Benefits of Fiber Optic Probes for Mid-IR Analysis

Dr. Viacheslav ‘Slava’ Artyushenko
President
art photonics GmbH
sa@artphotonics.com

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.

- **Near IR range** – transmission and reflection probes, optical path 1-10mm
- **Mid IR range** – ATR probes, optical path 1-10µm

Example: Acetone Absorption Bands

### Infrared Fibers

#### Chalcogenide IR fiber

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission range</td>
<td>3000 – 1550 cm⁻¹</td>
</tr>
<tr>
<td>Core/clad material</td>
<td>AgClBr</td>
</tr>
<tr>
<td>Core/clad diameter, µm</td>
<td>900/1000/1000</td>
</tr>
<tr>
<td>Protective jacket</td>
<td>Double polymer</td>
</tr>
<tr>
<td>Core refractive index</td>
<td>2.4</td>
</tr>
<tr>
<td>Numerical Aperture</td>
<td>0.3</td>
</tr>
<tr>
<td>Operating temperature, °C</td>
<td>270 + 95 + 90</td>
</tr>
<tr>
<td>Minimal bending radius, mm</td>
<td>120</td>
</tr>
</tbody>
</table>

#### Polycrystalline IR fiber

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Range</td>
<td>3100 – 600 cm⁻¹</td>
</tr>
<tr>
<td>Core/clad material</td>
<td>AgClBr</td>
</tr>
<tr>
<td>Core/clad diameter, µm</td>
<td>900/1000</td>
</tr>
<tr>
<td>No protective jacket</td>
<td></td>
</tr>
<tr>
<td>Core Refractive Index</td>
<td>2.15</td>
</tr>
<tr>
<td>Numerical Aperture</td>
<td>0.3</td>
</tr>
<tr>
<td>Operating temperature, °C</td>
<td>270 + 140</td>
</tr>
<tr>
<td>Minimum bend radius, mm</td>
<td>150</td>
</tr>
</tbody>
</table>
### Why Use Fiber Optics?

Flexible fiber probes enable remote spectroscopy in-situ – to see all key spectral bands with no need for sampling.

**ATR Accessory**

**ATR Fiber Optic Probe (1.5m long)**

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### ATR Probe – General Design

**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

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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

Schematic of ATR probe tip

ATR Crystal Choices

<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>600-1900cm⁻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>600-3100cm⁻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° Si - 3.4 Ge - 4</td>
<td>2</td>
<td>600-3100cm⁻¹</td>
<td>Si: pH range 0-10 Ge: pH range 1-12</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>60°</td>
<td>1.9</td>
<td>3</td>
<td>1550-9000cm⁻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>600-2500cm⁻¹ or 1550-6500cm⁻¹ depending on fiber in probe</td>
<td>pH range: 5-9 Complexing agents and SO₂ ions will also erode surface</td>
<td>Low</td>
</tr>
</tbody>
</table>
Detachable Loop Probe

How to replace loop tip

How to enhance sensitivity

Working Spectral Range for ATR-Cone Probes
Detection limit

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:
  7.5 µm

Example: diamond ATR crystals of different shape

Refractive index influence

- Calculated effective optical path in acetone:
  7.5 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

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.
Sensitivity for different ATR-tips

![Acetone peaks measured in transmission for different ATR tips](chart)

**Sensitivity for different ATR-tips**

Special probes

High Temperature Probe’s working range -150°C +250°C vs standard range 150°C +140°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.

PEEK-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 shaft (instead of PEEK) is available on request.
art photonics Probe Overview

<table>
<thead>
<tr>
<th>Design</th>
<th>Shaft Ø</th>
<th>ATR crystal</th>
<th>Si 650-950cm⁻¹</th>
<th>Ge 650-950cm⁻¹</th>
<th>ZnSe 650-950cm⁻¹</th>
<th>ZrO² with CIR 950/550 fiber, 1500-4000cm⁻¹</th>
<th>PIR-Loop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>12mm dia</td>
<td>12mm dia</td>
<td>7Bar, -150°C+80°C</td>
<td>7Bar, -150°C+80°C</td>
<td>7Bar, -150°C+80°C</td>
<td>100Bar, -150°C+90°C</td>
<td></td>
</tr>
<tr>
<td>PEEK Lab</td>
<td>6.3mm dia</td>
<td>200Bar, -150°C+140°C</td>
<td>100Bar, -100°C+140°C</td>
<td>100Bar, -100°C+140°C</td>
<td>100Bar, -100°C+140°C</td>
<td>PIR fiber 900/1000, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 600-2500cm⁻¹, ≤ 100°C</td>
<td></td>
</tr>
<tr>
<td>High Temperature</td>
<td>6.3mm dia</td>
<td>200Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>CIR fiber 900/550, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 1500-6500cm⁻¹, ≤ 90°C</td>
<td></td>
</tr>
<tr>
<td>Sterilizable</td>
<td>12mm dia</td>
<td>200Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>100Bar, -150°C+140°C</td>
<td>PIR fiber 900/1000, 30cm shaft Hastelloy C22, 150cm total, LTP conduit with SMA 905 connectors, detachable fiber cooling</td>
<td></td>
</tr>
</tbody>
</table>

Application: On-Line 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

Monitoring of extraction process (silicon oil by aceton)
Application: Dissolution Process Control

![Image of dissolution process control equipment]

- Graph showing transmission at certain wavenumber over time:
  - Transmission at 1315 cm⁻¹
  - Transmission at 1353 cm⁻¹

Application: Process Interfaces – Clean in Place

- SensoGate-FOS
- Ceramat-FOS

![Images of SensoGate-FOS and Ceramat-FOS]

Graph showing the cleaning process for rinsing and oil filling.
Application: Monitoring Chemical Reactions

- 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.

