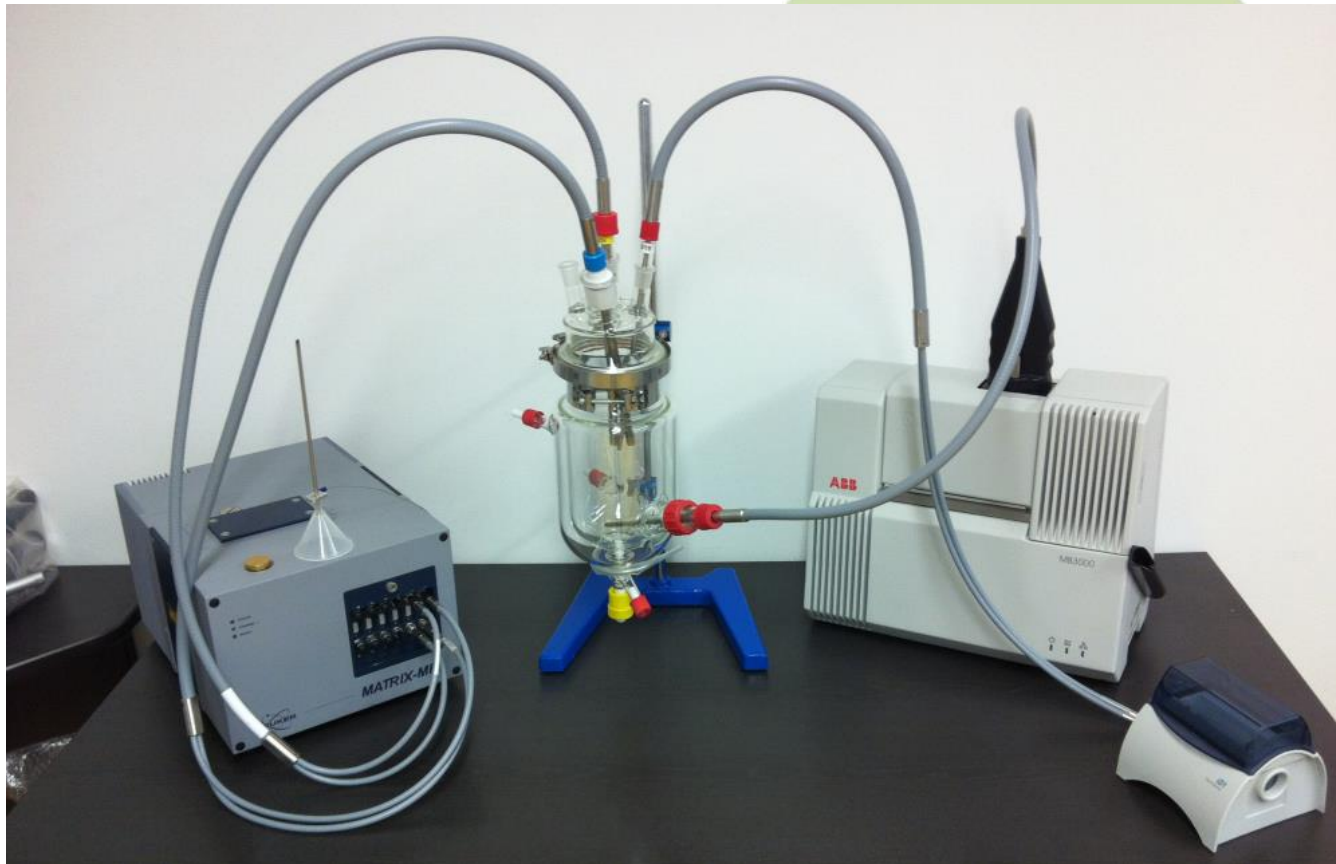


## OPTICAL FIBER PROBES FOR PROCESS SPECTROSCOPY



## OPTICAL FIBER PROBES FOR PROCESS SPECTROSCOPY

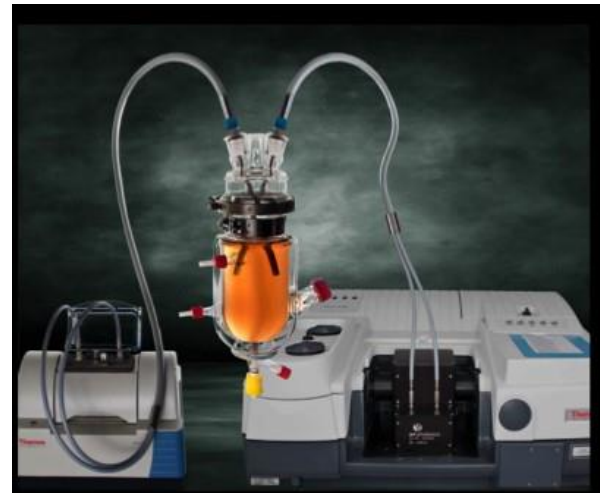
**FlexiSpec®** product line from **art photonics GmbH** is a cluster of innovative Fiber Optic Probes and Fiber Probe Couplers designed for in-line analytical analysis in broad spectral range – from UV to Mid-IR ( $550\text{cm}^{-1}$  to  $55550\text{cm}^{-1}$ ).

**FlexiSpec®** family of Immersion Fiber Probes includes ATR, Transmission, Transfection, Fluorescent and Diffuse Reflection probes - all compatible with any FT-MIR, FT-NIR or dispersion spectrometer, process-photometer, IR-LED or QCL spectral sensor to use in-line for PAT-applications.

**FlexiSpec®** Fiber Probe Couplers (FPC) couple any FTIR - spectrometer with various fiber optic probes and upgrade it to eliminate sampling and to run reaction monitoring in-line. Our fiber probe couplers provides high coupling efficiency for ATR-Absorption, Transmission or Reflection process-spectroscopy in a broad spectral range, from UV to Mid-Infrared – to use fiber coupled FTIR not only with LN-cooled MCT-detectors, but with uncooled detectors as well.

**FlexiSpec®** probes design is cleanable for many processes where probe optics can be contaminated by media. Industrial probes are compatible with process-interfaces SensoGate-FOS and Ceramat-FOS with approved fittings to secure their semi or full automated use in complete process control systems. They can be retracted, cleaned and calibrated during chemical process – to enable remote process-control in any liquid, gas or solid mixtures under harsh environmental conditions. Combined with FTIR or UV/Vis spectrophotometers, our fiber probes facilitate qualitative and quantitative product analysis and enable the determination of specific chemical and physical properties.

