CHEMICKÉ VLÁKNOVÉ SENZORY

Oddělení technologie optických vláken

Ústav fotoniky a elektroniky AVČR

I.Kasik & V.Matejec, M.Chomat

www.ufe.cz/~

Obsah

- **Úvod – **Základní pojmy, optické sensory

- **Metody – principy**
  - Absorpční, luminescenční metody
  - Metody založené na změnách indexu lomu
  - Metody založené na změnách fáze světla
  - Metody založené na stanovení změn v časové oblasti

- **Optický hardware – instrumentace**
  - Optická vlákna (planární vlnovody)
  - Optická vlákna – zpracování (odstraňování polymerního pláště, řezání, spojování, broušení, taperování, tvorba svazků, zápis mřížek)

- **Závěr** – obecné přístupy při návrhu optické detekce
  - použití optických vláknových sensorů – příklady

Úvod

Základní pojmy, optické sensory

(Bio)chemical optical (fiber) sensors

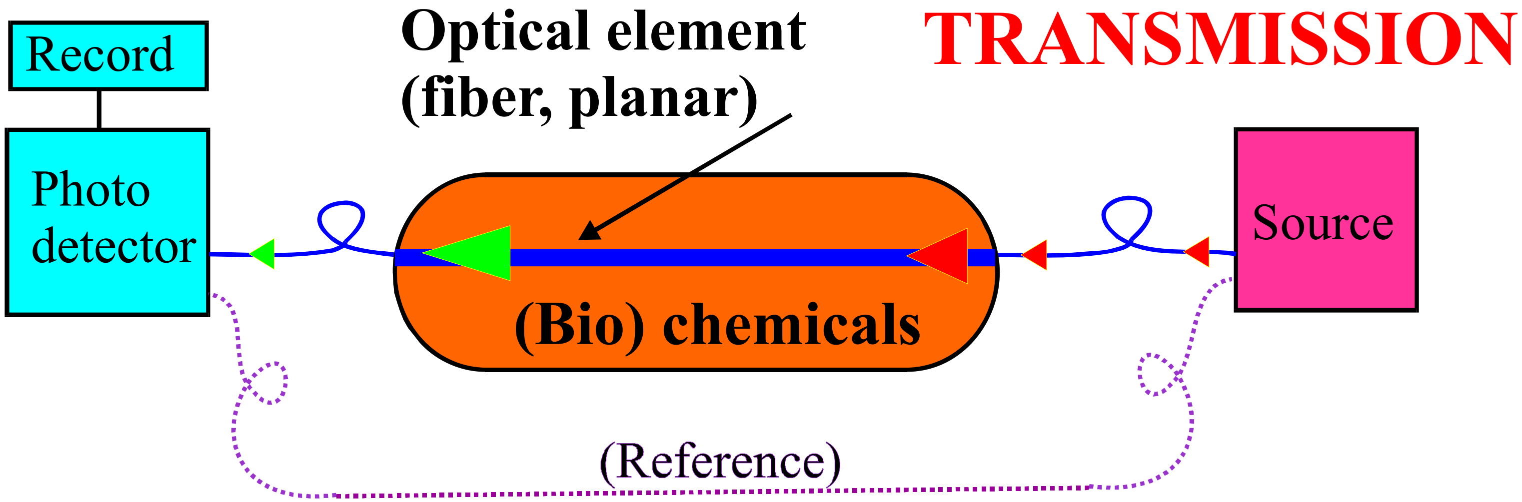
- **Sensors** (opto-chemical) : **conversion** of chemical changes to optical information in real time

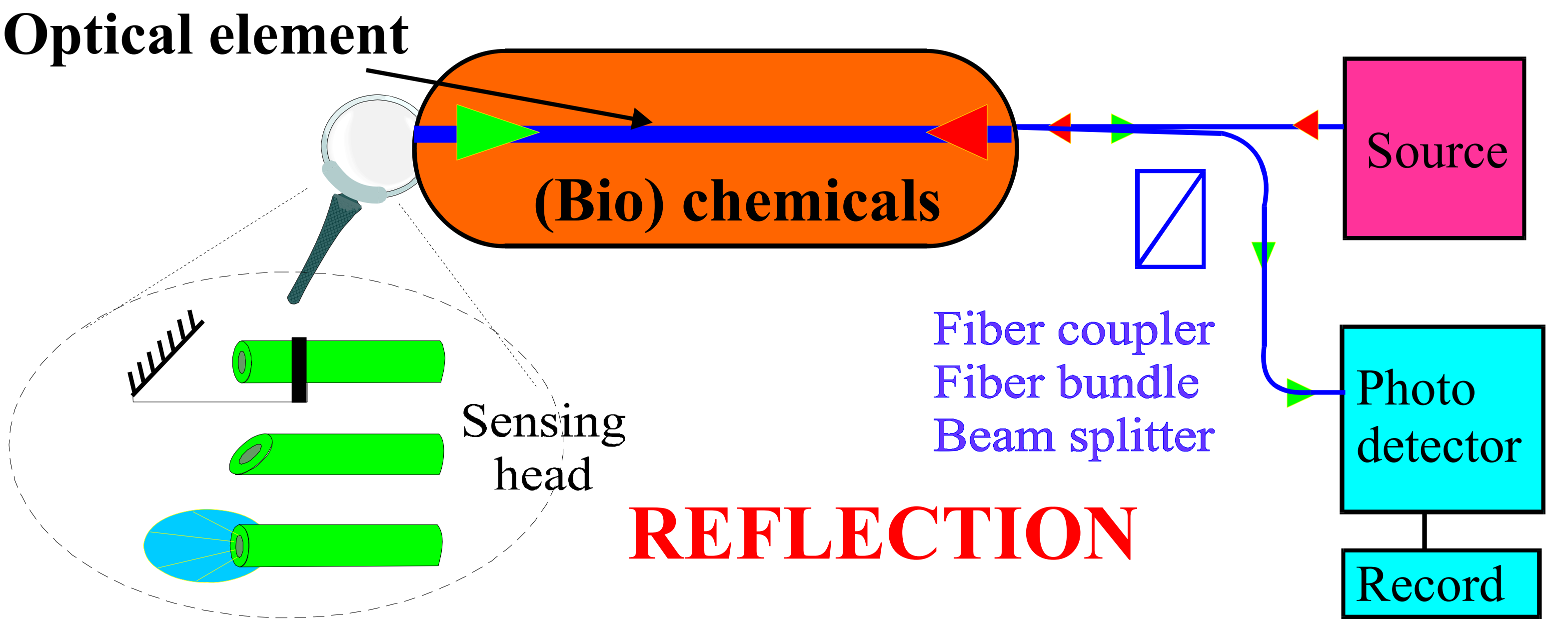
- Devices for optical monitoring of physical / (bio)chemical properties of a medium by means of optical elements

- Small devices
- **Continuous**
- **Reversible**
- Recording the concentration (changes) of a (bio)chemical species
- By means of optical fibers.

[O.S.Wolfbeis], [Boisde-Harmer]

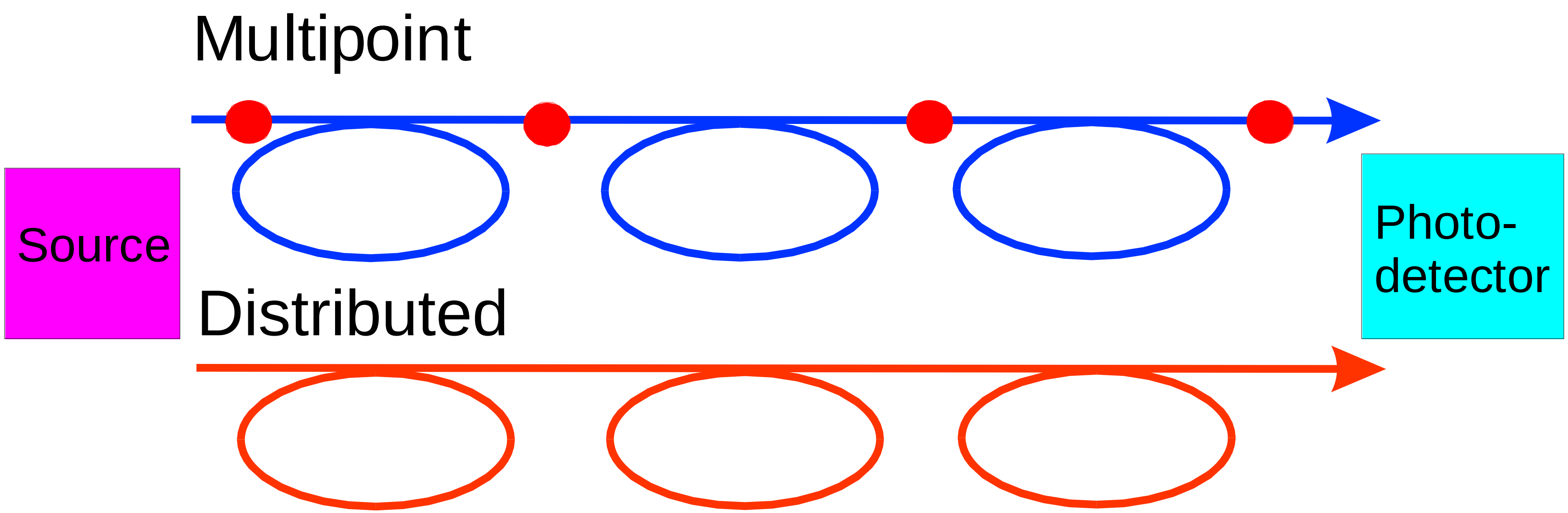
Optical sensors





Capabilities

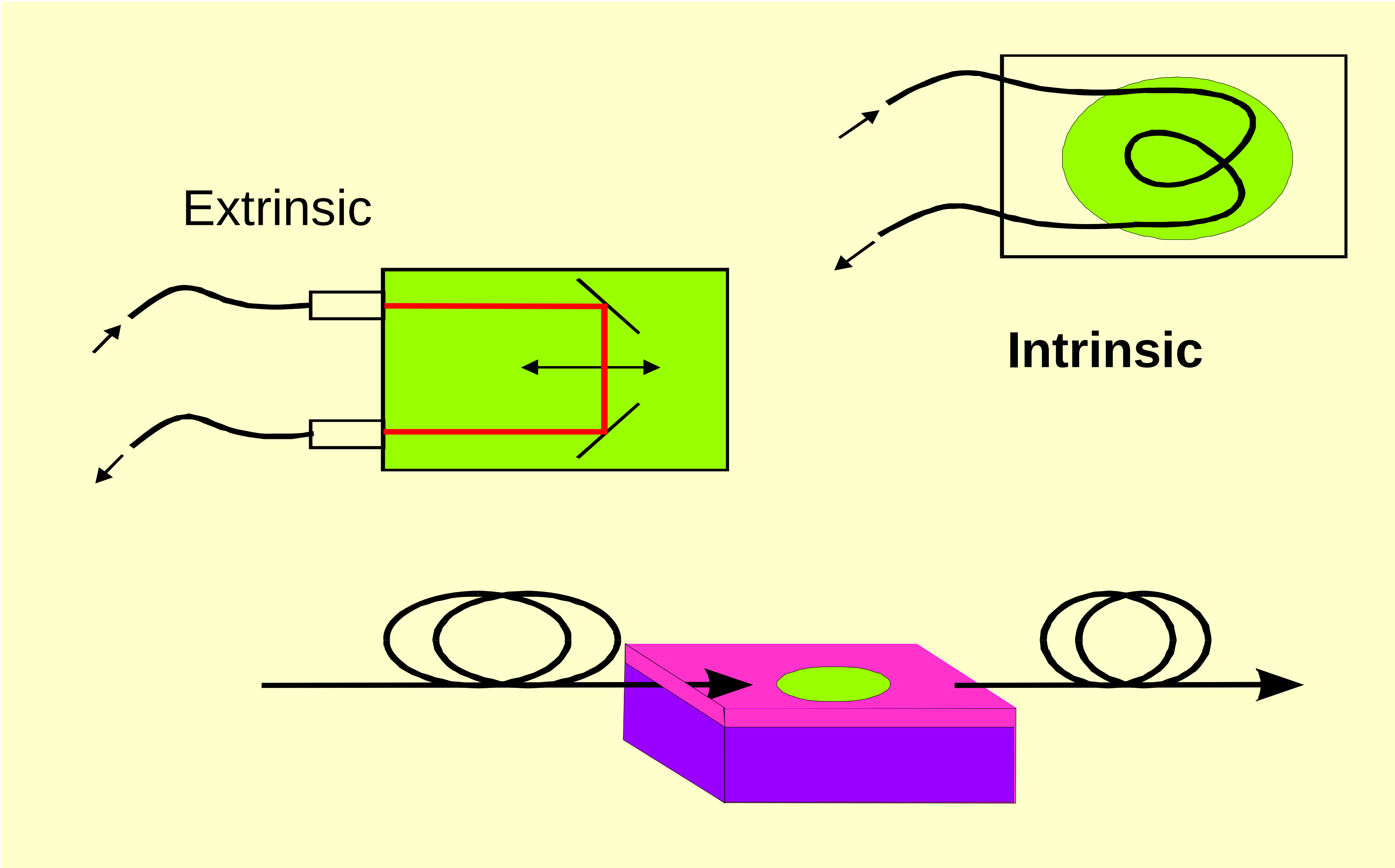
- High sensitivity [< ppm] in a wide dynamic range
- Immunity to electromagnetic interference
- Remote sensing
- Fibers : potential of distributed / multipoint detection



Limitations

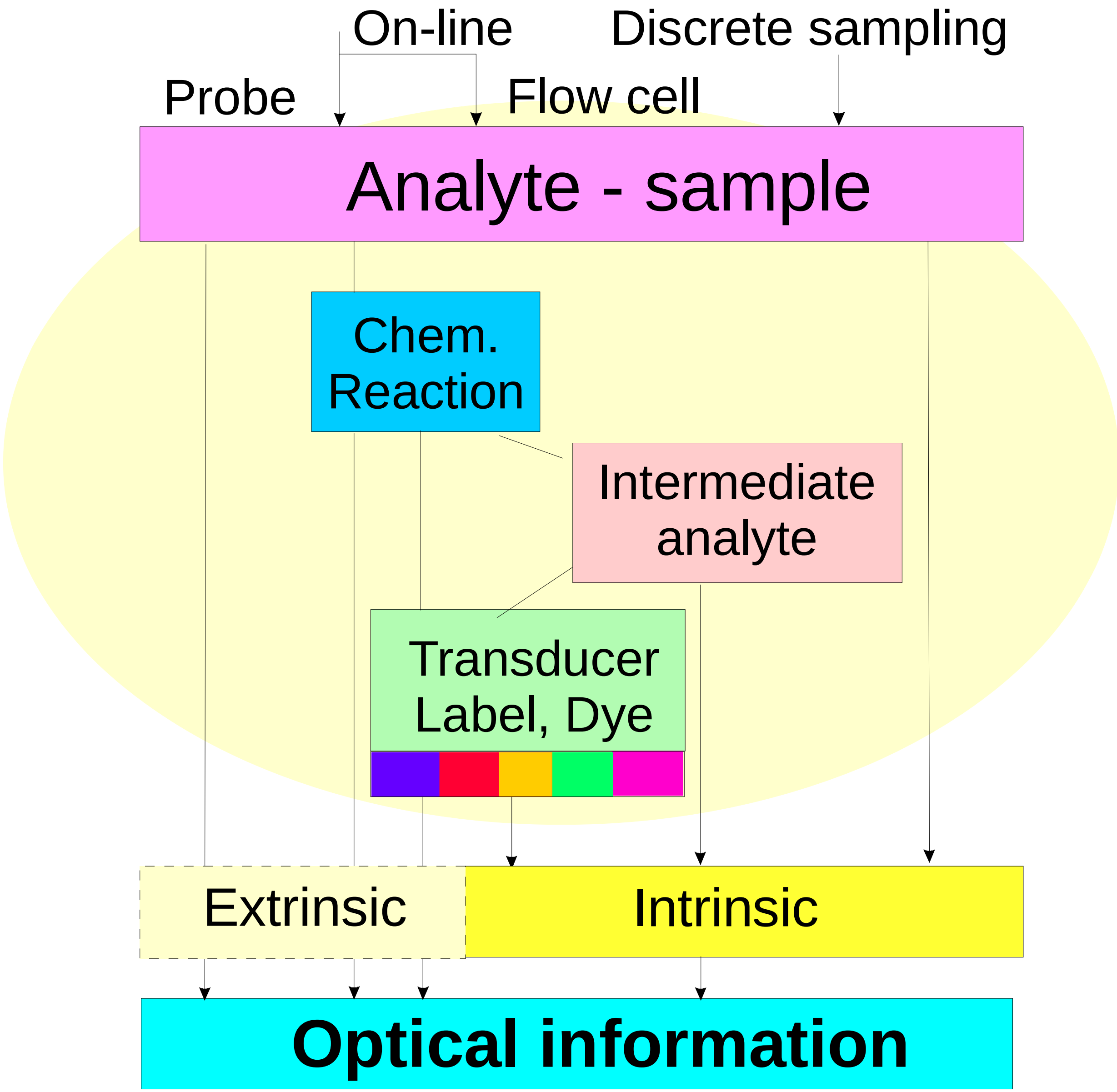
- Photodegradation of photosensitive samples
- Operation in harsh environment (dusty etc.)
- Parasitic signals (due to the light scattering in the medium)
- Unwanted background fluorescence (autofluorescence).

