probes for soft materials</td>
<td>Design of Shaft-in-shaft probes with removable inner shaft to enable outer shaft sterilization</td>
</tr>
</tbody>
</table>

They are still not a standard product but we can offer them already not as R&D.
Fiber Couplers

Fiber Probe Coupler for Nicolet iS5
~Includes SMA905 connectors
~Able to be purged
~Ready to install (iD form factor)
~Only for use in Mid-IR Region
~No MCT option available on iS5

Fiber Probe Coupler for Nicolet iS10/iS50
~Also compatible with Nicolet 5700/6700, and Avatar 360
~Includes SMA905 connectors
~Able to be purged
~Mounted on standard baseplate
~For use in Mid-IR and Near-IR regions
Fiber Probe Coupler for Nicolet iS5N
~Includes SMA905 connectors
~Able to be purged
~Ready to install (iD form factor)
~Only for use in Near-IR Region

Fiber Probe Universal Coupler
~Also compatible with any FTIR spectrometer
~Mounted on customized baseplate
~Includes SMA905 connectors
~Able to be purged
~For use in Mid-IR and Near-IR regions