We offer two categories of **FlexiSpec®** product portfolio: standard and customized. The standard products consist of preconfigured probes and probe couplers, which can be implemented in the laboratory, pilot plants or in production. The customized products allow users to custom configure fiber probes and couplers based on their unique process requirements.





future's  
in the making



# Part I

## Mid-IR Spectroscopy:

### ATR Fiber Probes & Probe Couplers

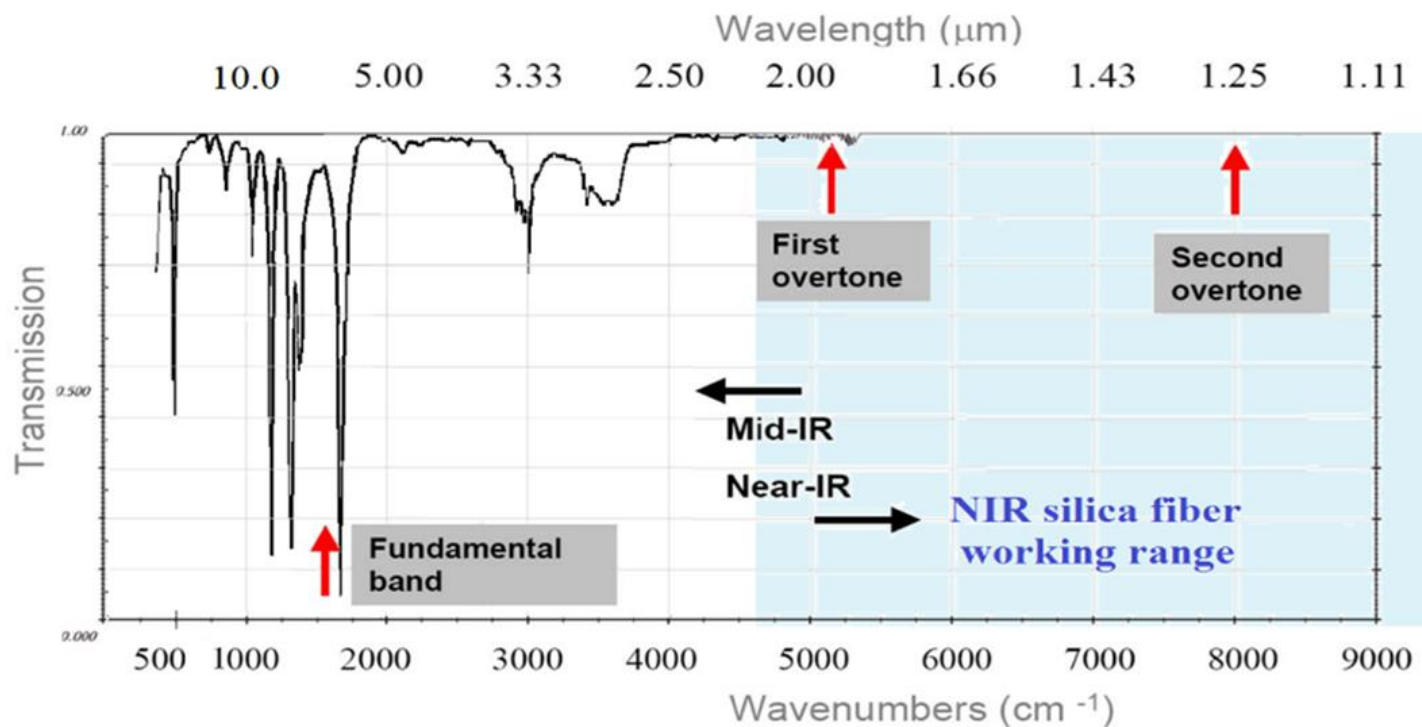
## Why Mid-Infrared Spectroscopy?

Infrared spectroscopy has been used to analyze materials since the middle of the last century. The infrared spectrum of the material is similar to a fingerprint with absorption peaks that correspond to vibrational frequencies between the bonds of the atoms that make up the material.

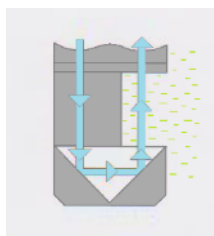
Since each individual material is a unique combination of atoms, no two compounds give exactly the same infrared spectrum. Therefore, infrared spectroscopy can lead to identification (qualitative analysis) of all types of materials. In addition, the peak size in the spectrum is a direct indicator of the amount of material presented. Thanks to modern software, the infrared port is an excellent tool for quantitative analysis.

The most intensive fundamental vibrational absorption bands are mainly present in so-called “fingerprint 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 5-50 $\mu$ m optical path in mid-IR range.

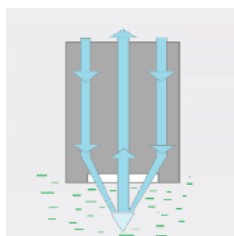
## Why Mid-Infrared Spectroscopy?



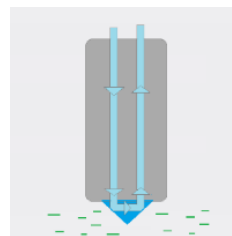
Example:  
Acetone Absorption Bands



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



Mid IR range – ATR probes, optical path 1-10 $\mu\text{m}$

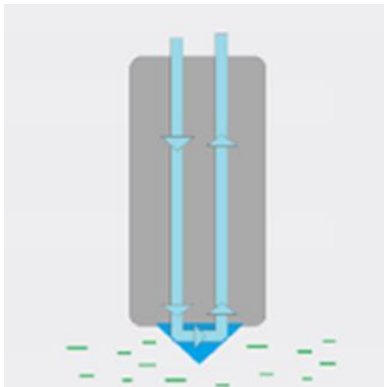


The optimum optical path length depends on the absorption coefficient of the substance



## What is FT-IR?

FT-IR (Fourier Transform InfraRed), the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.