Detection site



Place of interaction between light and analyte

Optical detection of chemicals



Opto-chemical transducers :

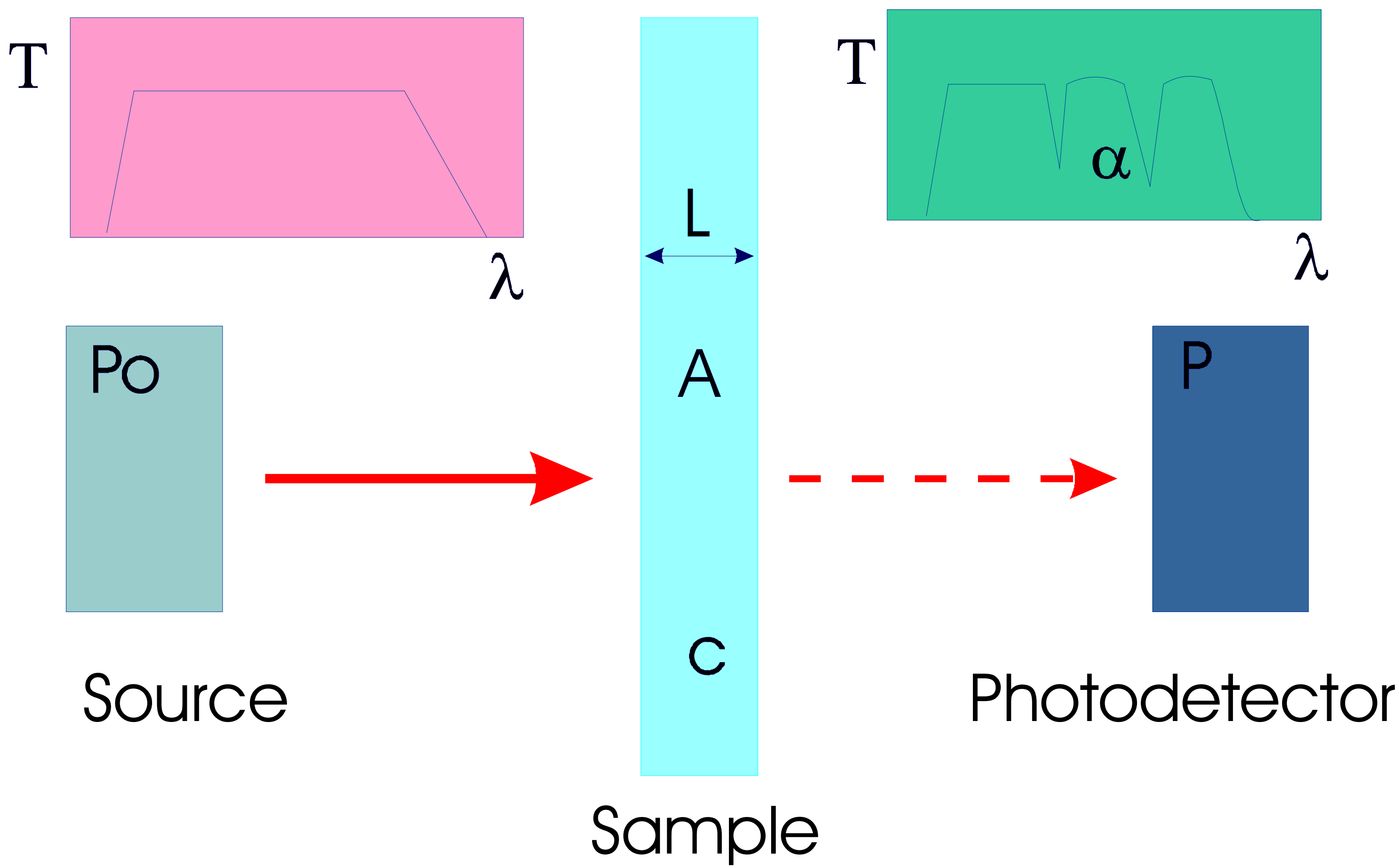
- selective membranes

-optical indicators

Metody – principy

Absorpční metody
Luminescenční metody
Metody založené na změnách indexu lomu
Metody založené na změnách fáze světla
Metody založené na stanovení změn v časové oblasti

Absorption-based methods

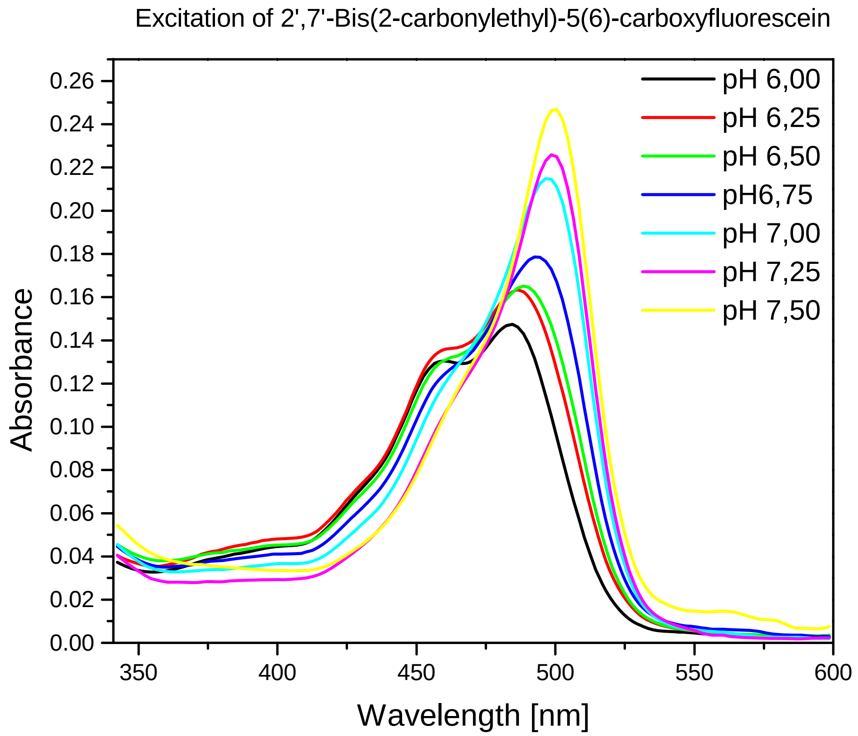


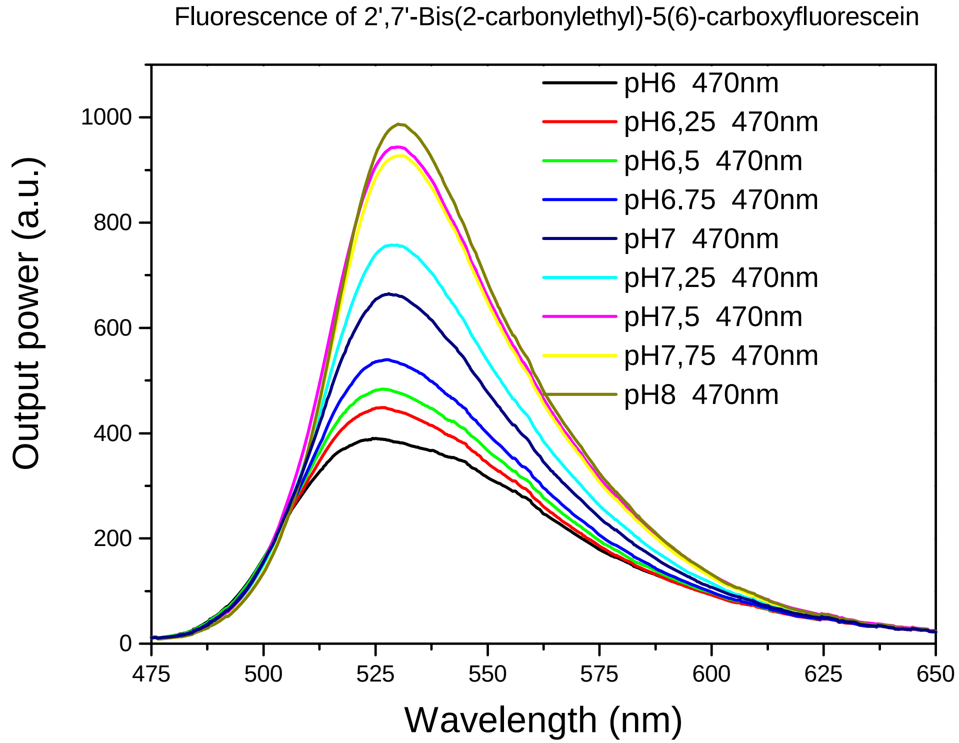
$A(\lambda) = \eta \cdot L \cdot C \cdot \alpha(\lambda)$ $\quad\quad$ $A = -\log(P/Po)$

Luminescence-based methods

- Luminescence : analytes (indicator) absorb excitation energy and emit characteristic light
  - fluorescence – excited by light (short lifetime [ns])
  - phosphorescence - excited by light (longer lifetime)
  - chemoluminescence – excited by chemical reactions

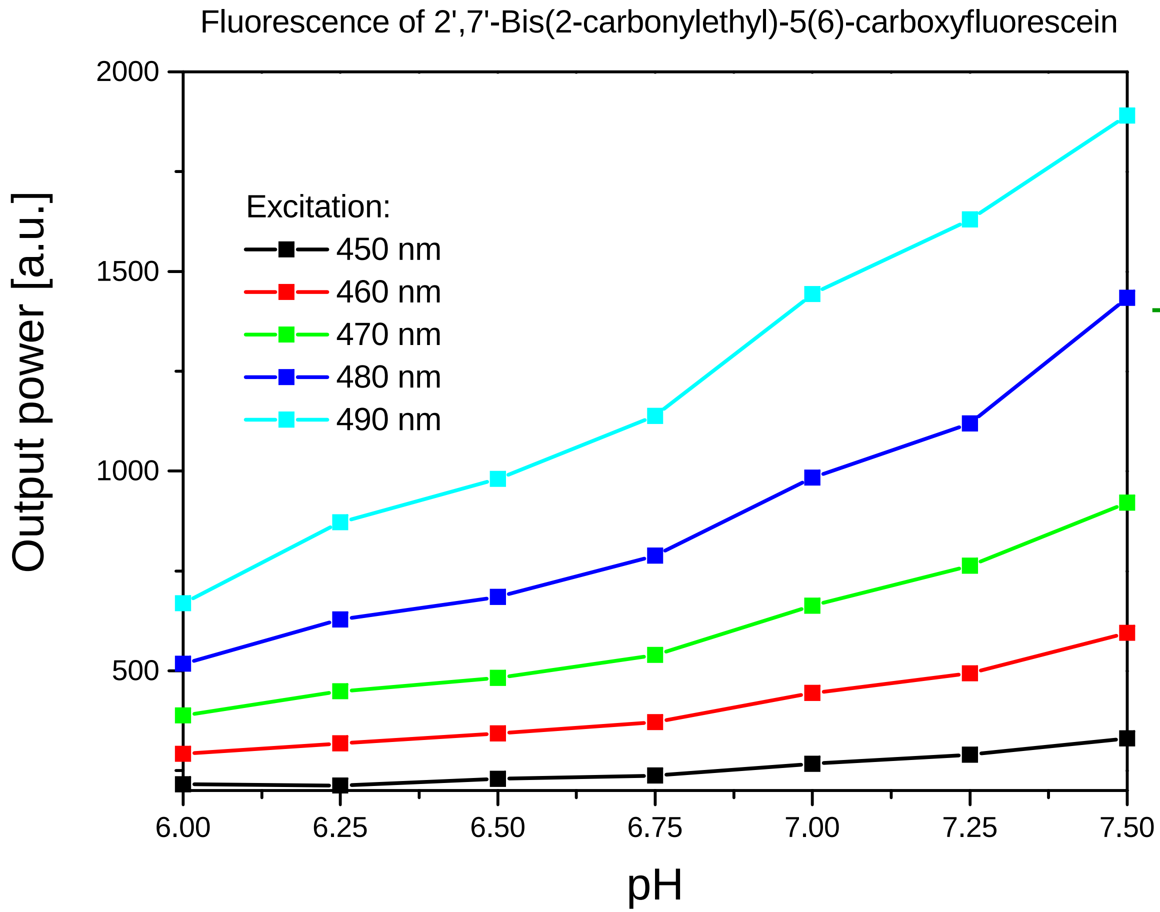
Luminescence-based methods

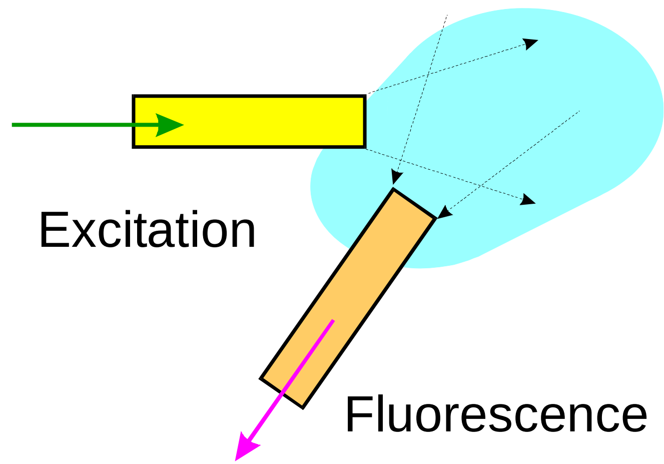




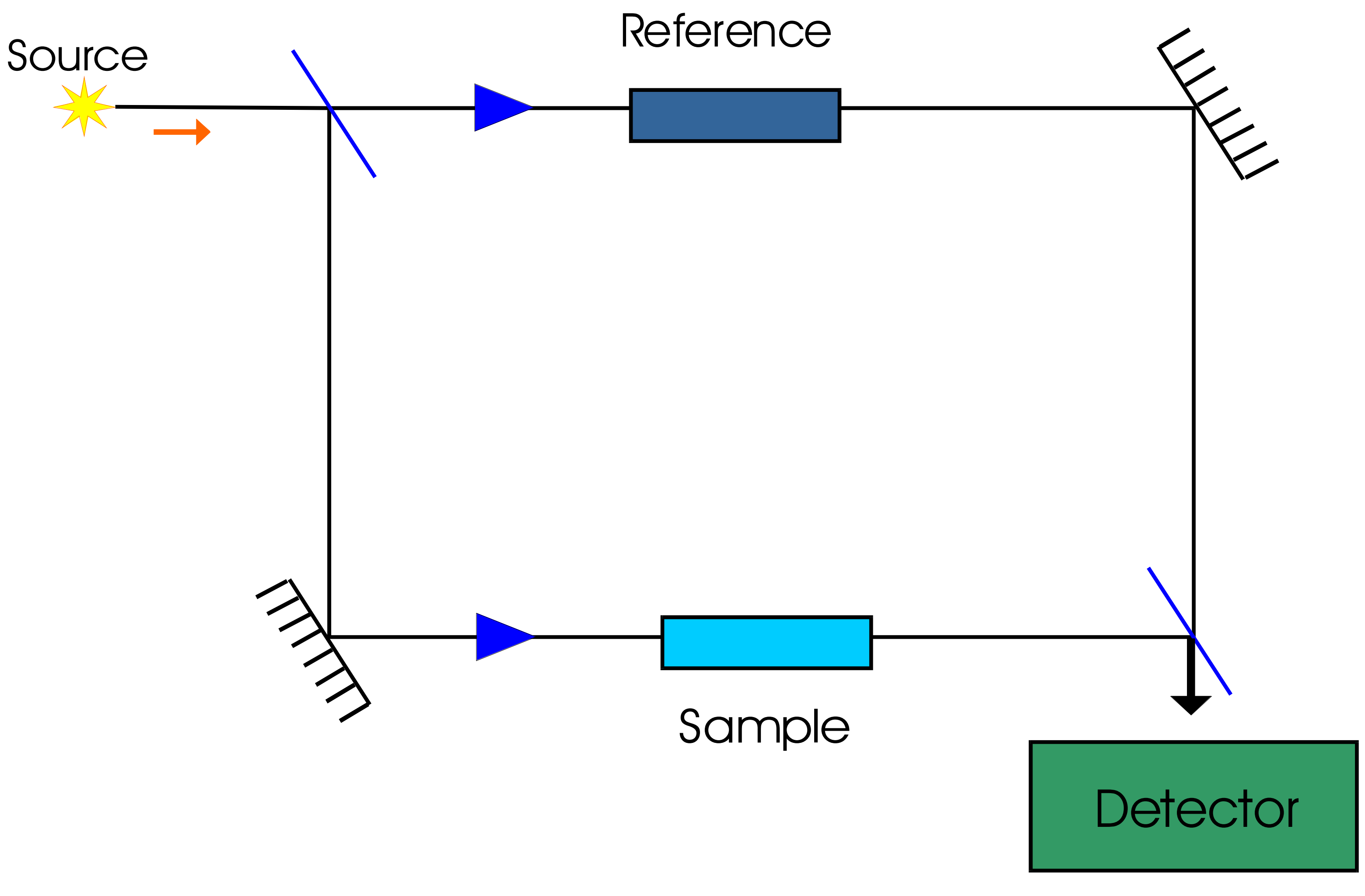
$$I = Io \,.\, \alpha \,.\, \Phi \,.\, c \,.\, K \,.\, L$$

Luminescence-based methods

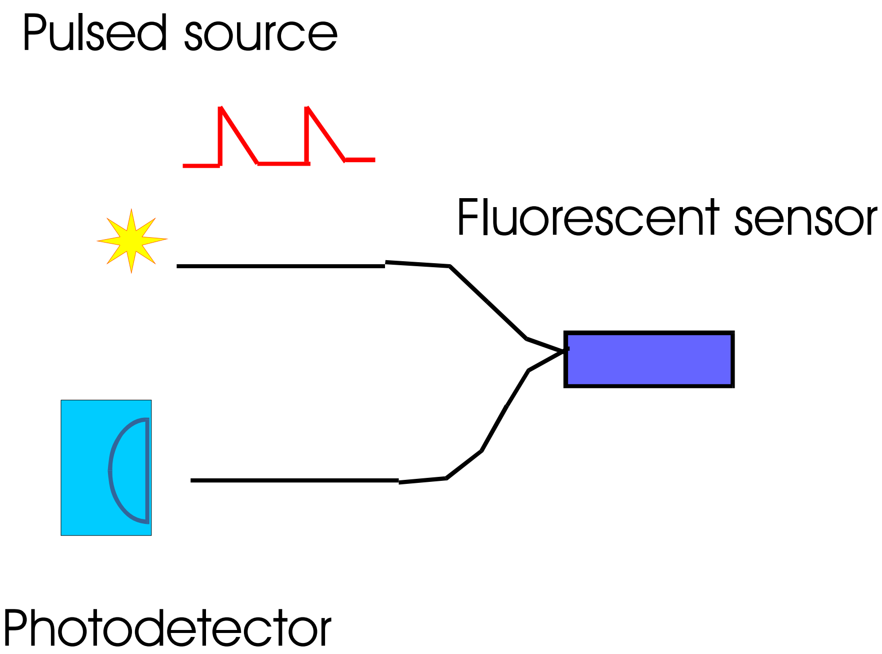


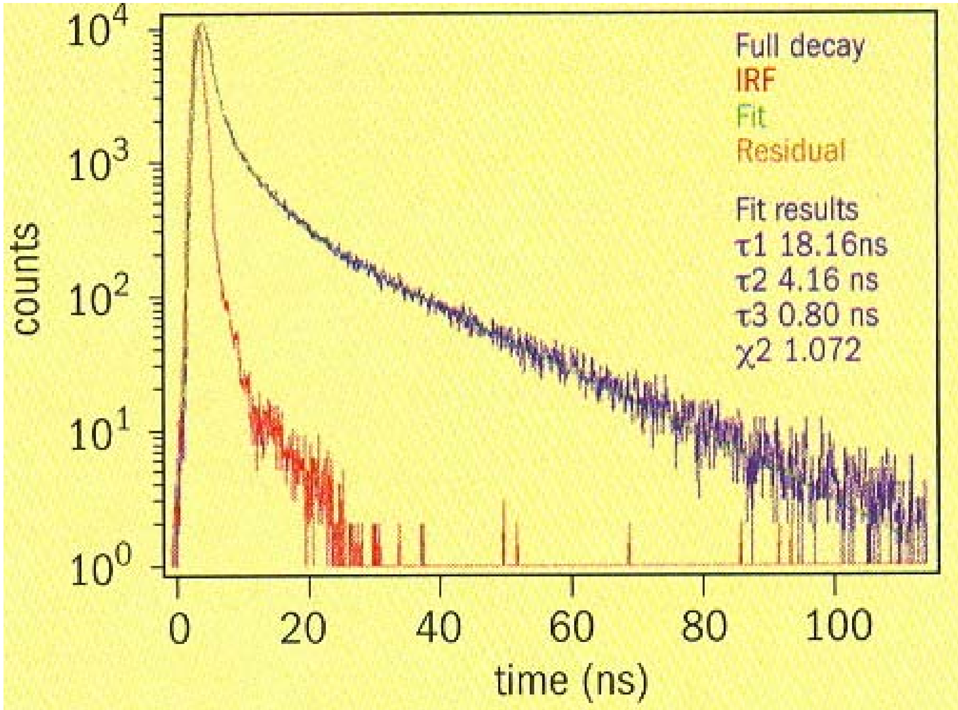


Methods based on phase changes



Methods based on changes in time domain





$It = Io \cdot \exp(-t/\tau_{lifetime})$ [ns]