![Graph](image1)

**Figure 1:** Deposition section experiment: formation of 3-bromophenol in a metal halogen exchange reaction from 2-bromophenol (MSU, THF, 40 °C).

![Graph](image2)

**Figure 4:** Intermediate 3 formation as extracted from the spectral data set via MCR-ALS algorithm: bis-exp. fit 2 ($t_1$: 6.9 s, $t_2$: 2.5 $\times$ 10^{-5} s, $R^2$: 0.99), bis-exp. fit 3 ($t_1$: 6.8 s, $t_2$: 3.3 $\times$ 10^{-5} s, $R^2$: 0.98).

Application: In Situ Characterization of Waste Sludge

**Double-Shell Tank**

<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$_2$PO$_4$</td>
<td>0.27</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>1.6</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>4.6</td>
</tr>
<tr>
<td>CsNO$_3$</td>
<td>0.00913</td>
</tr>
</tbody>
</table>

**IR-attenuation of Heavy Water solutions in Water**

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

Note: No radioactive.
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>Multi 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>
Mid-IR Fiber Optic Probes

A complete mid-IR fiber optic system includes one fiber coupler, one alignment cable, and one fiber optic probe.

1. Fiber Coupler  2. Alignment Cable  3. Fiber Optic Probe

<table>
<thead>
<tr>
<th>Fiber Couplers</th>
<th>869-177800 Fiber Probe Coupler for Nicolet iS5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>~Includes SMA905 connectors</td>
</tr>
<tr>
<td></td>
<td>~Able to be purged</td>
</tr>
<tr>
<td></td>
<td>~Ready to install (ID form factor)</td>
</tr>
<tr>
<td></td>
<td>~Alignment cable sold separately</td>
</tr>
<tr>
<td></td>
<td>~Only for use in Mid-IR Region</td>
</tr>
<tr>
<td></td>
<td>~No MCT option available on iS5</td>
</tr>
</tbody>
</table>

| 869-177900 Fiber Probe Coupler for Nicolet iS10/iS50 |
|~Also compatible with Nicolet 5700/6700, and Avatar 360 |
Fiber Alignment Cables

Types of Fiber Alignment Cables

- **Mid-IR Alignment Cable (PIR)**
  - PIR cable
  - Spectral range: 600-5000 cm⁻¹

- **Mid/Near-IR Alignment Cable (CIR)**
  - CIR cable
  - Spectral range: 1550-9000 cm⁻¹

- **Near-IR/Visible Alignment Cable (NIR)**
  - NIR cable
  - Spectral range: 4000-25,000 cm⁻¹

Fiber Optic Probe Material

- **PEEK**
- **Detachable Loop**
- **Hastelloy**
- **High-Temp & Pressure**
### iS5 vs. iS10 vs. iS50

<table>
<thead>
<tr>
<th>Model</th>
<th>Benefits</th>
<th>Applications</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicolet iS5</td>
<td>• Small size</td>
<td>• Reaction monitoring</td>
<td>• 1 – 5% concentration (DTGS Detector)</td>
</tr>
<tr>
<td></td>
<td>• Portable</td>
<td>• Fume hoods</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Rugged</td>
<td>• Reactor vessels</td>
<td></td>
</tr>
<tr>
<td>Nicolet iS10</td>
<td>• Workhorse spectrometer</td>
<td>• General probe applications</td>
<td>• 0.2 – 1% concentration (MCT Detector)</td>
</tr>
<tr>
<td></td>
<td>• Optional MCT detector</td>
<td>• Raw material screening</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Improved performance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicolet iS50</td>
<td>• Highest-performing optics</td>
<td></td>
<td>• 0.05 – 1% concentration (MCT Detector)</td>
</tr>
<tr>
<td></td>
<td>• Flexible configuration</td>
<td></td>
<td>• Sensitive, low concentration analysis</td>
</tr>
<tr>
<td></td>
<td>• Ability to adapt</td>
<td></td>
<td>• Low throughput analysis</td>
</tr>
<tr>
<td></td>
<td>• Multi-spectral ranges</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Connect With Us!

- **Contact our presenters with your questions:**
  - Dr. Viacheslav Artushenko, sa@artphotonics.com
  - Matt Gundlach, matthew.gundlach@thermofisher.com

- **Find us on the web:**
  - art photonics: [www.artphotonics.de](http://www.artphotonics.de)
  - Thermo Scientific FTIR product line: [www.thermofisher.com/ftir](http://www.thermofisher.com/ftir)
  - Thermo Scientific spectroscopy products: [www.thermofisher.com/spectroscopy](http://www.thermofisher.com/spectroscopy)
  - Spectroscopy videos: [https://www.youtube.com/thermoscientificspec](https://www.youtube.com/thermoscientificspec)
  - FTIR Spectroscopy Academy: [www.thermofisher.com/FTIRAcademy](http://www.thermofisher.com/FTIRAcademy)

- **More Events in 2016**
  - Webinar: **Driving Confidence with Tools for FTIR QA/QC** – November 2
  - On-demand Spectroscopy Webinars: [www.thermofisher.com/spectroscopywebinars](http://www.thermofisher.com/spectroscopywebinars)
  - Eastern Analytical Symposium (EAS), Somerset, NJ, Nov. 14-16
  - MRS Fall Meeting, Boston, MA, Nov. 27-Dec 2