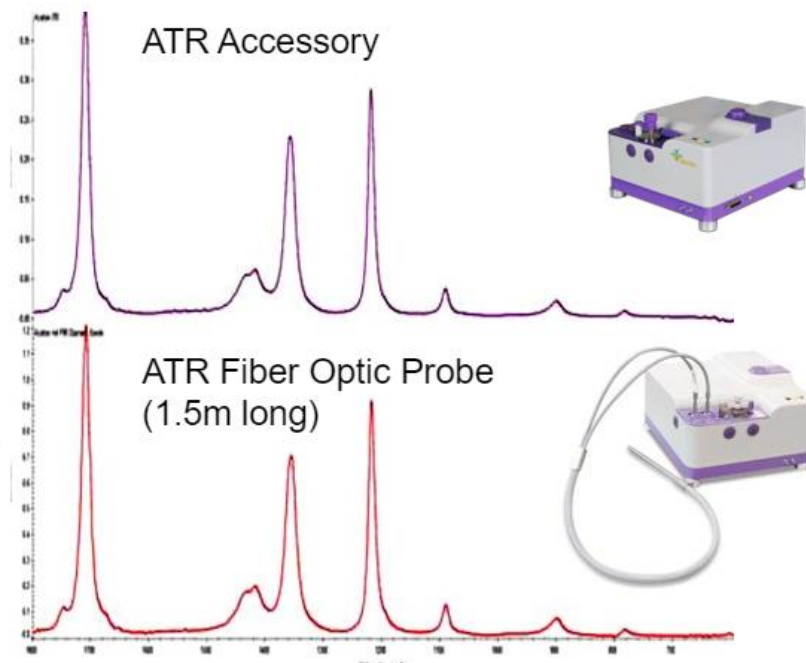
Ray-tracing is very simple – the radiation goes from the input fiber to the ATR crystal and reflects inside into the output fiber. The ATR crystal is reliably fixed inside metal or polymer parts of the tip, sealed with polymer ring and can not fall away.



## Why use fiber optics?

Flexible fiber probes enable a remote spectroscopy in-situ in real time to see all key spectral bands with no need to prepare samples and place them into the sample chamber, and makes remote analysis possible for molecular reaction monitoring in-line.

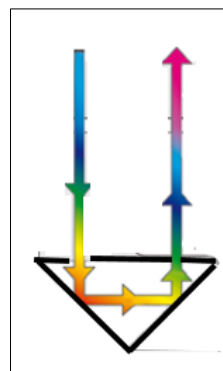
**Example:** no great difference is between liquid sample on ATR accessory in FTIR spectrometer and spectrum measured with fiber optic ATR probe coupled with the same spectrometer.



## Choosing the Right ATR Fiber Probe

The most important issue in the FTIR analysis is right choice of type of the ATR fiber probe. The best probe type depends on the nature of the sample and environment conditions.

Regardless of the fiber probe, the concept is still the same – light from the FT-IR analyzer is guided by the optical fiber probe onto the sample. From there the light with the sample spectra is captured by a fiber optic detection line and returned to the analyzer where the data is analyzed.

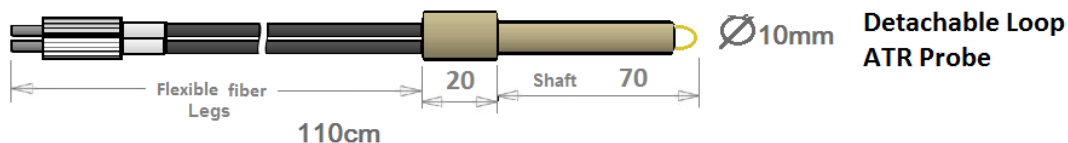
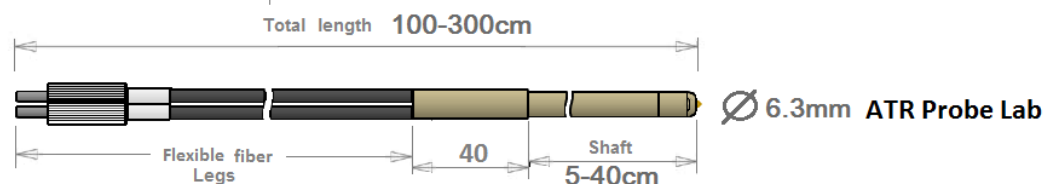
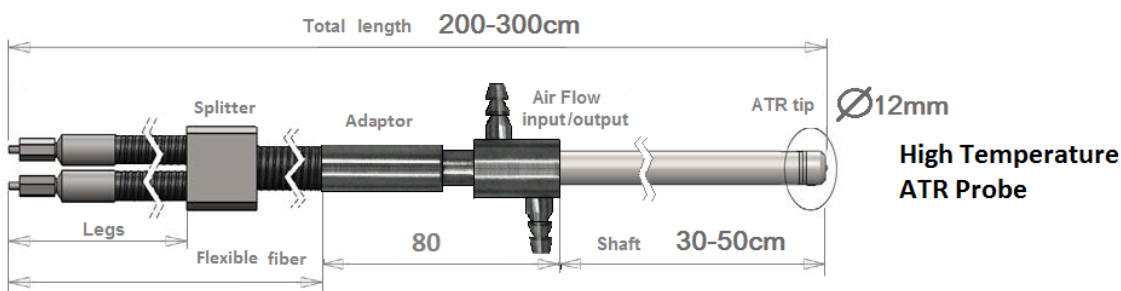
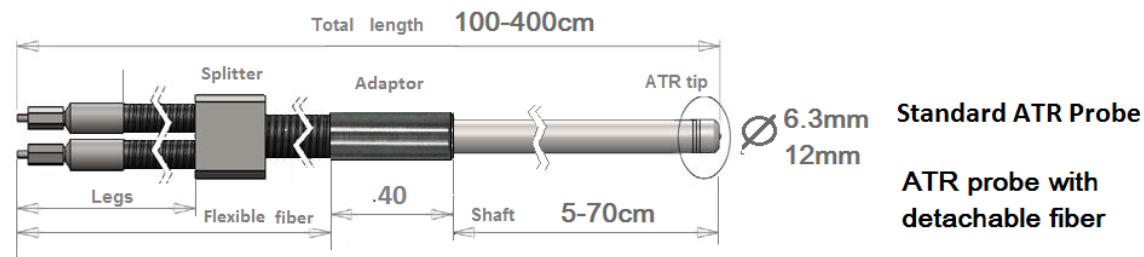