E.Blackwood, Opt.&Laser Europe 1/2007, p. 25

Methods based on refractive-index changes

- Changes of numerical aperture of waveguide

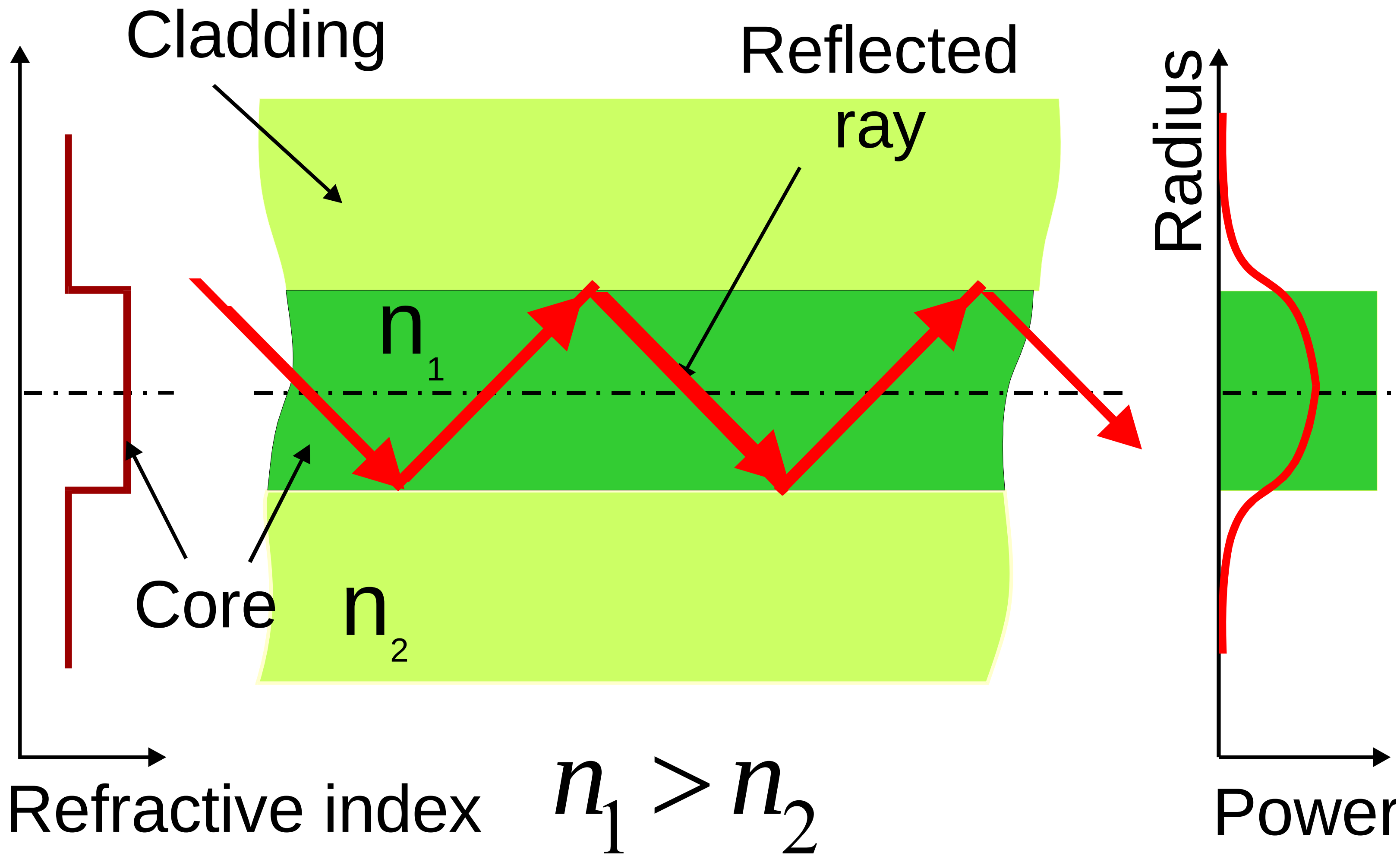
Optický hardware – instrumentace

Optická vlákna (planární vlnovody)

Optická vlákna – zpracování

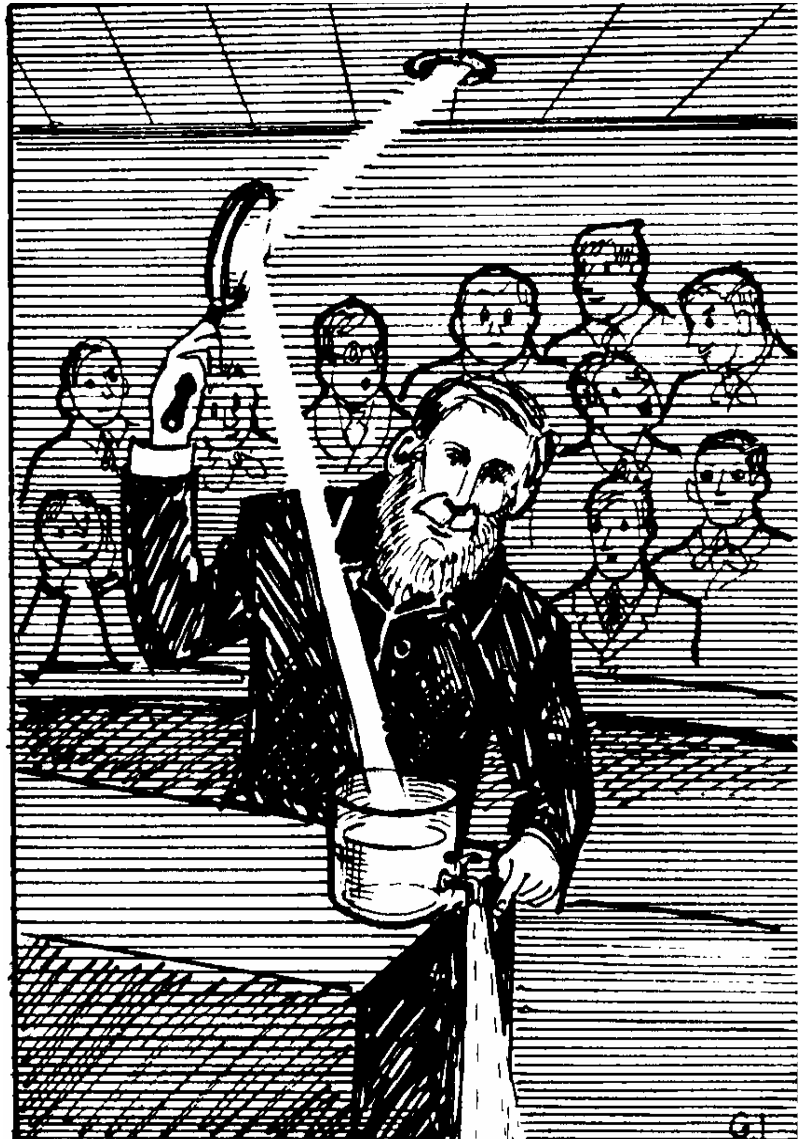
- odstraňování polymerního pláště
- řezání
- spojování
- broušení
- taperování
- tvorba svazků
- zápis mřížek

Principle of optical fiber performance - total reflection



$$n_1 > n_2$$

Snell's Law & Total Reflection



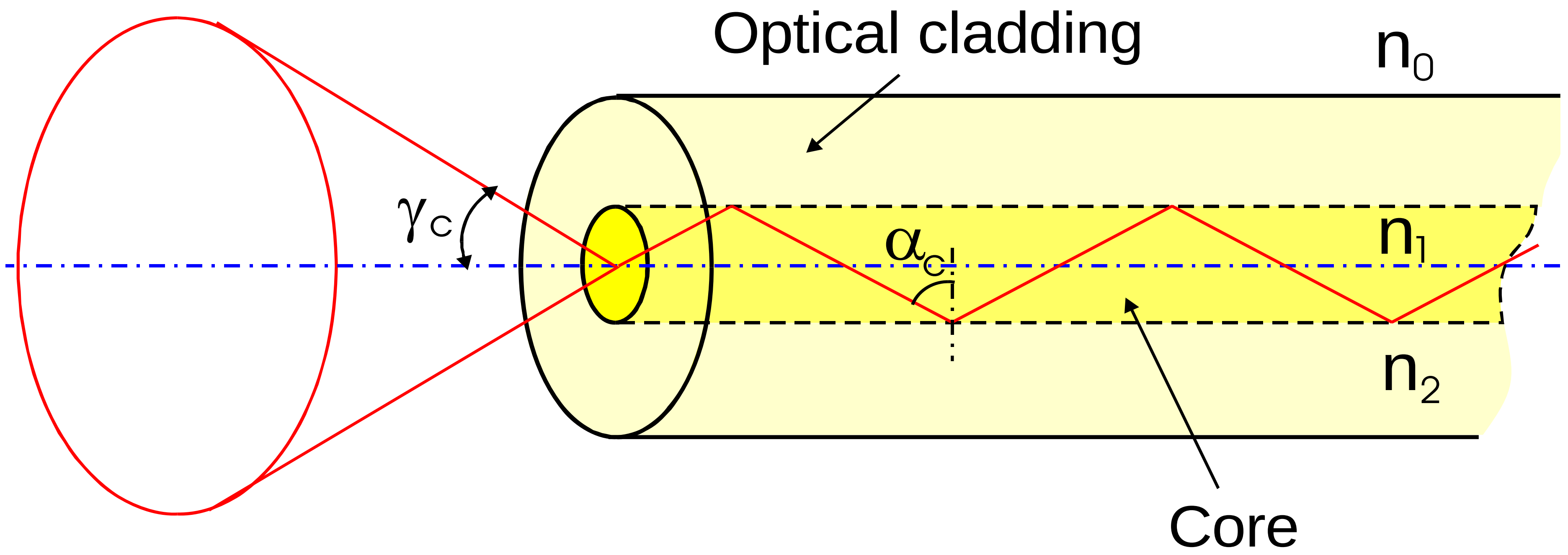
$$\frac{n_1}{n_0} = \frac{\sin\alpha}{\sin\beta} \quad \rightarrow$$

$$\frac{n_1}{n_0} = \sin\alpha_C$$

Snell Willebrord 1580-**1626**

Tyndall John 1820-**1893**

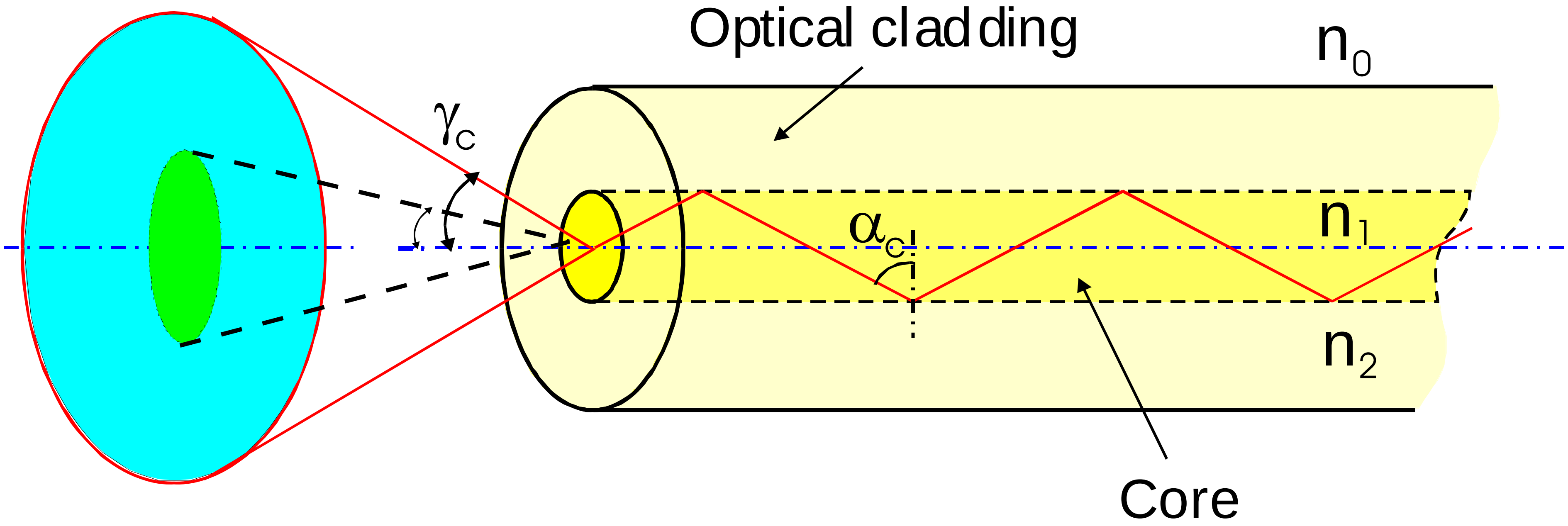
Numerical aperture



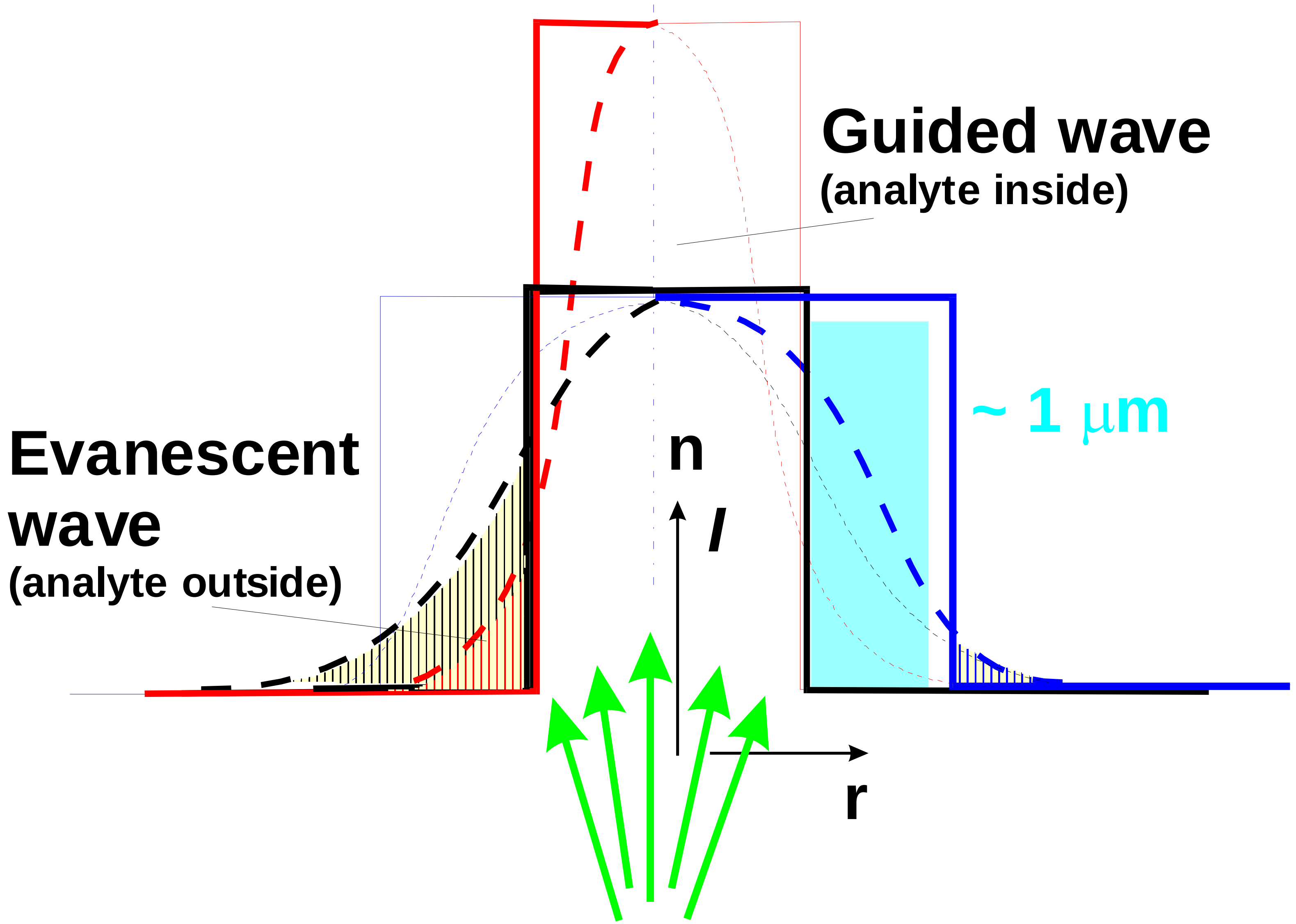
$$NA = n_0 \sin \gamma_c = \sqrt{n_1^2 - n_2^2}$$

Typical values of NA: 0.1 – 0.5

Methods based on refractive-index changes

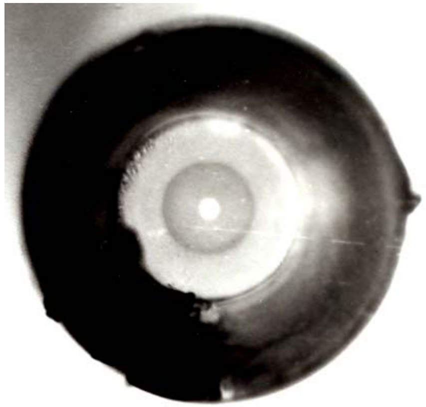


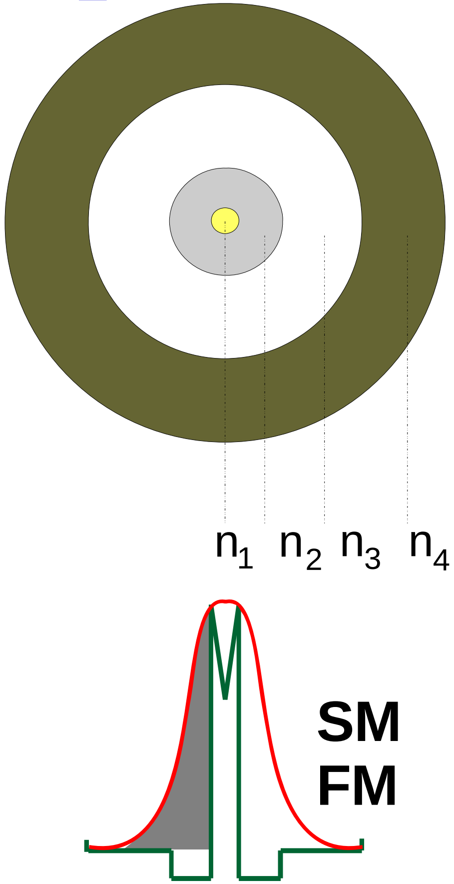
Evanescent and guided wave

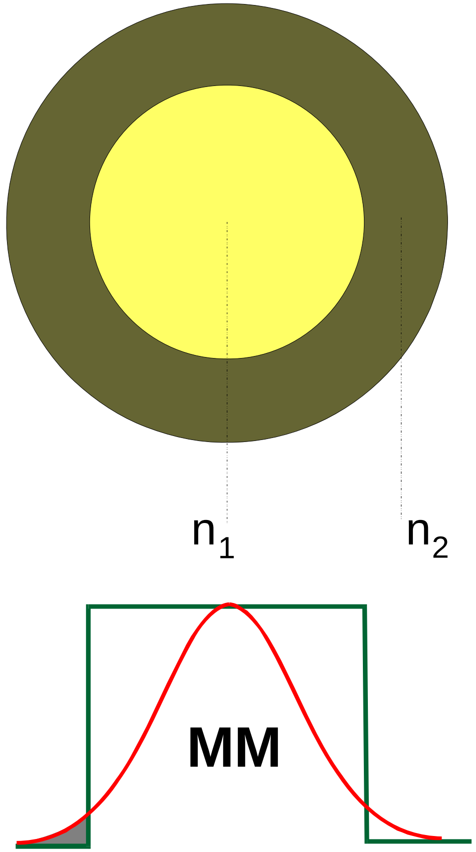


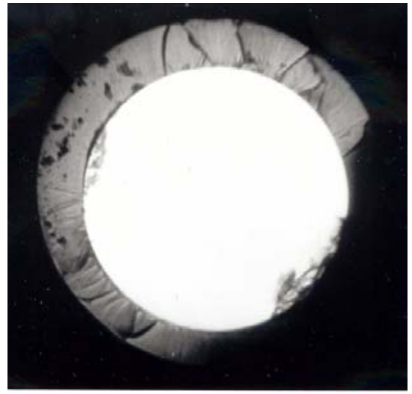
Evanescent-wave sensors : ageing, composites …[T.Navratil]