## Fiber Optic ATR Probes: Overview

	PIR fiber 900/1000, 30cm shaft Hastelloy C22, 150cm total, LTP conduit with SMA 905 connectors		PIR fiber 900/1000, 15cm shaft PEEK, 150cm total, PEEK protective tubing with SMA 905 connectors	PIR fiber 900/1000, 30cm shaft Hastelloy C22, 200cm total, LTP conduit with SMA 905 connectors, air flow cooling	PIR fiber 900/1000, 30cm shaft, 150cm total, LTP conduit with SMA 905 connectors, detachable fiber	
Design	Standard		PEEK Lab	High Temperature	Sterilizable	
Shaft Ø	6,3mm dia	12mm dia	6,3mm dia	12mm dia	6,3mm dia	12mm dia
ATR crystal						
Diamond, 600-1900cm <sup>-1</sup>	200Bar, -150°C +140°C	200Bar, -150°C +140°C		200Bar, -150°C +250°C	200Bar, -150°C +140°C	200Bar, -150°C +140°C
Si, 600-3100cm <sup>-1</sup>	100Bar, -150°C +140°C	100Bar, -150°C +140°C	7Bar, -100°C +140°C	100Bar, -150°C +250°C	100Bar, -150°C +140°C	100Bar, -150°C +140°C
Ge, 600-3100cm <sup>-1</sup>	10Bar, -150°C +80°C	10Bar, -150°C +80°C	7Bar, -100°C +80°C		10Bar, -150°C +80°C	10Bar, -150°C +80°C
ZnSe, 600-3100cm <sup>-1</sup>		10Bar, -150°C +140°C	7Bar, -100°C +140°C	10Bar, -150°C +250°C		
ZrO2 with CIR 500/550 fiber, 1550-9000cm <sup>-1</sup>	100Bar, -150°C +90°C	100Bar, -150°C +90°C	7Bar, -100°C +90°C	100Bar, -150°C +200°C	100Bar, -150°C +90°C	100Bar, -150°C +90°C
Detachable Loop	PIR fiber 900/1000, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 600-2500cm <sup>-1</sup> , -50°C +90°C Disposable ATR-Loop Tip					
	CIR fiber 500/550, 10cm shaft PEEK, 110cm total, PEEK tubing with SMA 905 connectors, 1550-6500cm <sup>-1</sup> , -50°C +90°C Disposable ATR-Loop Tip					



## ATR fiber probe – general design



### Standard build materials:

Fiber - Polycrystalline  
- Chalcogenide  
- Silica

ATR crystal - Diamond  
- Silicon  
- Germanium  
- ZnSe  
- Cubic Zirconia ( $ZrO_2$ )  
- Sapphire on request

Shaft - PEEK (poly-ether-ether-keton),  
- Hastelloy C-22

Protective tube - PEEK,  
- Liquid Tight tube  
with limited bending radius  
- KOPEX industrial applic.

Sealing - laser welding,  
- PEEK, PTFE, FKM rings,  
- gold on request

Adapters and connectors - S. Steel  
- Titanium  
- Brass

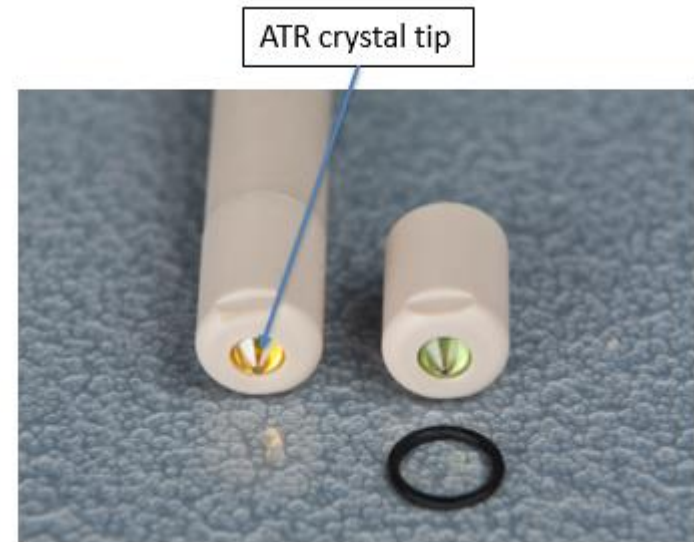
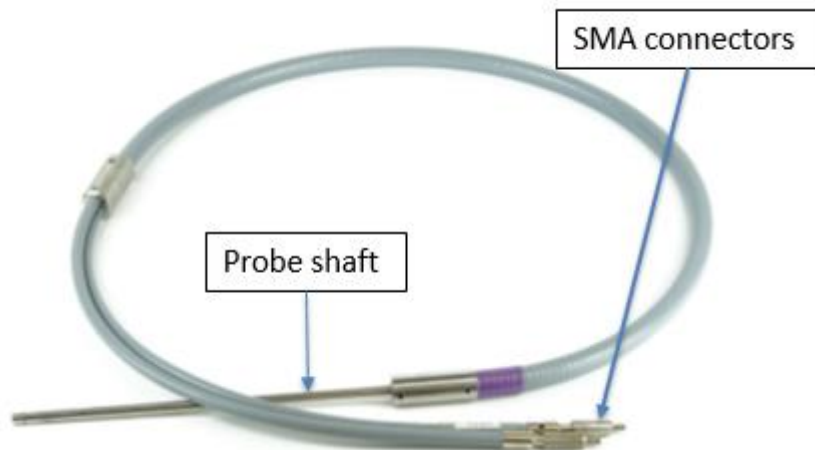
## ATR fiber probe – general design (continuation)

ATR probe consists of: **ATR crystal tip** at the end of immersible part (so-called shaft) and **Mid-IR optical fiber** bifurcated to 2 legs with SMA connectors.

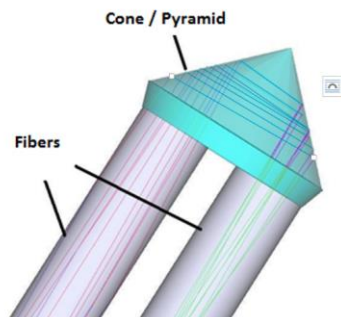
**ATR crystal tip** and **Mid-IR optical fiber** are the most important parts of the probe

Probes with metal shaft and robust 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.