Optical fiber structures









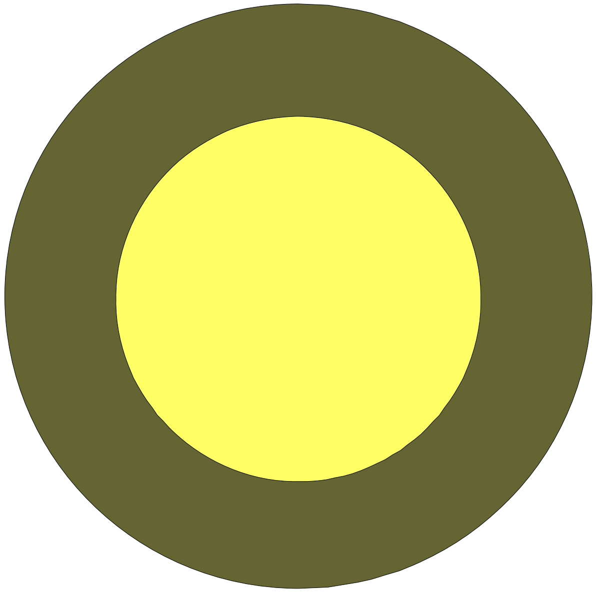
NA_{SM} (0.1-0.25) << NA_{MM} (0.2-0.5)

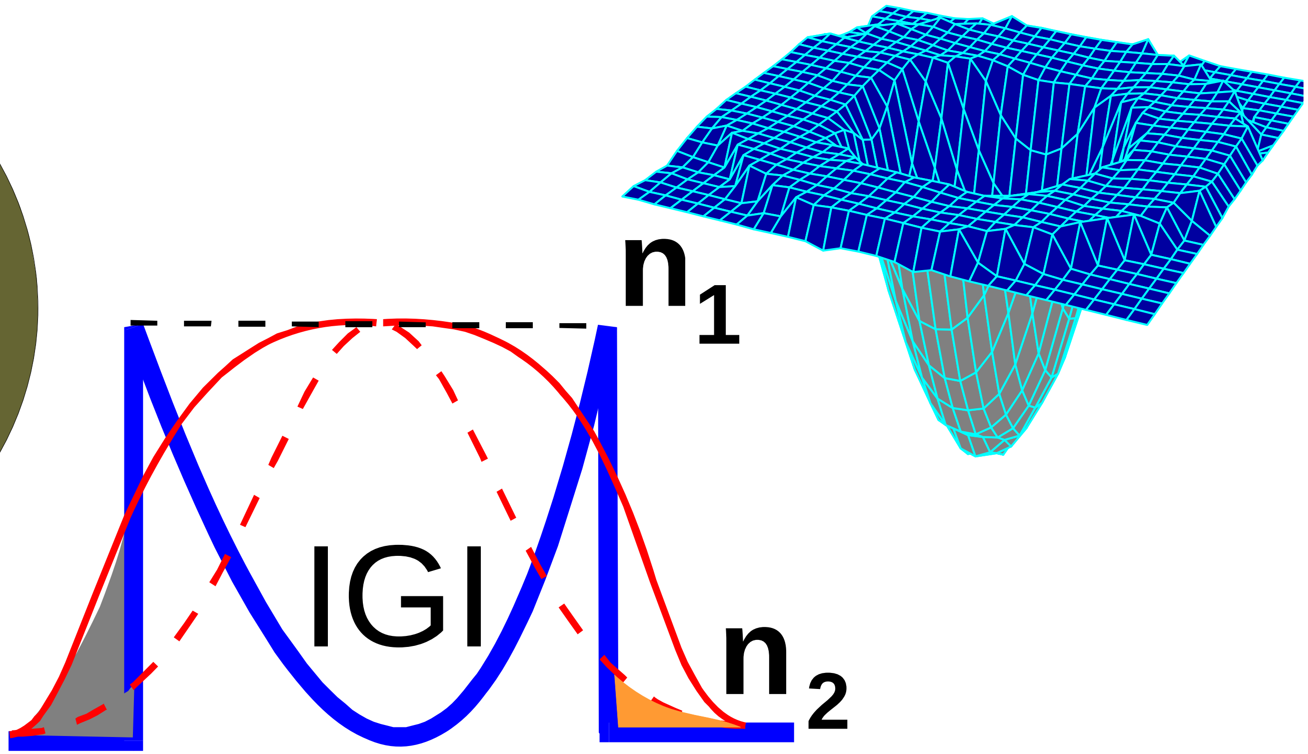
$Ø_{core}$SM-FM (2-15 µm) << $Ø_{core}$MM (50-1000 µm)

- Intensive evanescent field
- No access of the analyte to the core

- Polymer-clad-silica (**PCS**)
  Polymer-clad-glass (**PCG**)
  Plastic optical fiber (**POF**)
- Poor evanescent field !

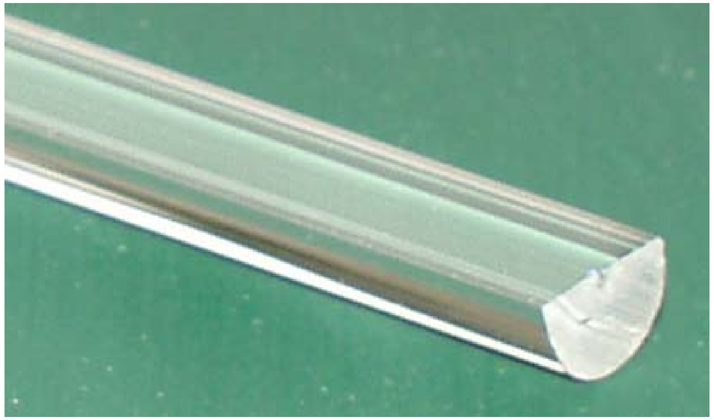
Enhancement of MM structures for evanescent-wave detection

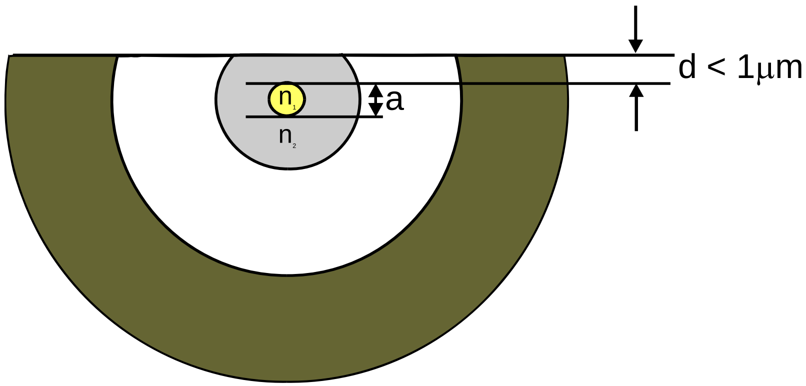


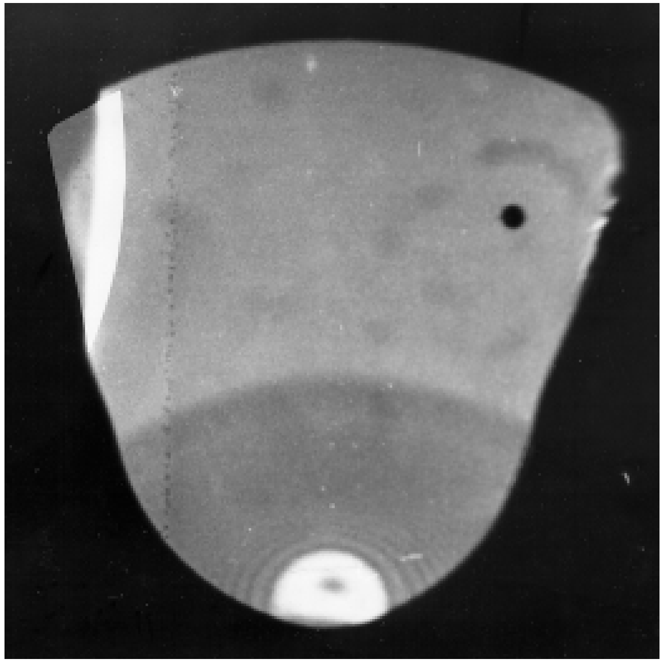


Inverted Graded-Index (**IGI**) structures; evanescent wave 0.5% => 5-7%, depending on conditions of excitation/detection (selective-axial) [IPE]

D-shaped fibers, S-fibers

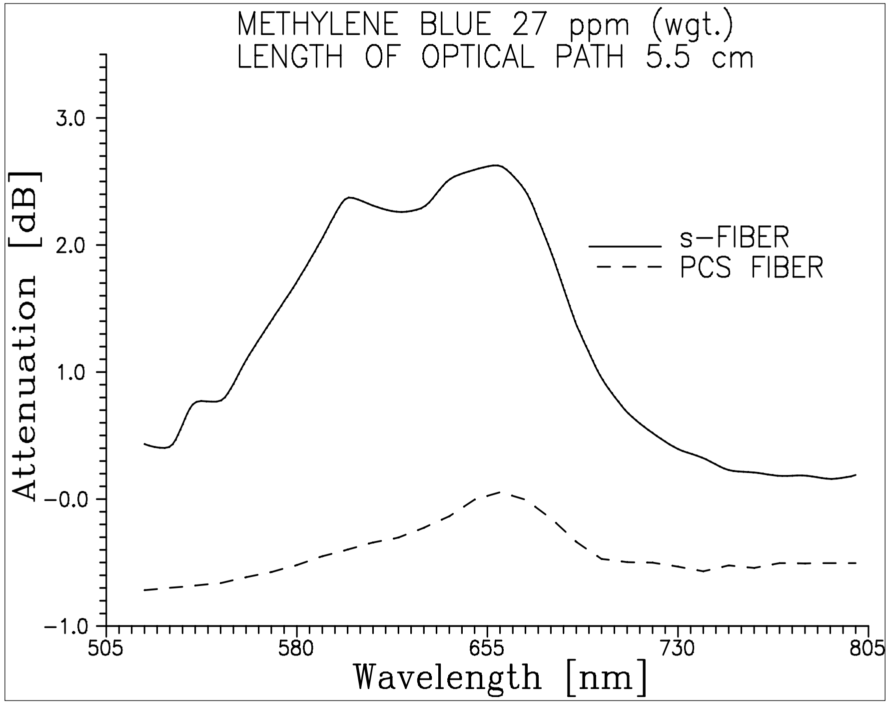


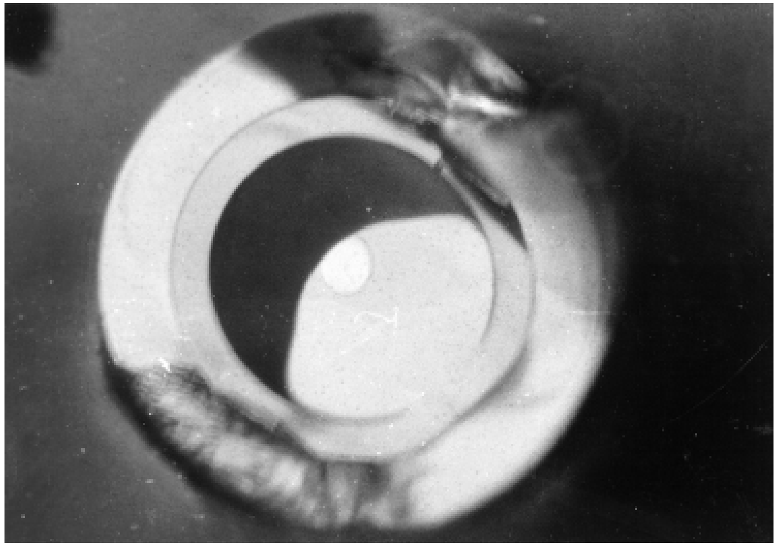




- Non-circularly symmetric, robust, size of the detection site
[G.Stewart, IPE-M.Chomat]

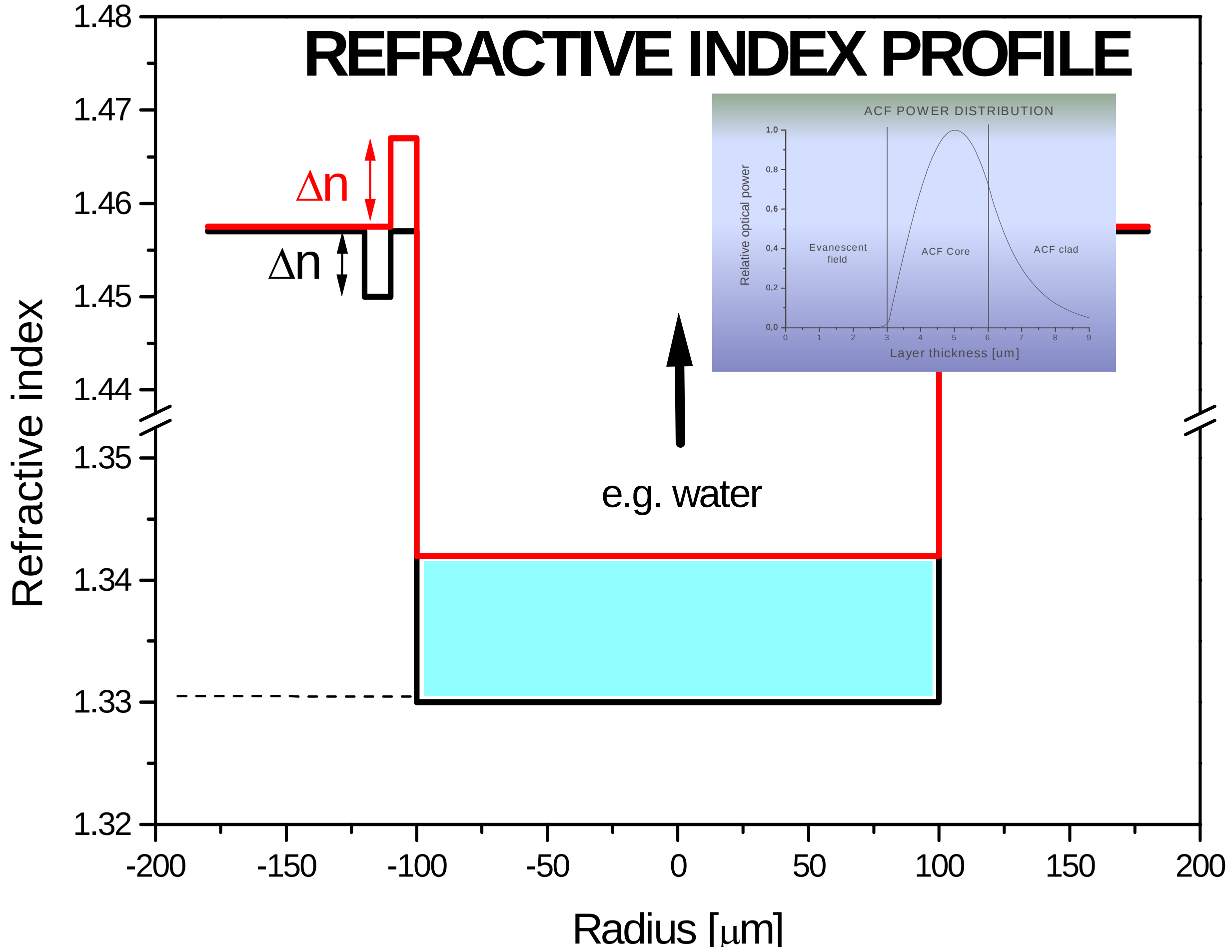
S-fibers, Capillary S-fibers

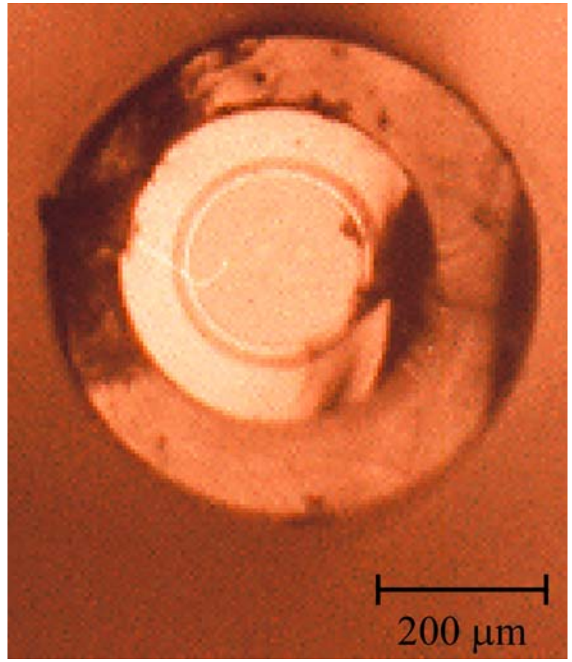




- Symmetric, compatible with silica fibers [IPE-V.Matejec]

SM (FM) annual core fiber capillaries & hollow fibers



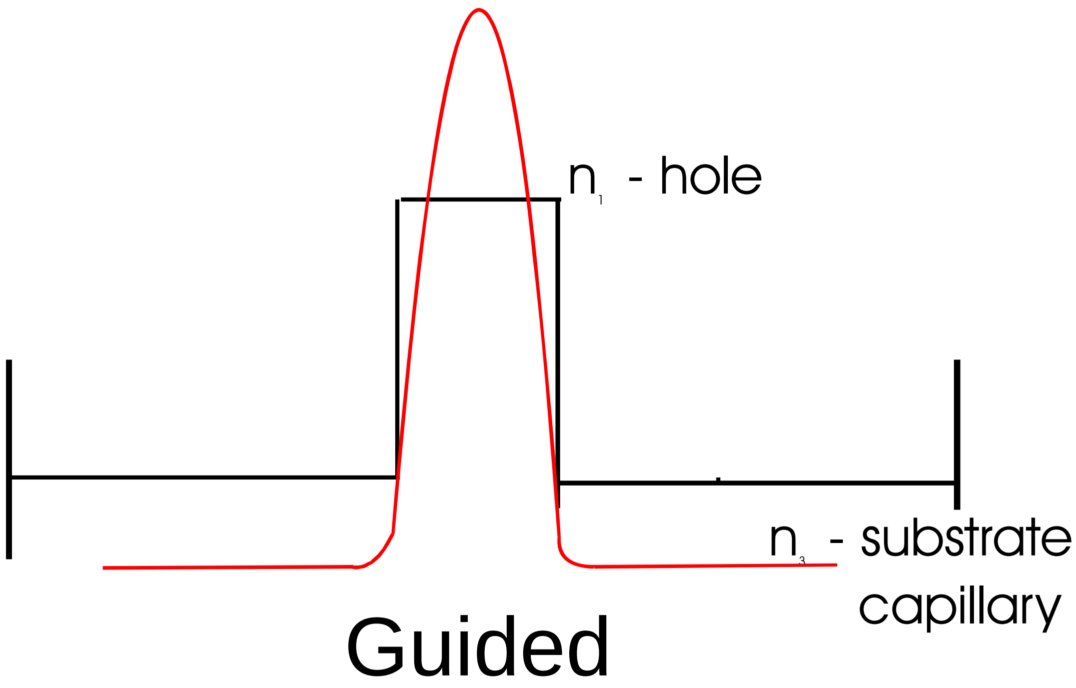


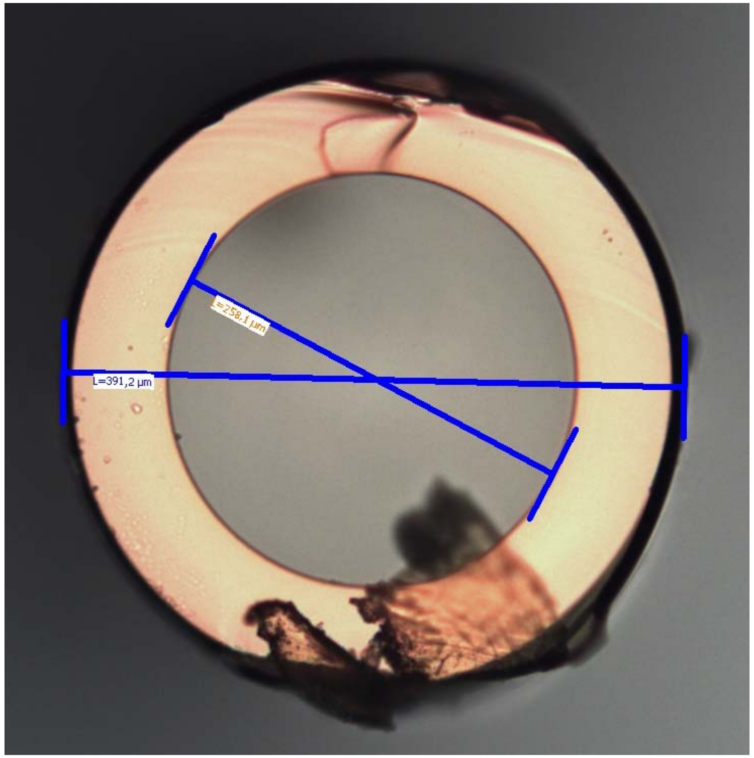
ACF-fiber capillary

380/210 μm

- Gases : (+) low viscosity but (-) low refractive index [K. Stulik]
- Liquids : (-) high viscosity but (+) suitable refractive index
- Dimension requirement : 365 / 250 μm [IPE]

Fiber capillaries & hollow fibers

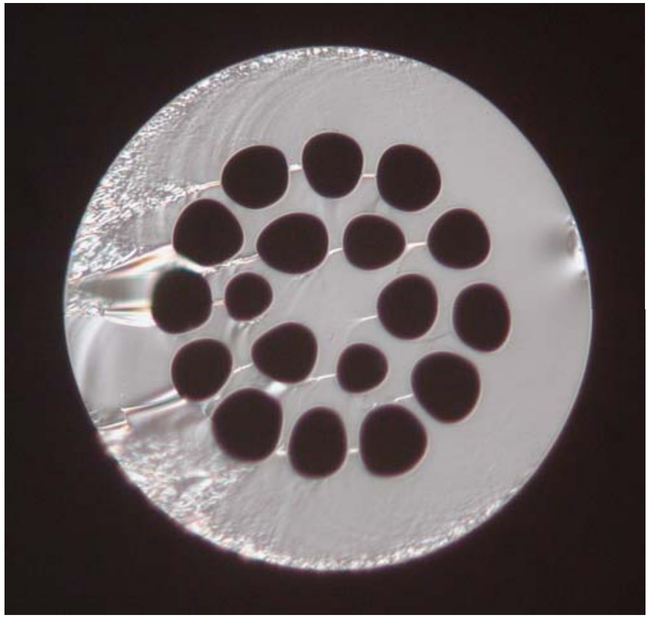


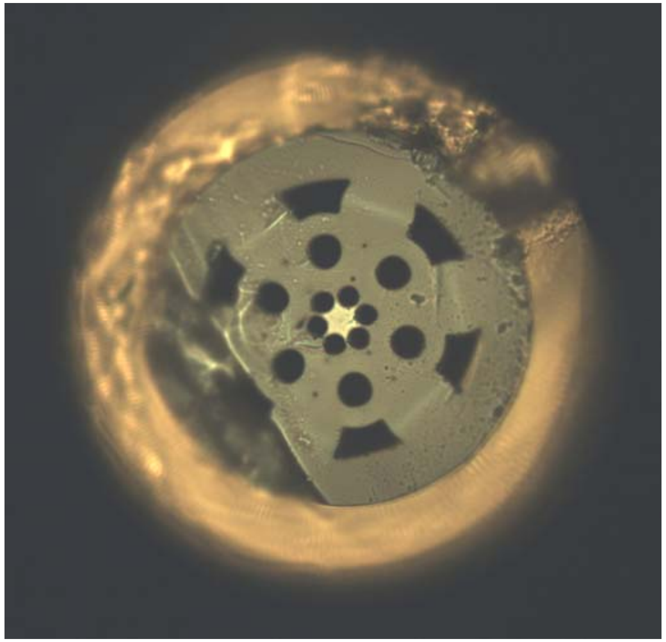


- Liquid-core fiber capillary

- Silica fiber capillary 365/360/60 µm
- [polymicro.com, verrillon.com, IPE …]

Photonic crystal fibers (PCF)





- P.Russel, A.Bjarklev; [crystal-fibre.com, IPE...]
- micro => NANO [J. Labuda], intensive evanescent field

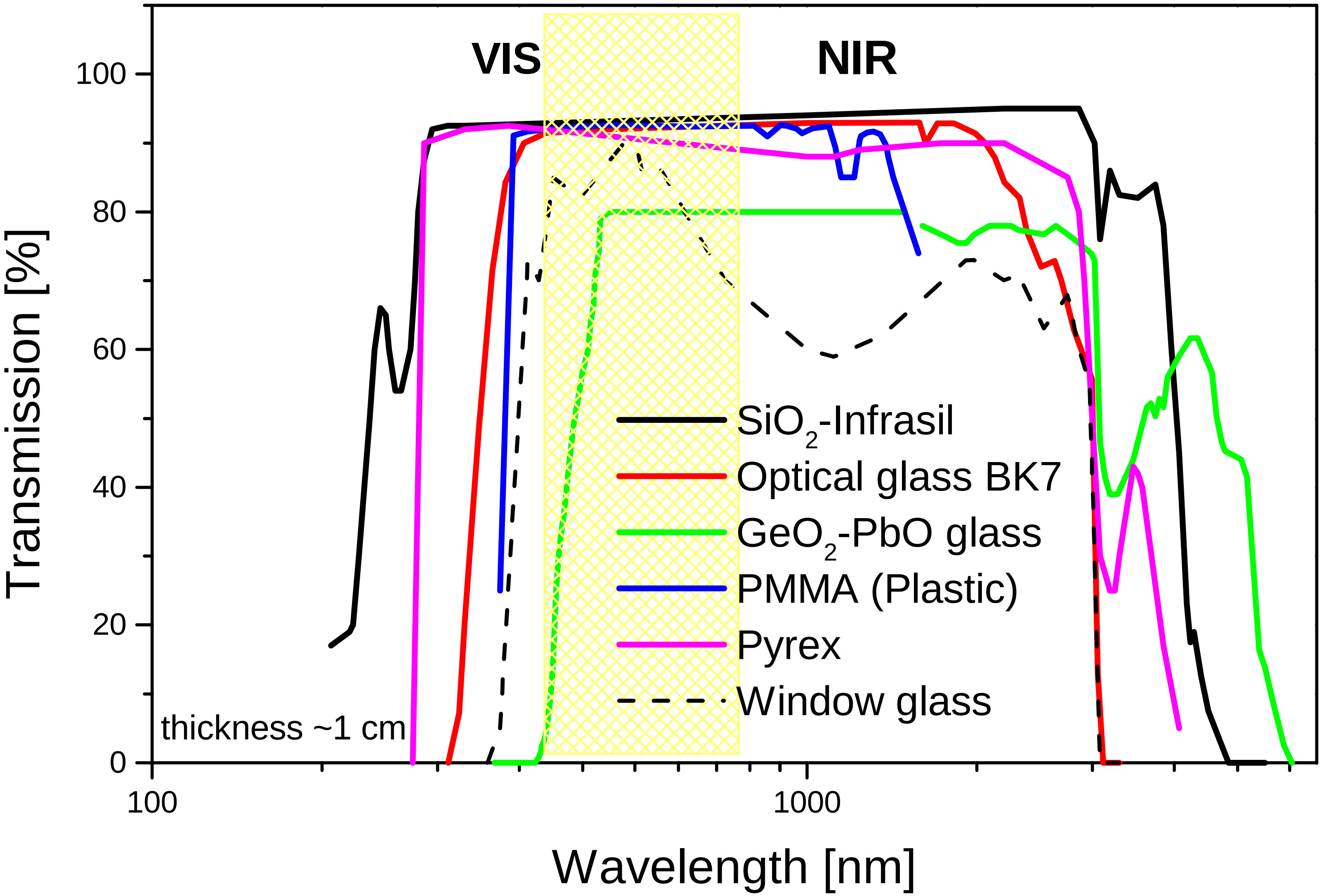
Requirements

- **Durability** to the analyte
  - (glasses > polymers > crystals)
- High **transparency** in a wide spectral range
  - (VIS-NIR > UV and IR)
- Common **availability** of optical hw
  - (conventional > special; VIS-NIR > UV & IR)

- Choice of material, structure, coating of optical element

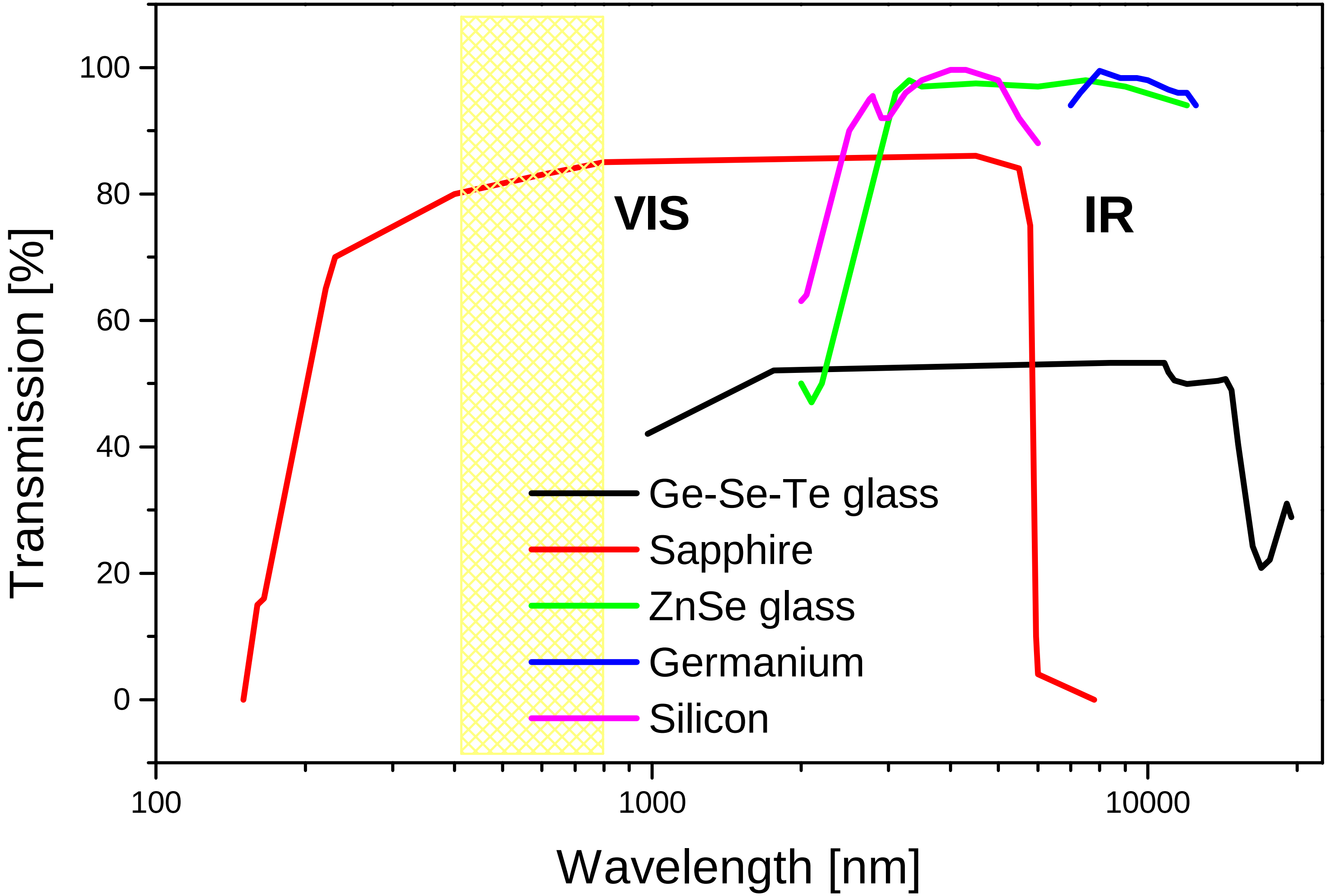
Spectral transparency

VIS-NIR – transparent



Spectral transparency

- IR – transparent



Optical fiber coatings

- **Conventional**
  - **Mechanical protection**
- **Special**
  - **Immobilising** of opto-chemical transducers
  - **Tailoring of access of analyte** to the detection site (porosity, thickness, phobicity) - membranes

<u>Conventional</u> (primary) - on-line coating

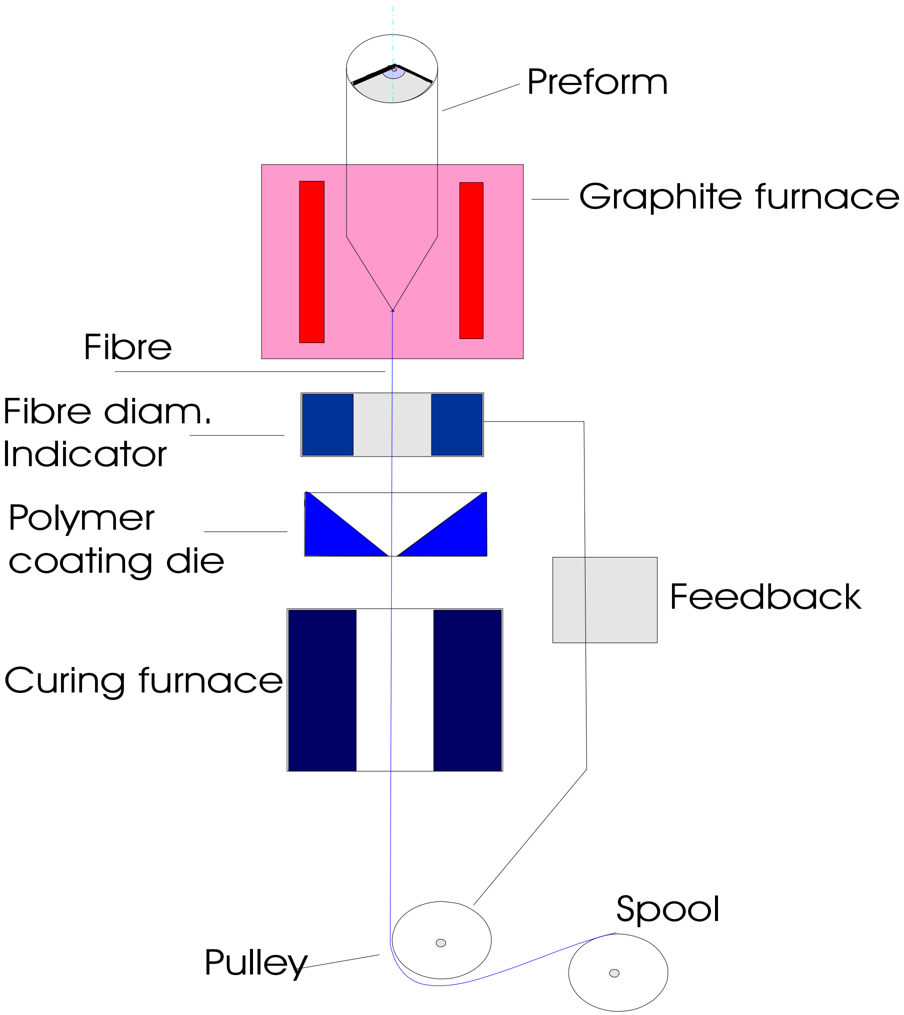
- Polysiloxane (n_D = 1,41), soft [PCS]
- UV-acrylate (n_D = 1,65), hard
- PTF– polytereftalate (n_D>1,46), hard
- PI – polyimide (n_D>1,46), hard
- PTFE – teflon (n_D = 1,29)
  - thickness 4 μm (hard) – 100 μm (soft)

<u>Special coatings</u> - additionally coated : sol-gel and/or polymers

  - thickness ~10^2 nm (!) – several μm

- Nano-materials [J. Labuda], tailored receptors [V. Kral]

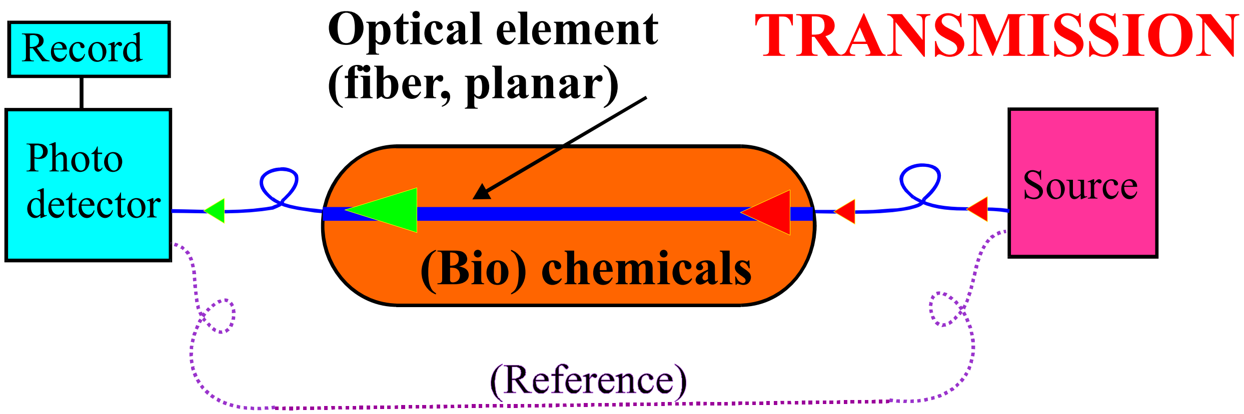
Optical fiber coatings

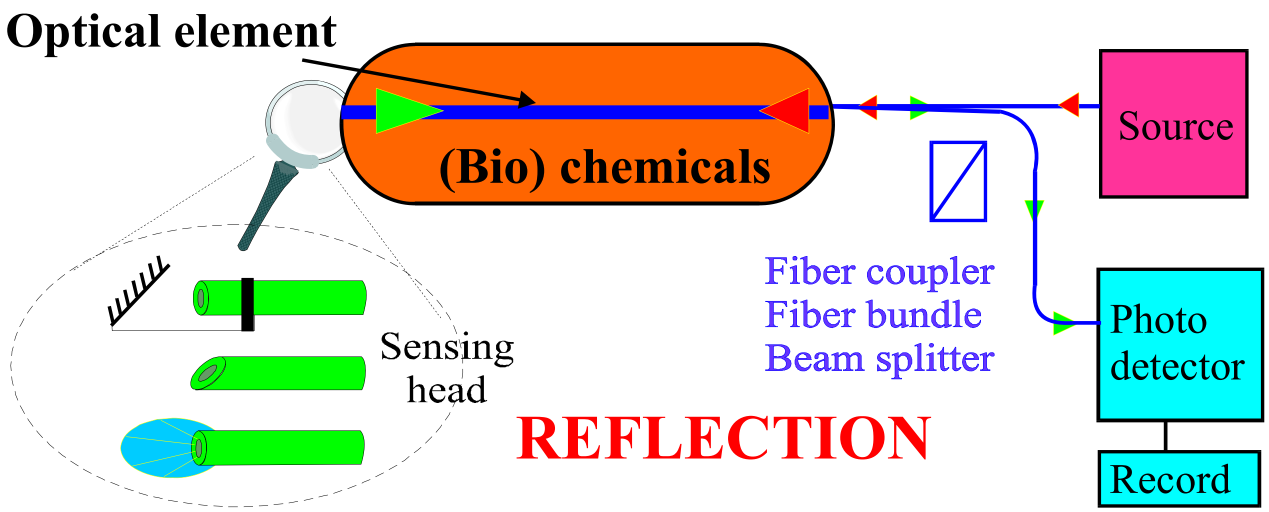


Direct continuous coating [IPE]