## ATR probe tip – General design

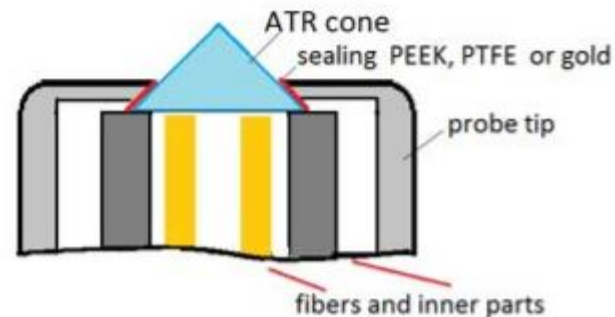


## Standard Design






- Two-bounce reflection ATR crystals
- Input and output fiber
- ATR crystals of conic and pyramid shape
- Special design to withstand high outer pressure
- Special design of ATR crystal to provide better sensitivity according refraction index

## Special Design for Lab application

- Replaceable ATR tip
- Lower price
- Possibility to manufacture dielectrical shaft



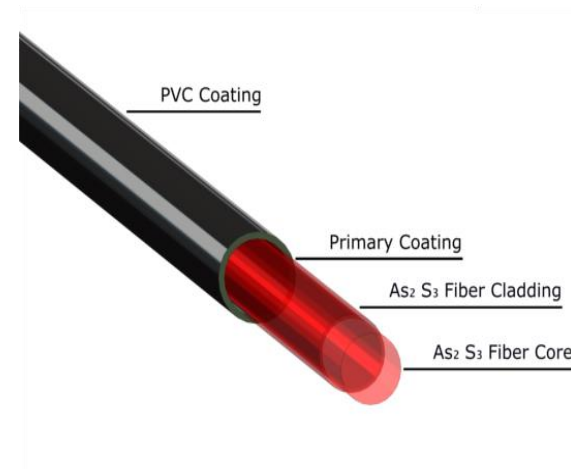
## ATR probe tip – General design

ATR Crystal Choices						
Material of the tip	Angle at the Top	Refractive Index	Number of Reflections	Spectral Range	Chemical Resistance	Mechanical Strength / Durability
 <b>Diamond</b>	90°	2.4	2	600-1900cm <sup>-1</sup>	Highest - can be used in any liquid	Ultimate
 <b>ZnSe</b>	90°	2.4	2	600-3100cm <sup>-1</sup>	pH range: 5-9 <u>Complexing agents</u> (ammonia and EDTA) will also erode surface	Low
 <b>Si &amp; Ge</b>	120°	Si - 3.4 <u>Ge</u> - 4	2	600-3100cm <sup>-1</sup>	Si: pH range 0-10 <u>Ge</u> : pH range 1-12	Moderate Moderate
 <b>ZrO<sub>2</sub></b>	60°	1.9	3	1550-9000cm <sup>-1</sup>	pH range: 0-14 Do not use with strong acids and <u>alkalies</u>	High
 <b>Detachable Loops</b>	<u>Not defined</u>	2.1	Multiple	600-2500cm <sup>-1</sup> or 1550-6500cm <sup>-1</sup> <u>depending on fiber in probe</u>	pH range: 5-9 <u>Complexing agents</u> and SO <sub>2</sub> ions will also erode surface	Low

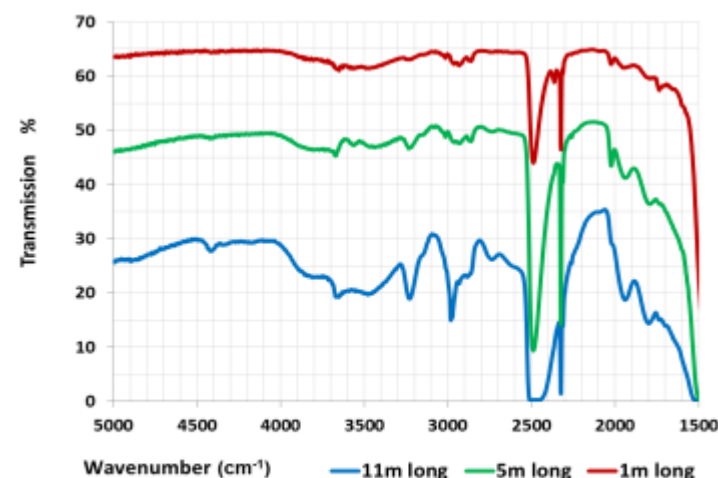
## Mid-IR Optical Fibers

### Chalcogenide IR-Fibers

Chalcogenide As-S glass fiber transmits IR-radiation in the spectral range of 1.1 – 6.5 $\mu$ m. High performance CIR core/clad fiber are drawn with core diameters span from 8 $\mu$ m to 500 $\mu$ m. Advanced drawing process with double polymer jacket provides a superior mechanical strength and high flexibility of CIR- fibers. Low optical losses and small absorption peaks over the mentioned spectral range ensure a successful use of CIR-fiber for a wide range of applications.



<b>Transmission range</b>	<b>9000 – 1550cm<sup>-1</sup></b>
<b>Core/Clad material</b>	As <sub>2</sub> S <sub>3</sub> /As-S
<b>Core/Clad/ jacket diameter, <math>\mu</math>m</b>	500/550/690
<b>Protective jacket</b>	Double polymer
<b>Core refractive index</b>	2.4
<b>Numerical Aperture</b>	0.3
<b>Operating temperature, °C</b>	-200 < T < 90
<b>Minimal bending radius, mm</b>	120



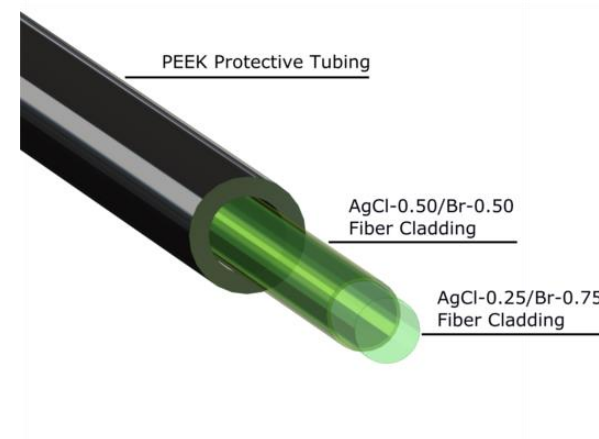
Transmission vs Wavenumber in As-S CIR fiber of different length