Additional dip-coating [IPE]

Optical sensors



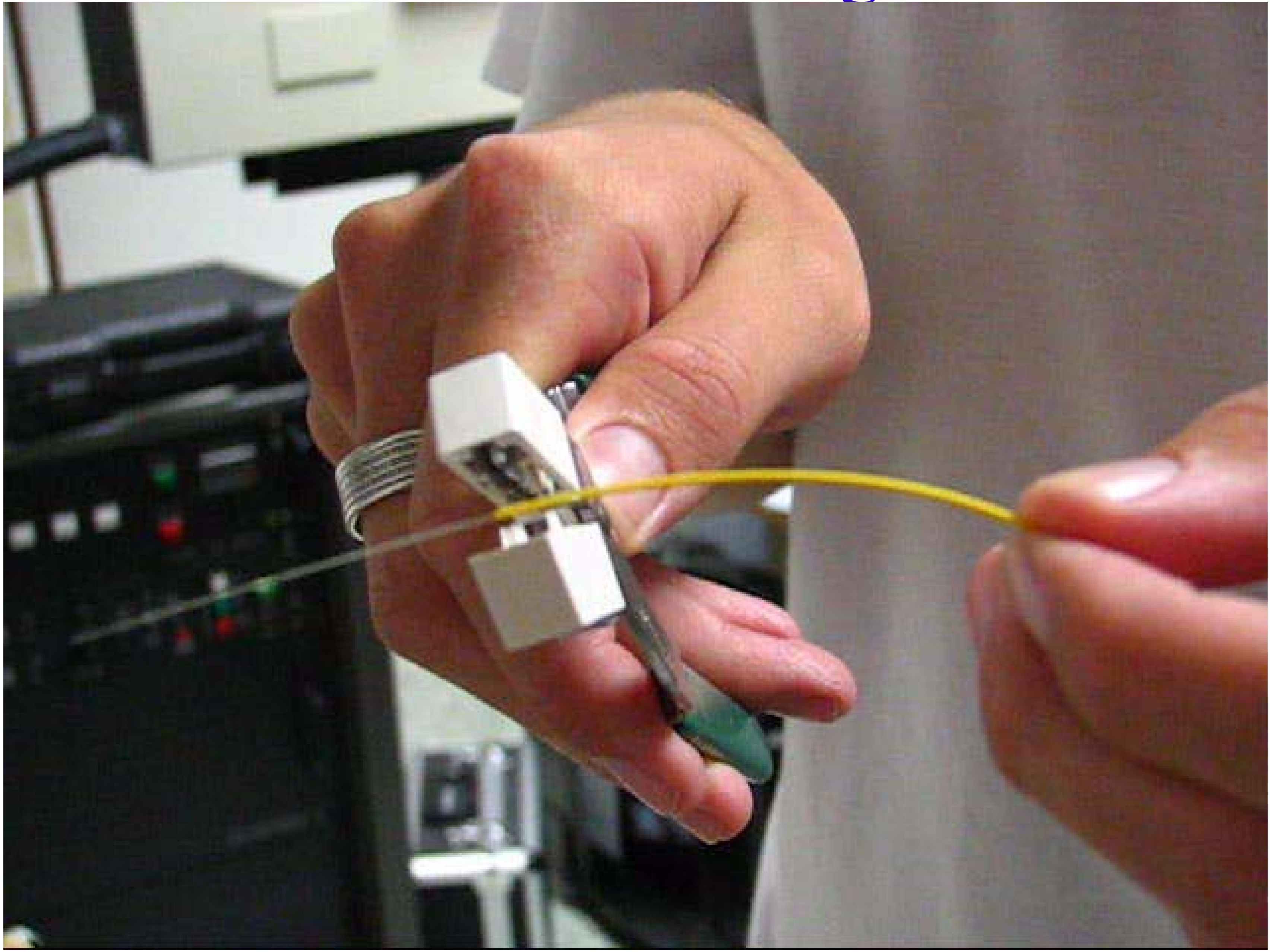


Optical fiber decladding

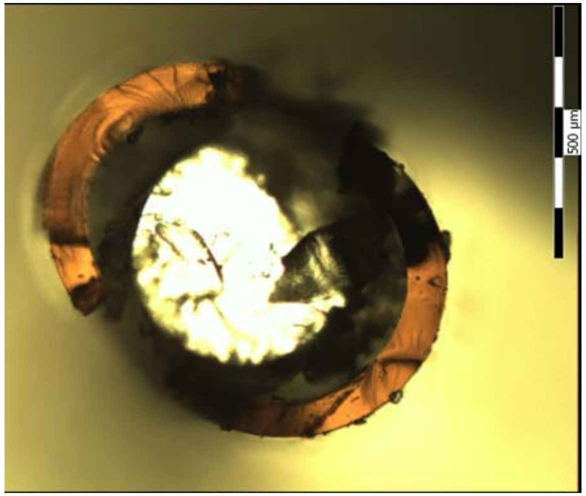
- mechanically – stripping tool (pliers)
- chemically - leaching
  - trichloethylene (acrylates)
  - HF acid (siloxanes)
  - exposition – seconds-minute

Optical fibers to be handled with care = “No drop on floor” [NPL, UK]

Fiber decladding

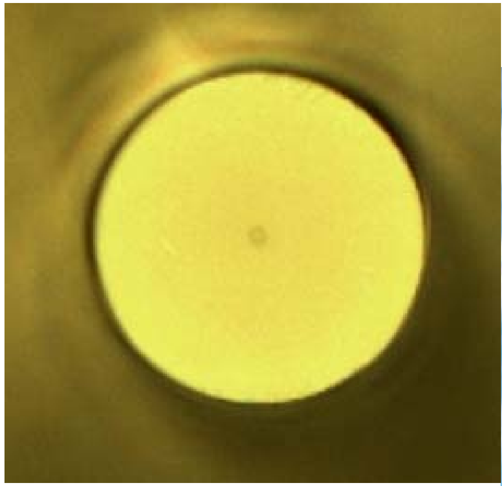


Fiber cutting



- primitively :

  scissors, knife, razor blade
  (suitable only for POF)
- more primitively: fire



- correctly :
  - **fiber cleaver** FK11 (York Tech, UK, Ericsson, S)
    [IPE]

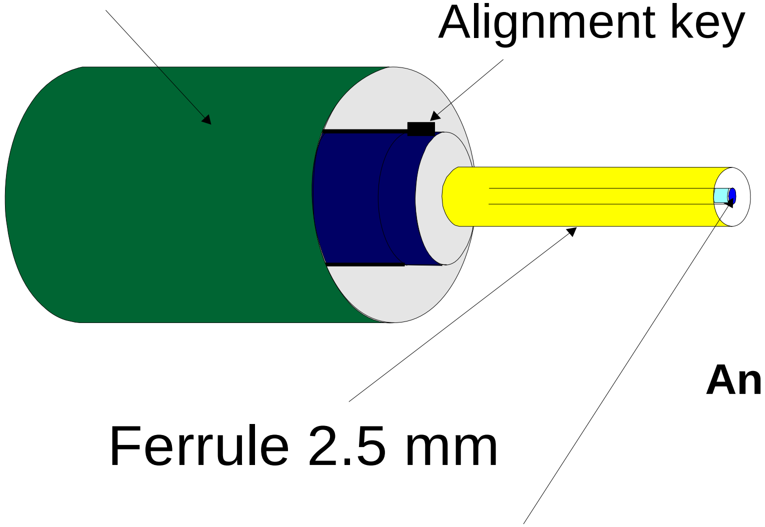
Fiber cutting

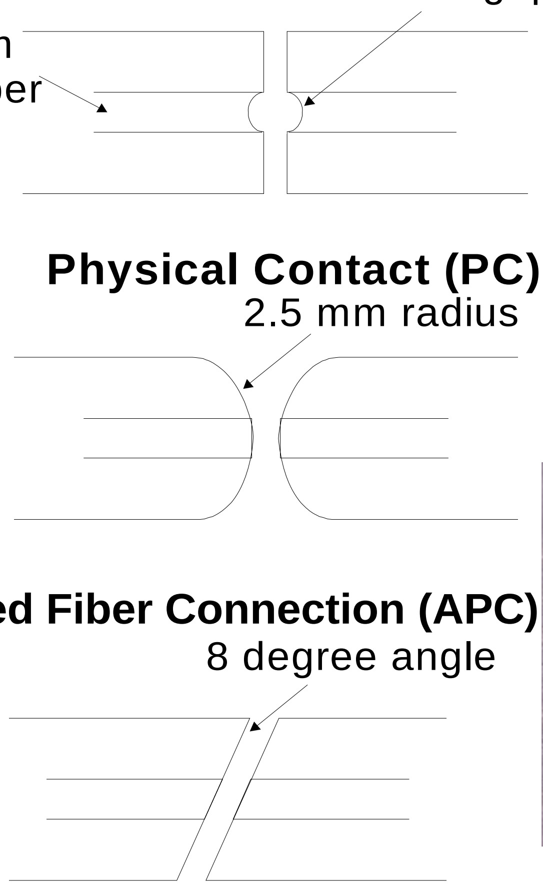
Optical fiber joining : splicing

- Splicing device (Fujikura, Ericsson) [IPE], silica-based fibers only; losses ~0.1 dB

Optical fiber joining : splicing

Optical fiber joining : connectoring





- FC, HMS-10, PC, D4, SMA, SC, DIN ST …; losses ~0.2 dB

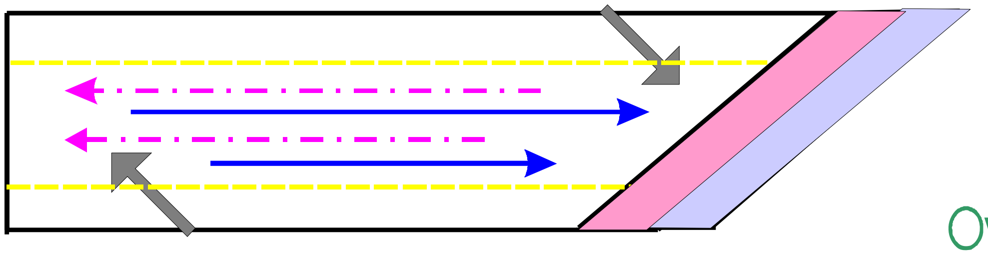
Optical fiber grinding, bevelling

- Diamond tools [Logitech…] or lapping films [3M…]; HOLDERS !

Optical fiber grinding, bevelling

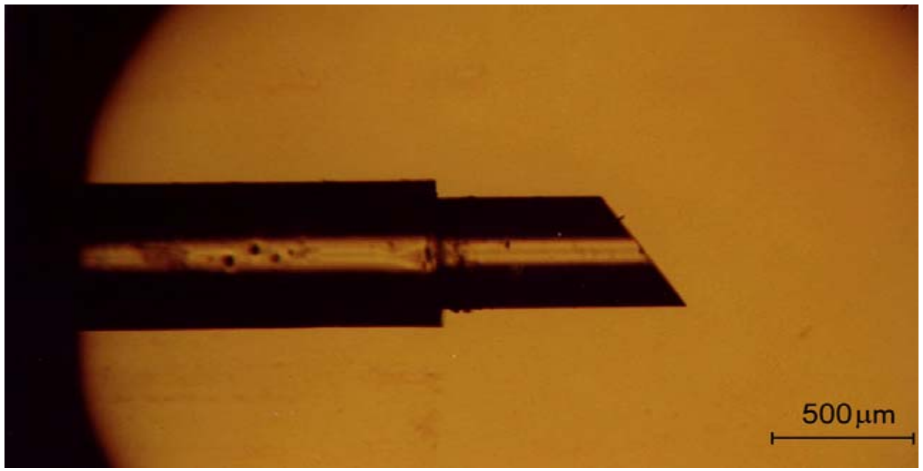
Light from the blue LED
going to the probe tip

Sol-gel

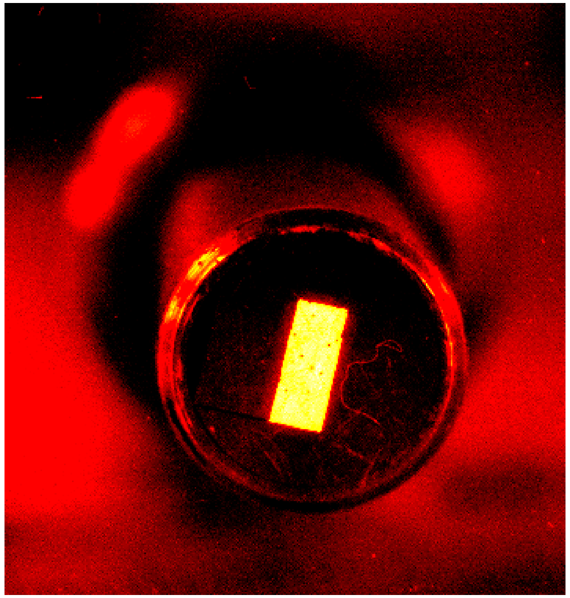


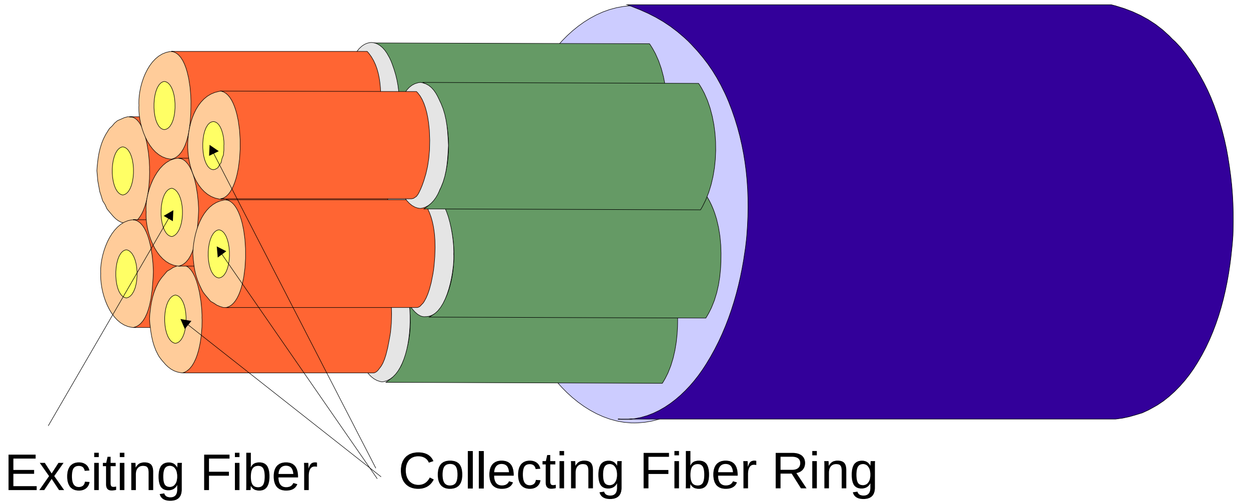
Overcoat

Collected fluorescence
going to the spectrometer



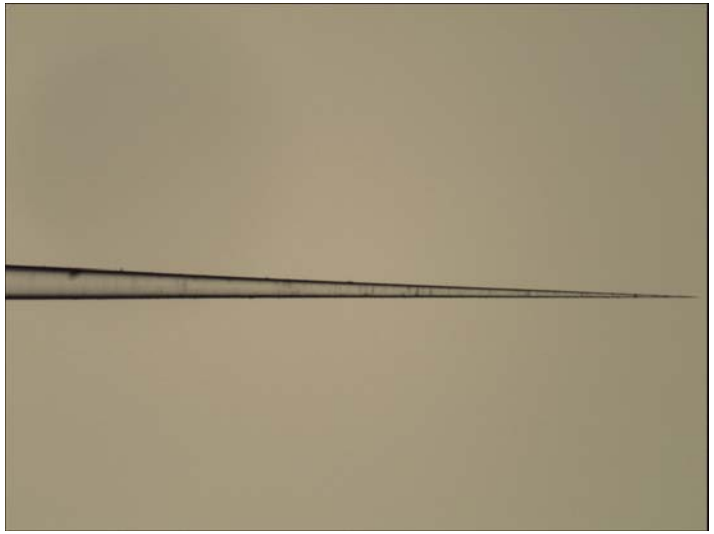
Fiber bundling





- Reflection sensing arrangement
- Imaging [IPE]
- Multianalyte analysis, large area monitoring

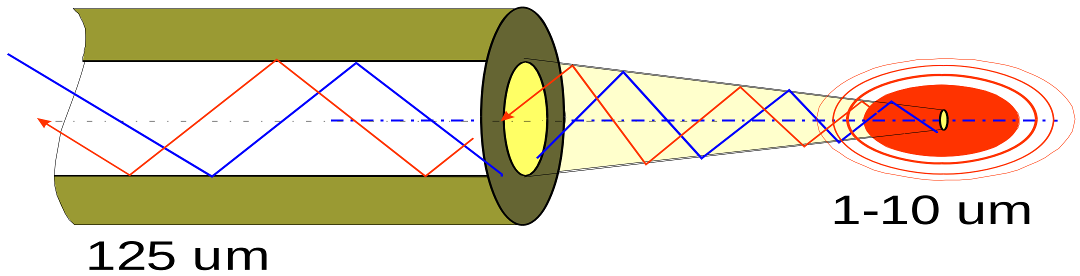
Optical fiber tapering



- TAPER :
- 1. Small area monitoring ~ μm^2
- 2. Multipoint monitoring
-
- Preparation
  - Flame processing
  - Slow withdrawing from acidic HF-containing solution
- [B.D.Gupta, C.D.Singh, F.Ligler, D.Kopelmann]