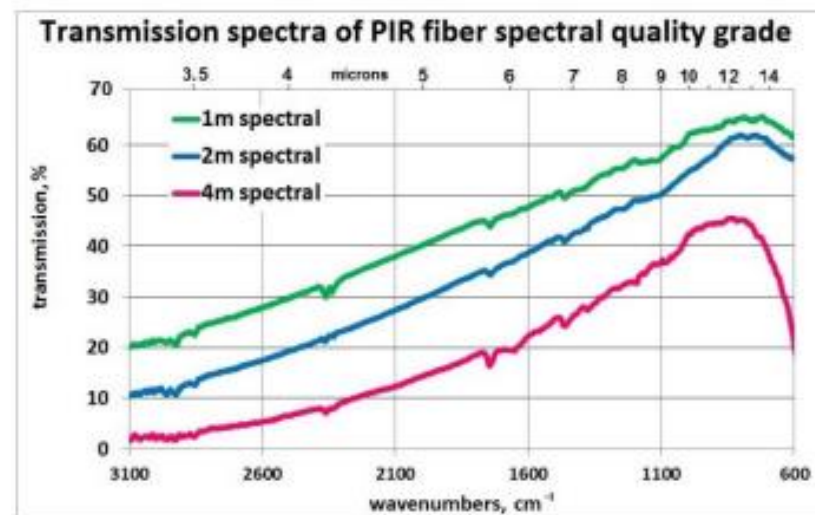
## Mid-IR Optical Fibers

### Polycrystalline IR-fibers

**art photonics** developed a volume production technology of a unique product – Core / Clad Polycrystalline Infra-Red (PIR-) fibers transparent over a broad spectral range 3 – 18  $\mu\text{m}$ . Highest performance PIR core/clad fiber are extruded with core diameters span from 240 $\mu\text{m}$  to 860 $\mu\text{m}$ . Continuously improved extrusion process provides a superior optical quality and mechanical strength of PIR- fibers. Low optical losses without absorption peaks over the mentioned spectral range ensure a successful use of PIR- fiber for a broad range of applications.



Transmission Range	3100- 600 cm <sup>-1</sup>
Core/clad material	AgClBr
Core/clad diameter, $\mu\text{m}$	900/1000
No protective jacket	
Core Refractive Index	2.15
Numerical Aperture	0.5
Operating temperature, $^{\circ}\text{C}$	$-270 < T < 140$
Minimum bend radius, mm	150



## Standard ATR probe

Near & Mid IR-fiber ATR-Probes produced for any type of FT-NIR, FT-IR and other IR-spectrometers, photometers and IR-LED or QCL spectral sensors.

ATR immersion fiber optic probes are suitable for reaction monitoring in lab, pilot plant and for full automated process control.

### Features

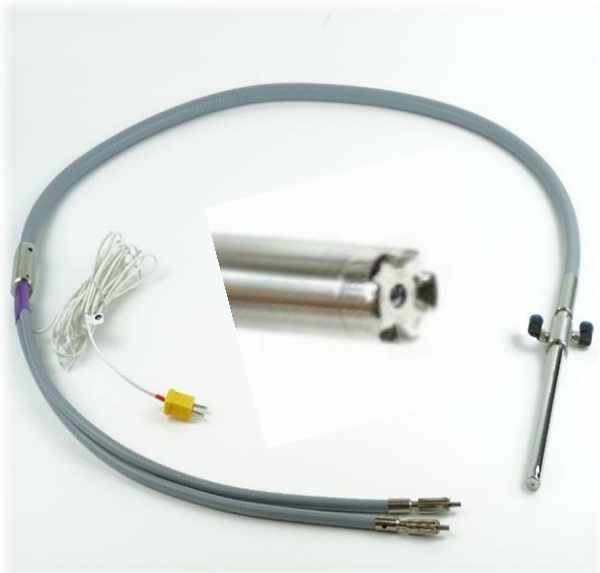
- High throughput in any part of Near & Mid InfraRed-spectrum
- ATR-tip shaped for immersion in liquid flow without dead zone
- Flexible and robust for industrial applications in harsh environment
- Compatible with all spectrometers and automated process-interfaces

### Applications

- Reaction Monitoring in real time
- Process Analytical Technologies (PAT)
- Remote Polymerization Control
- Crystallization Process Screening In-situ IR-Spectroscopy for PAT in Chemical, Petrochemical, Atomic, Biopharmaceutical & Food Industry



## Special ATR probes



Fiber Optic ATR-Probes for harsh environment can be used for process-spectroscopy in Near & Mid IR range to monitor reactions in-line in a broad temperature range from  $-100^{\circ}$  to  $+250^{\circ}$  C. They can resist to high pressures up to 200Bar and used with FTIR or any other IR-spectrometers and spectral sensors in automated process control with process-interfaces. The air flow cools polycrystalline fibers inside the probe shaft. A thermocouple controls the temperature of the fibers to avoid overheating. High Temperature probe is available only with 12 mm diameter shaft.

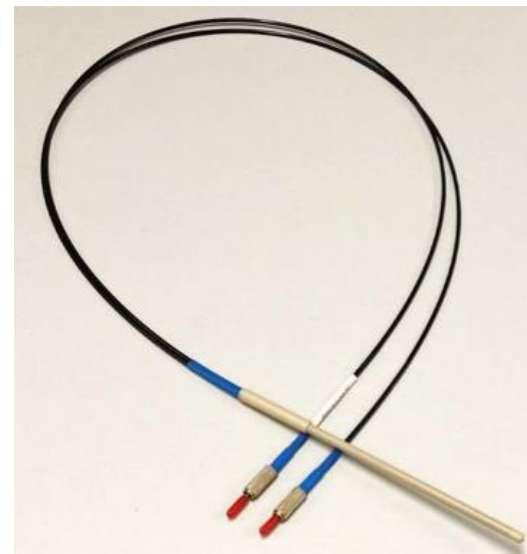


Touch-Probes are built with a flat ATR tip and are intended for the measurement of pellets, polymers, powders, etc. The cleaning of such probe tip is much easier in comparison with conical ATR crystal.

## Special ATR probes



ATR Probe with thin 3mm OD shaft are intended for micro-reactors.  
High Temperature probe is available only with 12mm diameter shaft.



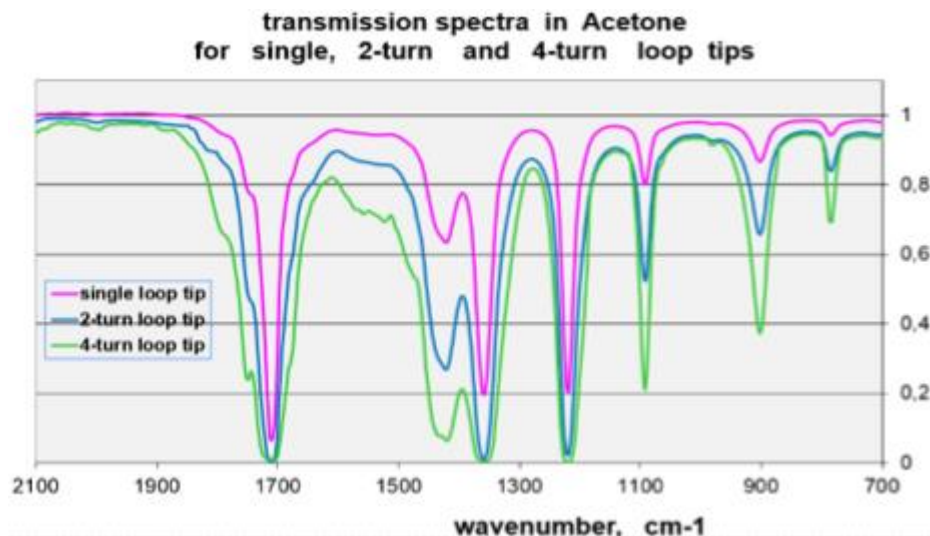
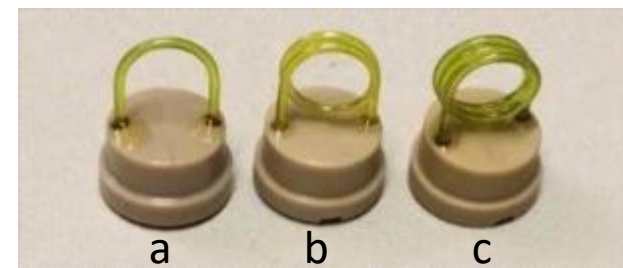
ATR Probes for laboratory applications with PEEK shaft are cost effective and perfect to use in small lab reactors and open vessels. They do not contain metal parts in the tip and can be used for the monitoring of electrochemical reactions, potentiometric cells, measurements in high-frequency fields.  
PTFE tip is available on request.

## Special ATR probes

### Detachable ATR Loop Probe

ATR-Loop PIR-fiber probes are perfect for remote analysis of composition of liquids, pastes and soft surfaces with no need in sample preparation. An unusual ATR tip is a Polycrystalline fiber loop. It is attached to fibers and is replaceable/ or disposable.

Kits of 5 or 10 fiber loop tips can be purchased separately to be used with the fiber probe bought once. Loop tips can be made with several fiber turns to enhance sensitivity of such tip.



Detachable PIR-Loops

a) single      b) dual      c) triple



## Special ATR probes

### Sterilizable ATR-Probe



Sterilizable ATR Fiber Probe are produced with any type of ATR element and for any type of FTIR spectrometers.

Unique Shaft-in-Shaft design enables use of ATR Probe in Bio process where sterilization is required without having to forgo the renowned advantages of Mid-IR FTIR spectroscopy.



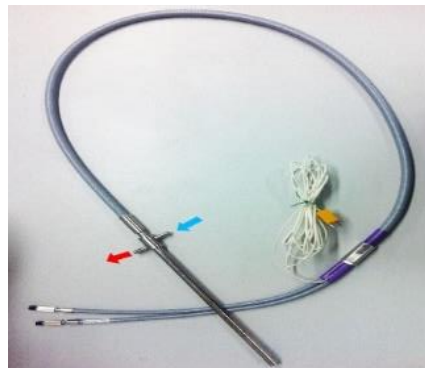
#### Features

- Fiber assembly is easy detachable.
- No need to retract the whole probe out of the fermenter, just pull the fiber assembly out of the operational shaft and store it separately.
- Sealing the operational shaft is possible for the sterilization, cleaning, deactivation or any other treatment.

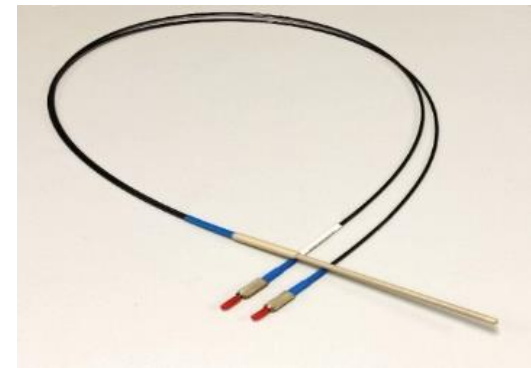
## Summary: The Family of Fiber Optic ATR-Probes



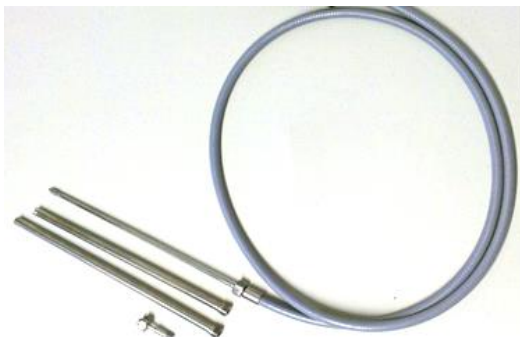
**Standard ATR probe**



**High Temperature ATR probe**



**Standard Lab ATR-Probe**



**Sterilizable ATR-Probe**



**ATR-Loop Probe**

## Fiber Probe Couplers

**FlexiSpec®** Fiber Probe Couplers from **art photonics GmbH** enables easy coupling of fiber probes with any FTIR spectrometer. Coupling of **FlexiSpec®** probes with FT-spectrometers eliminates the need to prepare samples and place them into the sample chamber, and makes remote analysis possible for molecular reaction monitoring in-line.



## Fiber Probe Couplers

### Fiber coupler FPC-2M

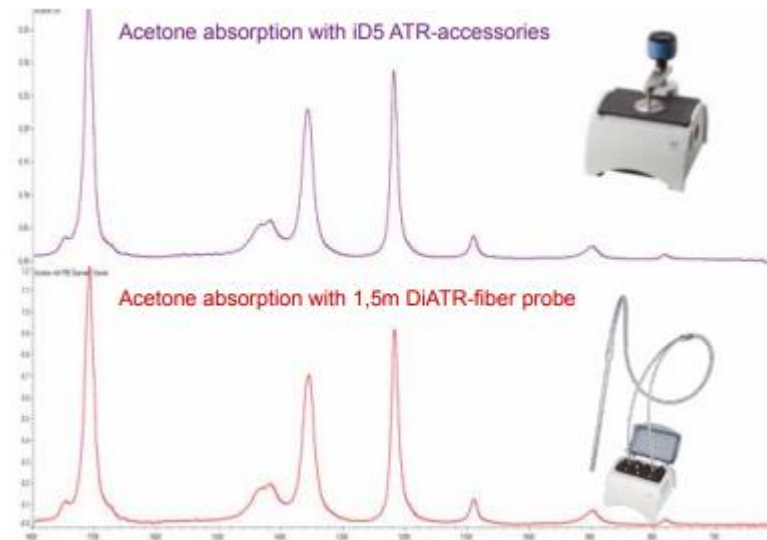
Fiber coupler FPC-2M enables efficient coupling of fiber probes with iS5 – the smallest FTIR-spectrometer from Thermo. FPC-2M design is based on two off-axis parabolic mirrors inside the standard accessories iD1 which can be adjusted for maximum signal from SMA-terminated probe.