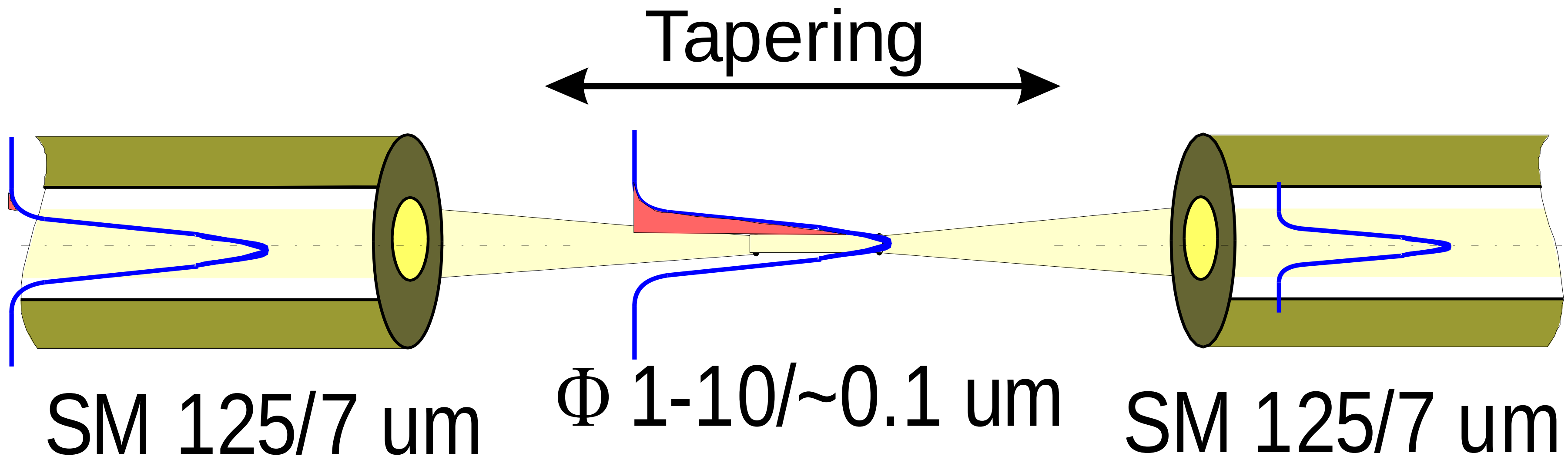
- 1. Small area monitoring

Tapered optical fiber



Optical fiber tapering

- 2. Multipoint monitoring
- Principle :



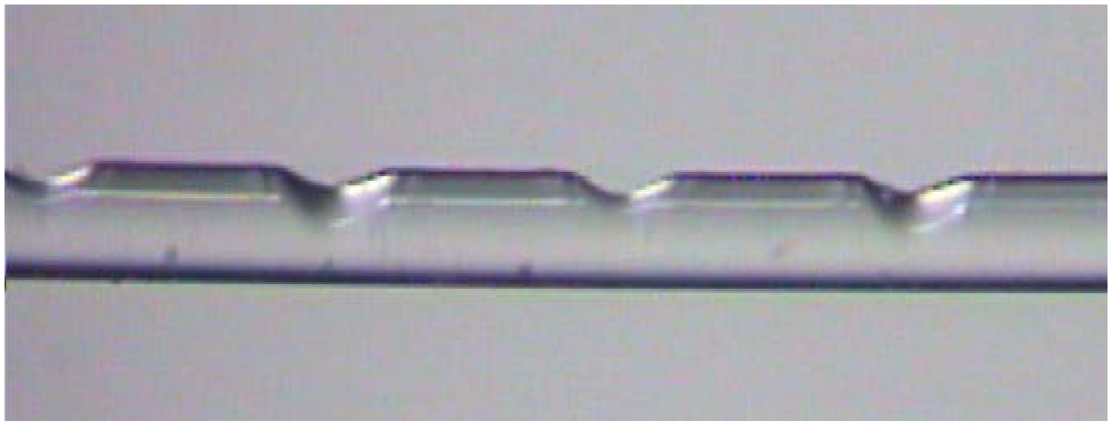
Optical losses : SM ~ 0.1 dB

Optical fiber tapering

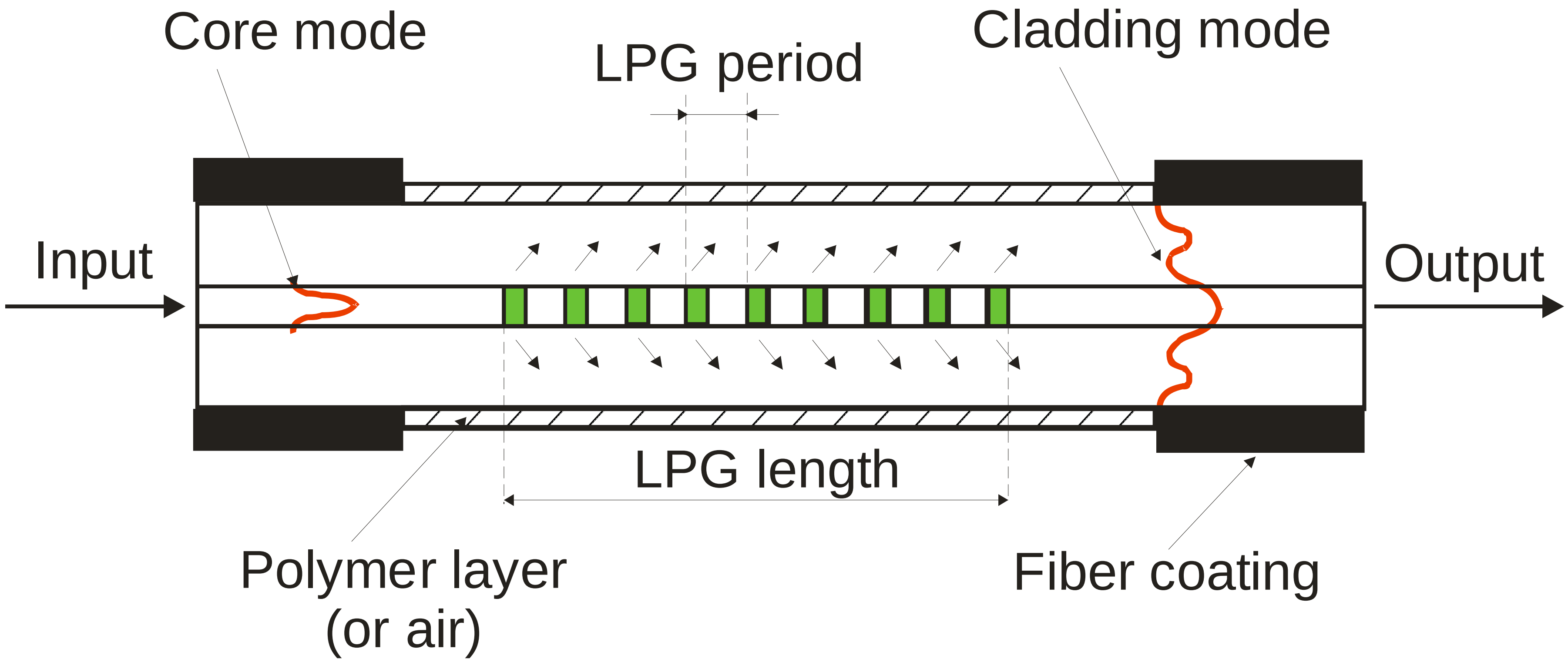
Gratings

- Multipoint monitoring
- Fibre Bragg Gratings **FBG**
  - short period, side-polished, forward mode => backward mode
- Long Period Gratings **LPG**
  - ~ mm period, whole structure, forward clad mode => forward mode

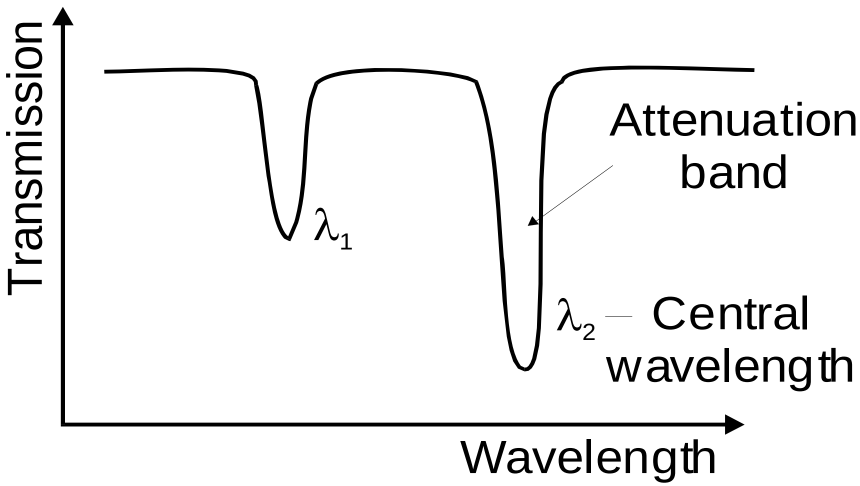
- UV/CO_2 laser scanning inscription / via mask / on-line
- Condition : strain => highly doped fibers



Long Period Gratings (LPG)



LPG

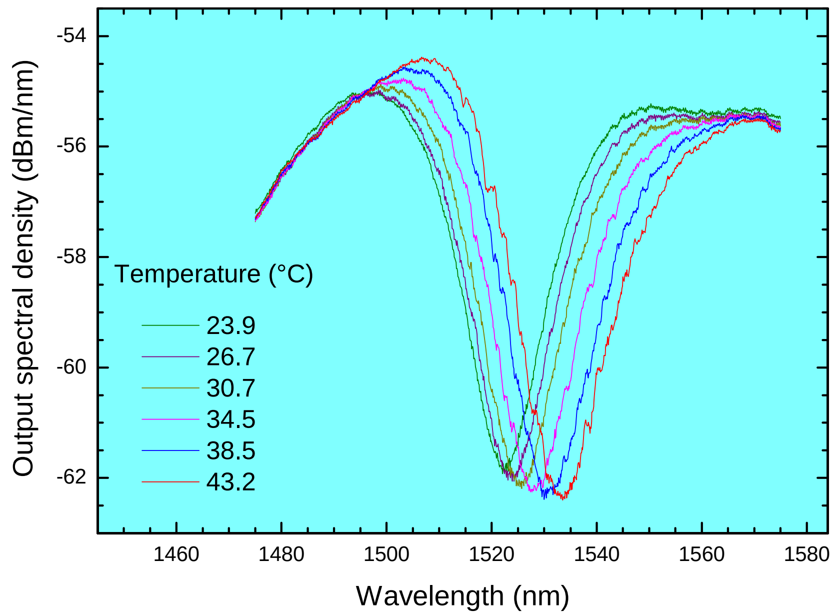


Transmission spectrum of LPG

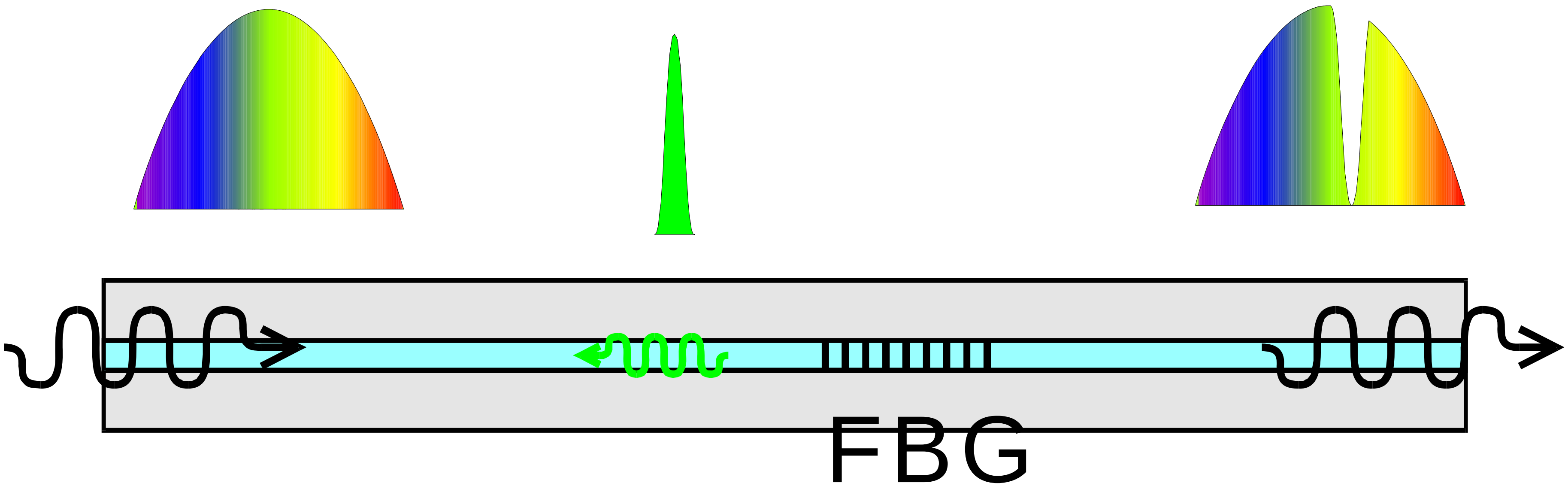
Phase-matching condition

$$\lambda_i = \Lambda\left(n_{eff}^{co} - {}^{(i)}n_{eff}^{cl}\right)$$

Λ - LPG period

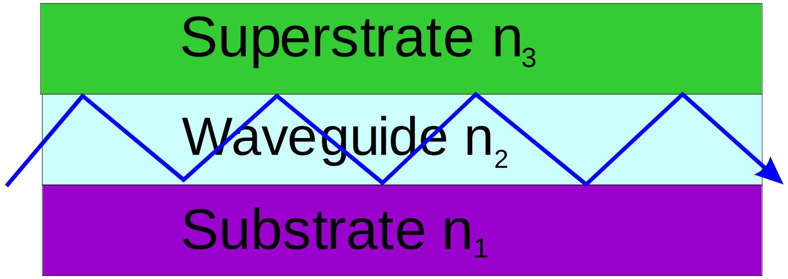


Fiber Bragg Gratings (FBG)

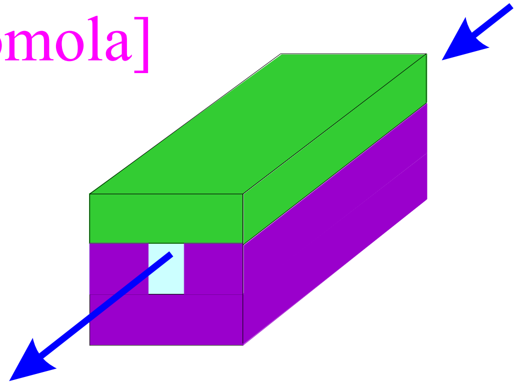


Planar waveguides

[J. Homola]



Planar waveguide



Channel waveguide

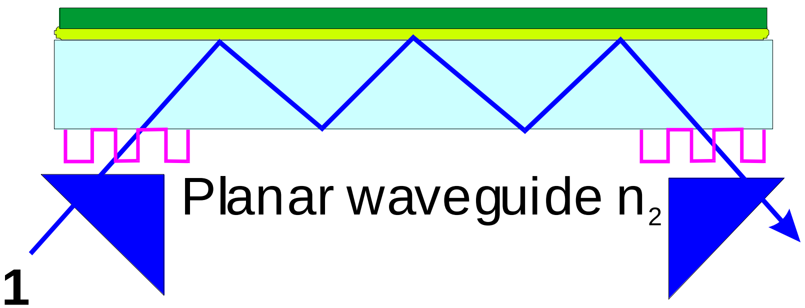
$n_1 < n_2 > n_3$

Total reflection

Snell's Law

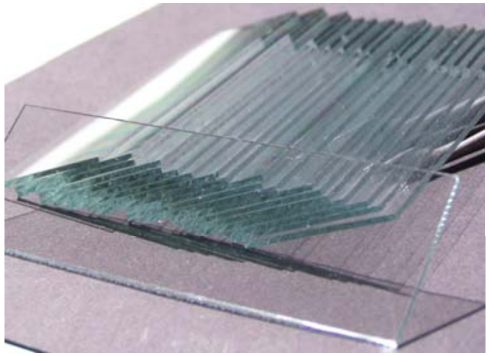
Coupling of light

Analyte (coating) n_3

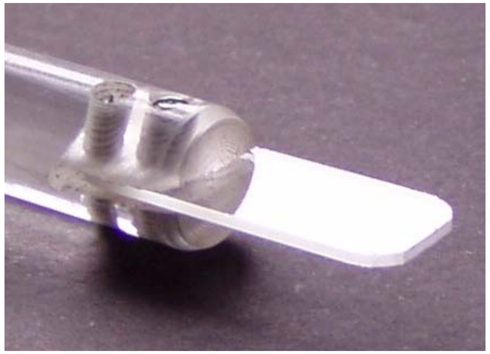


$n_1 = 1$

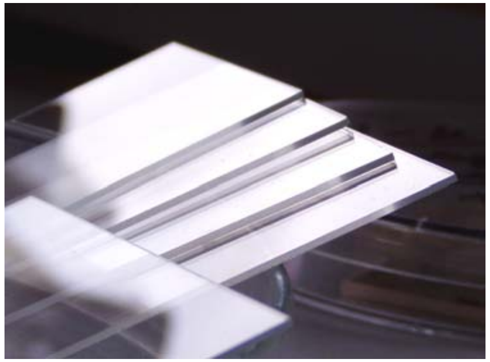
Grating / prism

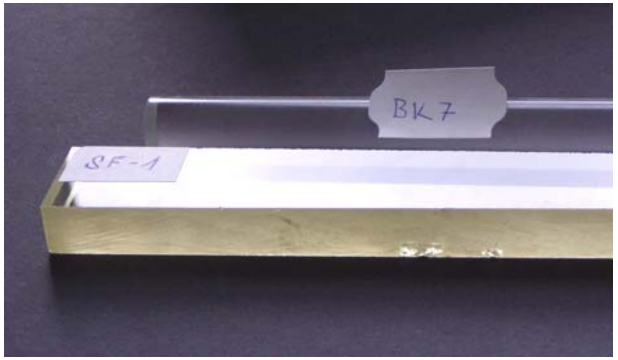


Planar substrates



- PMMA





- Silica

Microscope slides - alkali-rich glass of undefined properties

Simax (Pyrex, Vycor) borosilicate low-alkali glass, n_{589nm}= 1.472 [kavalier.cz, pyrex-wafers.com, pgo-online.com ...]

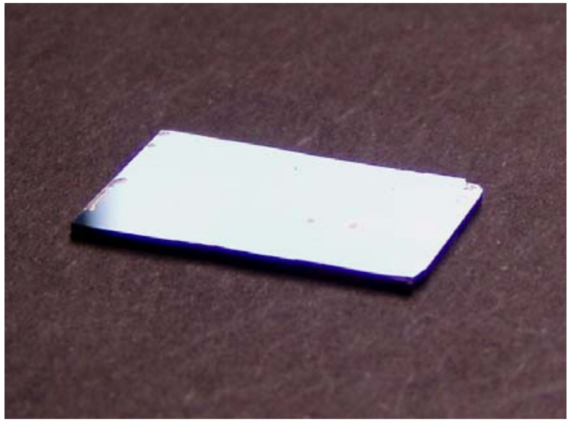
BK7 optical glass, n_D= 1.5168 [edmundoptics.de, thorlabs.com ...]

Optical soft glasses - F, SF, LF, FKK, n_D= 1.5–1.95 [schotglass.de …]

HERASIL - silica, n_{633nm}= 1.457, [heraeus.com, corning.com]

PMMA, PE, PVC, PS - polymers, $n_D \sim$ 1.5-1.6) [plasticoptics.com …]

Planar substrates



- Si -wafer

- GeO_2-PbO glass

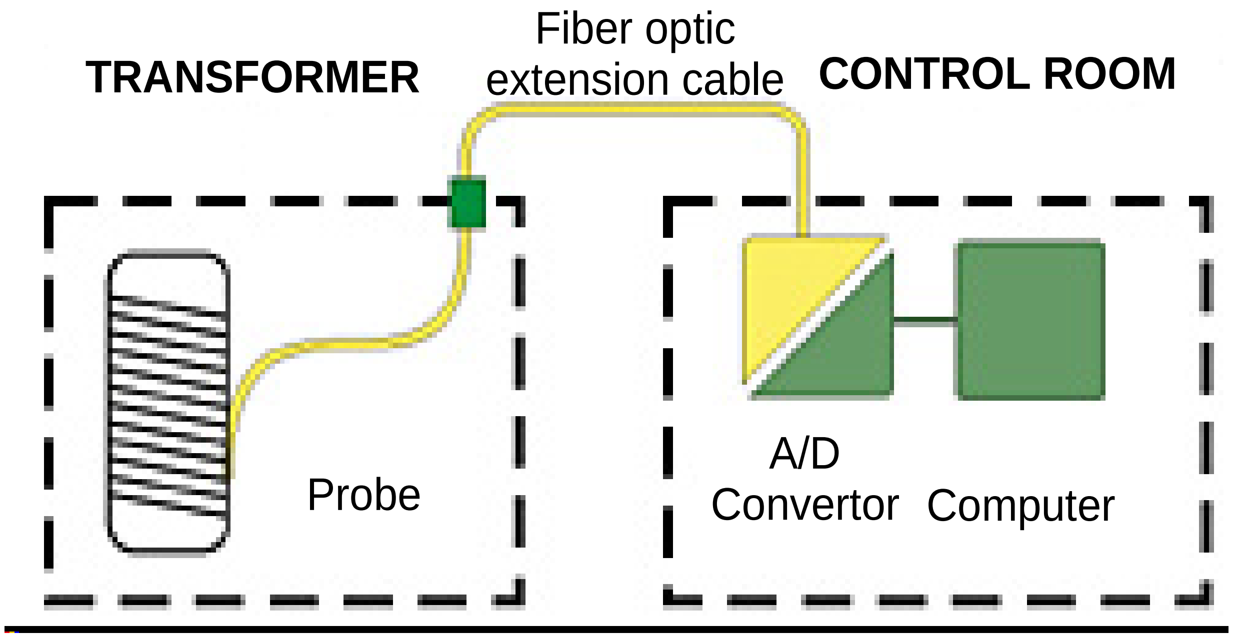
- As_2S_3 glass

Závěr

- obecné přístupy při návrhu optické detekce
- použití optických vláknových sensorů – příklady

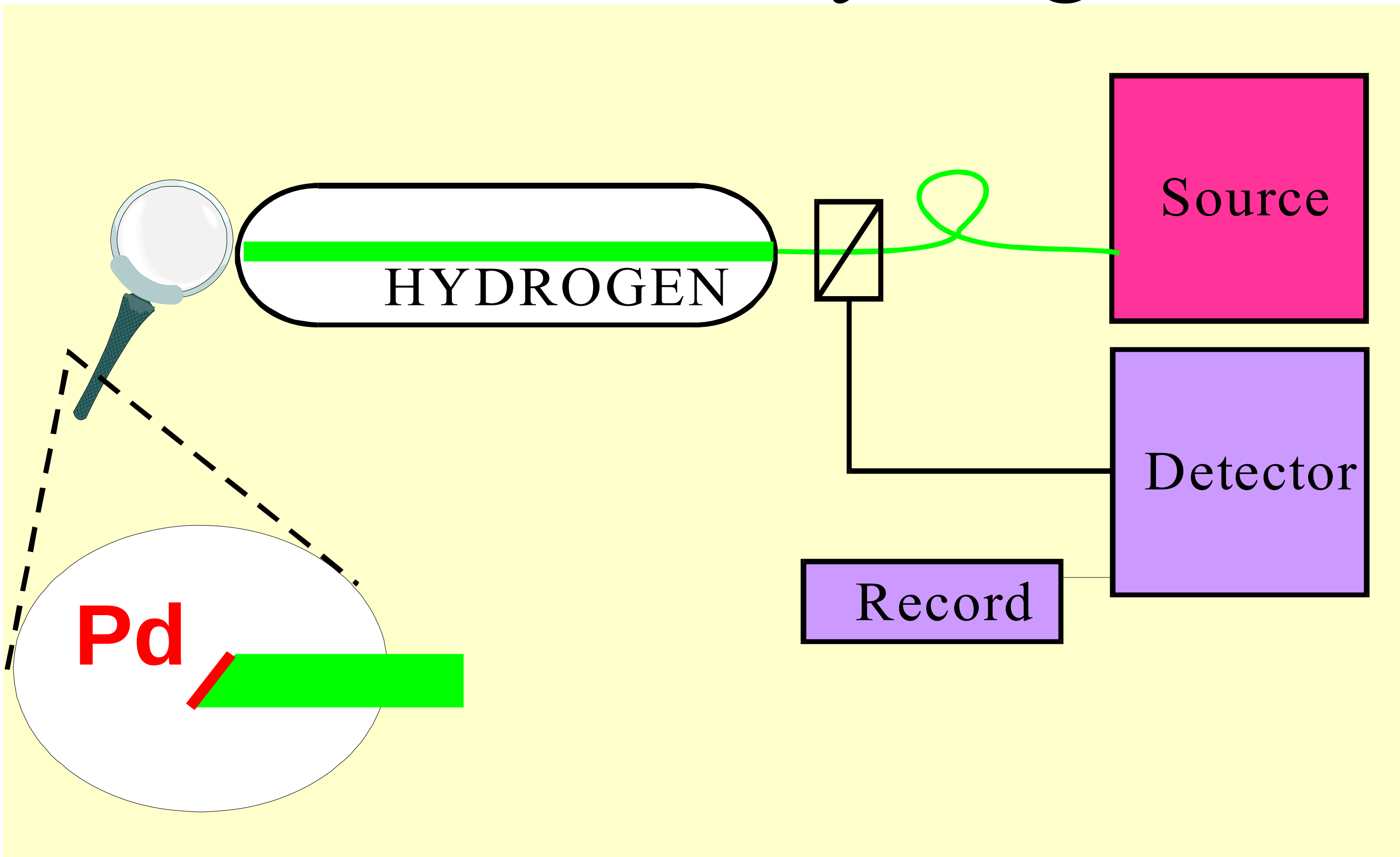
1. Indispensability of optical fibers

- **Medicine** [Baldini]
- **High-voltage areas** [www.FISO.com]



- **Explosives**, easily **flammable** or corrosive substances detection

Detection of hydrogen



- [X.Bevenot, H.Gagnaire, R. Willsch]
- **SUITABLE : distributed or multipoint** sensing
  - *~5 USD/1 m PCS$_{200}$ vers. 50 USD / 1”-silica substrate*
- *75% of production of laser sources are fiber lasers (compatible)*

2. Spectral range

- Availability of optical hardware

  UV<< VIS+NIR >> IR

- Optical losses of optical hw

  UV<< VIS+NIR >> IR

- **VIS-NIR**
- compatibility with conventional fiber optics = available sources, detectors, accessories on acceptable price

- **UV, IR**
- more expensive and more complicated instrumentation, nevertheless valuable results can be obtained

3. Optical fiber structure

- Multimode – **MM**
- + larger core & higher NA => cheap LED sources, fibers, accessories
- + robustness – easy handling, processing
- + compatibility with conventional fiber optics
- - sensitivity => enhancement by coating, optics

- Single-mode, few-mode – **SM/FM**
- + high sensitivity
- + compatibility with conventional fiber optics
- - more expensive components
    - *25 % sensing applications SM x 75% MM*

- Availability : **conventional >> specialty**
- *conventional solution* *x* *unconventional, advanced, valuable ... solution*

Optical hardware consideration

Requirements :

- sensitivity – LOD
- selectivity
- reproducibility
- dynamics - time response
- reliability

- **Method**

  (optical, ultrasonic, electronics...)

- **Optical hw** & chemical sw
  - 1. **Planar / fiber-optic**
  - **2. Spectral range**
  - **3. Structure OF**
  - **4. Coatings & transducers**

- **Feasible and easy ??***

* Parkinson : The more complicated system, the higher probability of its failure.

*Murphy : What can go wrong, it will.

- Expected utilization (market)
- Price

Problem :
leakage of petro-chem products (break downs)

=>

Task : 24/7 monitoring of technology and transport of product (tanks, tubing)

Consideration – solution

- flammable analytes (petrol)

  => prevention of overheating, sparking => optical method
- distributed (along tubes – long distances)

  => optical fiber
- industrial scale

  => not too expensive => VIS-NIR, multimode structure
- method : evanescent-wave sensing

  refractometry suitable :

  $(n_{hydrocarbons}/n_{water} \sim 1.48/1.33 > n_{silica} \sim 1.46)$

Consideration – solution

1. solution

- conventional MM-PCS fiber coil (active length ~8 m), axially excited

- COSTS :
  - LED + silicon detector
  - 8 m PCS fiber

  < 1000 E
- bottleneck : -

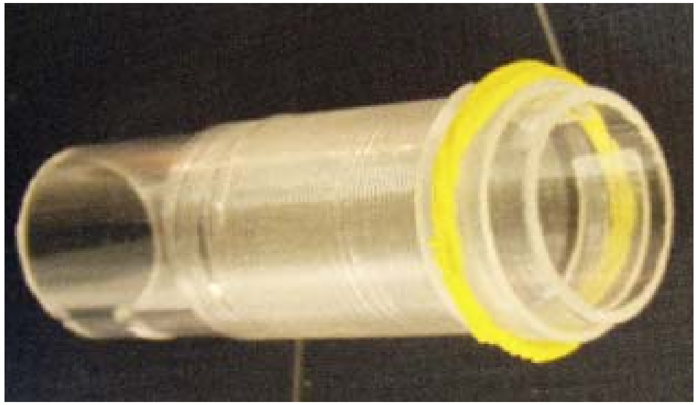
2. solution

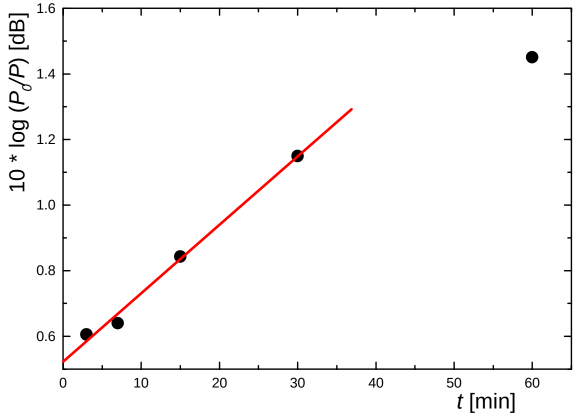
- specialty MM-IGI fiber (active length ~5-10 cm), declad and additionally coated with PDMS, selectively excited by inclined collimated beam of red LED delivered by beveled fiber

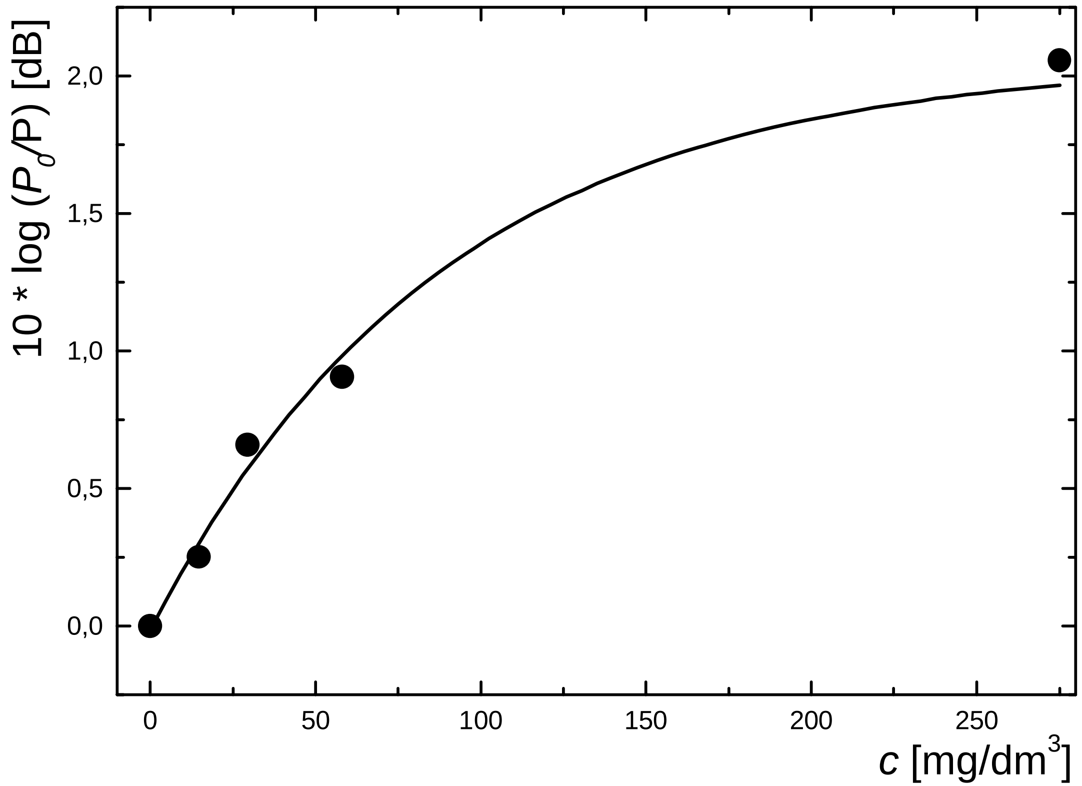
- COSTS :
  - LED + silicon detector
  - 20 cm IGI fiber

  < 1000 E
- bottleneck : specialty fiber + coating PDMS $\neq$10 μm [IPE]

Results 1 : PCS-coil







\+ **sensitivity** : $LOD_{1688\ nm} \sim 1$ mg/l, $LOD_{670\ nm} \sim 10$ mg/l

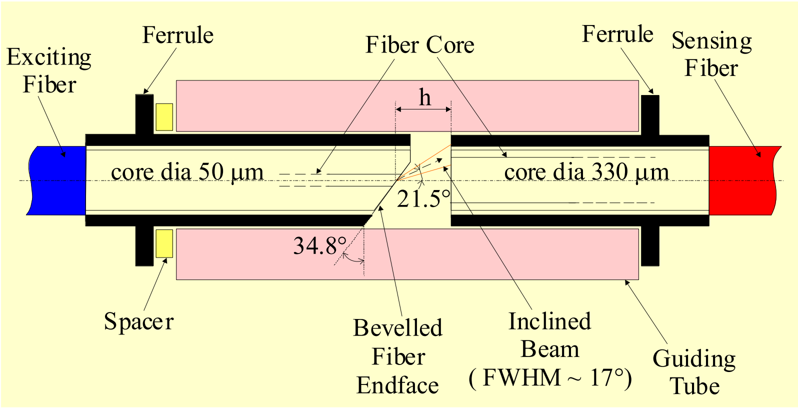
~ comparable with EU ecological limit

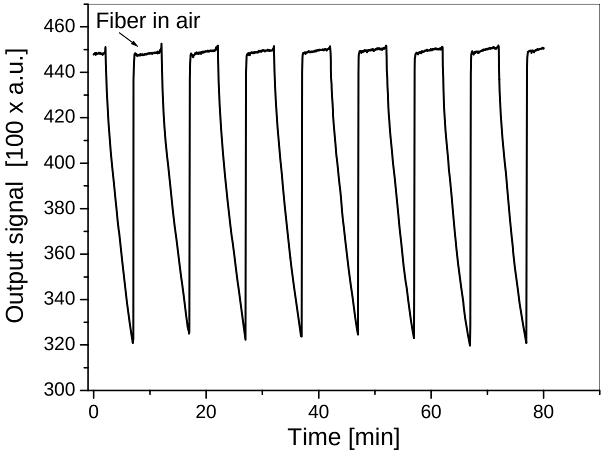
\- **time response** : minutes

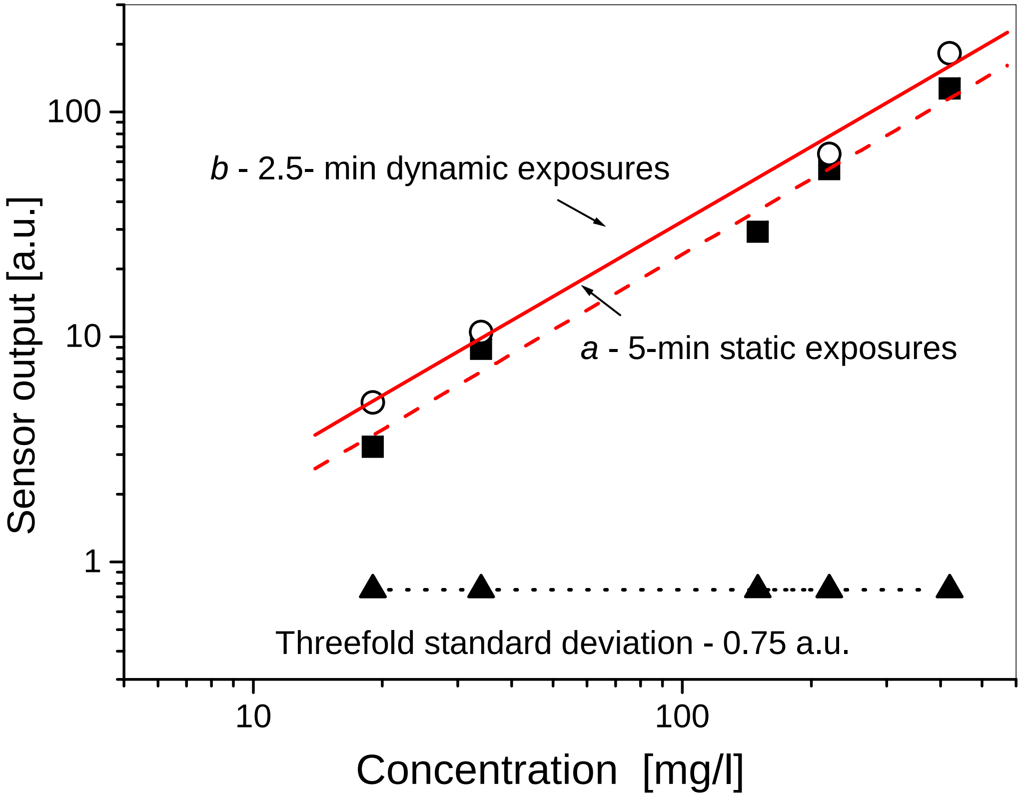
\- **stability - reproducibility :** ~ hours

\-**selectivity** : temperature – referencing, generally sensitive to R-I changes

Results 2 : IGI-fiber







+ **sensitivity** : LOD ~ 3-5 mg/l ~ comparable with EU ecological limit
+ **time response** : seconds
+ **stability - reproducibility** : < months
- **selectivity** : temperature – referencing, protective membrane

Optically detected analytes

Chemical analytes

- Oxygen
- pH
- Carbon dioxide
- Ammonia
- Hydrogen
- Sulfur dioxide
- Nitrogen dioxide
- Hydrocarbons
- Chlorinated hydrocarbons
- Chlorine
- Sulfites
- Cations – K^+, heavy metal ions
- Anions – chlorides, nitrates …

Organic (biochemical) analytes

Alcohols

Glucose

Lactate

Creatinine

Esters

Urea

Glutamate

Oxalate

Phenols

Cholesterol

Ascorbate, Bilirubin,Xantin …

SUMMARY

- **Optical sensors**
- - devices for optical monitoring of physical / (bio)**chemical** properties of a medium by means of optical elements (real-time and reversible)
  - - high sensitivity [< ppm] in a wide dynamic range
  - - immunity to electromagnetic interference
  - - remote sensing
- Optical fiber sensors
- - potential of distributed / multipoint detection
- - indespesability in medicine, high-voltage areas, explosives
- **Methods** : absorption, luminescence, phase, time domain
- **Optical elements :** optical **fibers, planar** waveguides**, bulk** optics
- - principle of performance - total reflection
- - structures and materials

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