### Fiber Probe Coupler for Nicolet iS5N

- In/Out ports made compatible with SMA-terminated fiber probe
- Able to be purged
- Ready to install (iD form factor)
- **Only for use in Near-IR Region**

### Fiber Probe Coupler for Nicolet iS5

- In/Out ports made compatible with SMA-terminated fiber probe
- Able to be purged
- Ready to install (iD form factor)
- **Only for use in Mid-IR Region**



## Fiber Probe Couplers

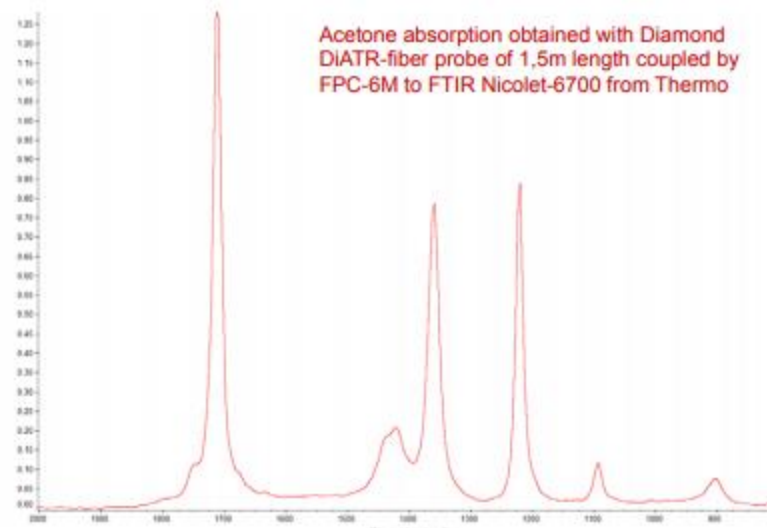
### Fiber coupler FPC-6M

Fiber probe coupler FPC-6M provides the highest efficiency coupling of any fiber probe with bench FTIR-spectrometer when it's installed in its sample chamber. Thus FPC-6M enables in-line reaction monitoring in lab, while it can be also modified for process-control with industrial FTIR and robust probes with SMA or other customized connectors



### Fiber Probe Coupler for Nicolet iS10/iS50

- Compatible with Nicolet 5700/6700, and Avatar 360
- In/Out ports made compatible with SMA-terminated fiber probe
- Able to be purged
- Mounted on standard baseplate
- For use in Mid-IR and Near-IR regions

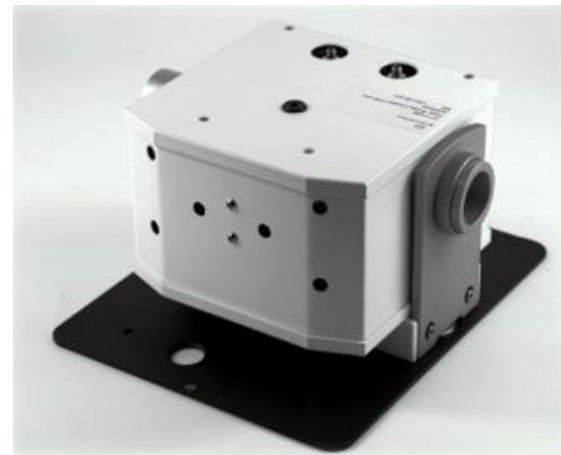




## Fiber Probe Couplers

### Fiber Probe Universal Coupler

- Compatible with any FTIR spectrometer
- Mounted on customized baseplate
- In/Out ports made compatible with SMA-terminated fiber probe
- Able to be purged
- For use in Mid-IR and Near-IR regions



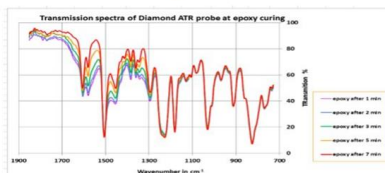
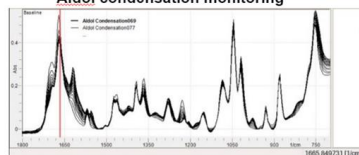
## Coming next - APPLICATIONS

### 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

#### Aldol condensation monitoring



Conical design of ATR crystal makes it easy to retract the tip out of the cured epoxy.  
The transmission in the range  $1\ 600 - 1\ 900\text{cm}^{-1}$  is enough to see absorption bands of C=O groups even using FTIR spectrometer iS5 from Thermo with DTGS detector.

#### Polyurethane synthesis

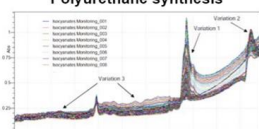
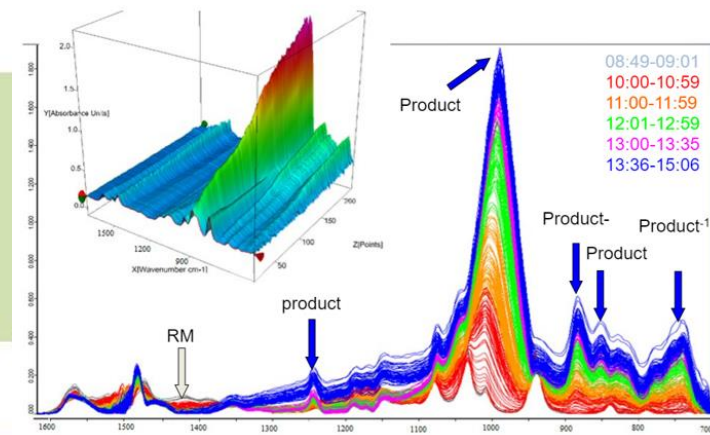


Figure 2: Reaction cell FTIR spectra acquired during the reaction and major variation observed

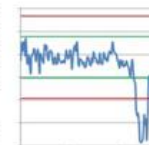
### Application: synthesis monitoring



### Application: fermentation process control



Process interface is a special unit for the automatic cleaning and calibration of the probe tip. For example, **Ceramat** unit from Knick is shown in work for biogas production. The matching of the probe to such unit should be checked in each case.





future's  
in the making



**Thank you for your attention!**

