Spektrometrie v blízké infračervené oblasti

Pavel Matějka

NIR spectrometry

- molecular absorption/reflection spectrometry
- **non-destructive** method used in process analysis, QC/AC
- practical method that can replace more expensive, more time-consuming and more laboured methods – GC, HPLC, titrimetry
- relatively fast method for a routine use in technological applications

NIR spectrometry

- qualitative information – **NIR libraries** – identification of pure substances and/or check of pre-defined mixtures
  - pharmaceuticals, polymers etc.

- **quantitative analysis** – multivariate calibration models
  - **multi-component analysis** - organic, inorganic

NIR spectrometry

NIR

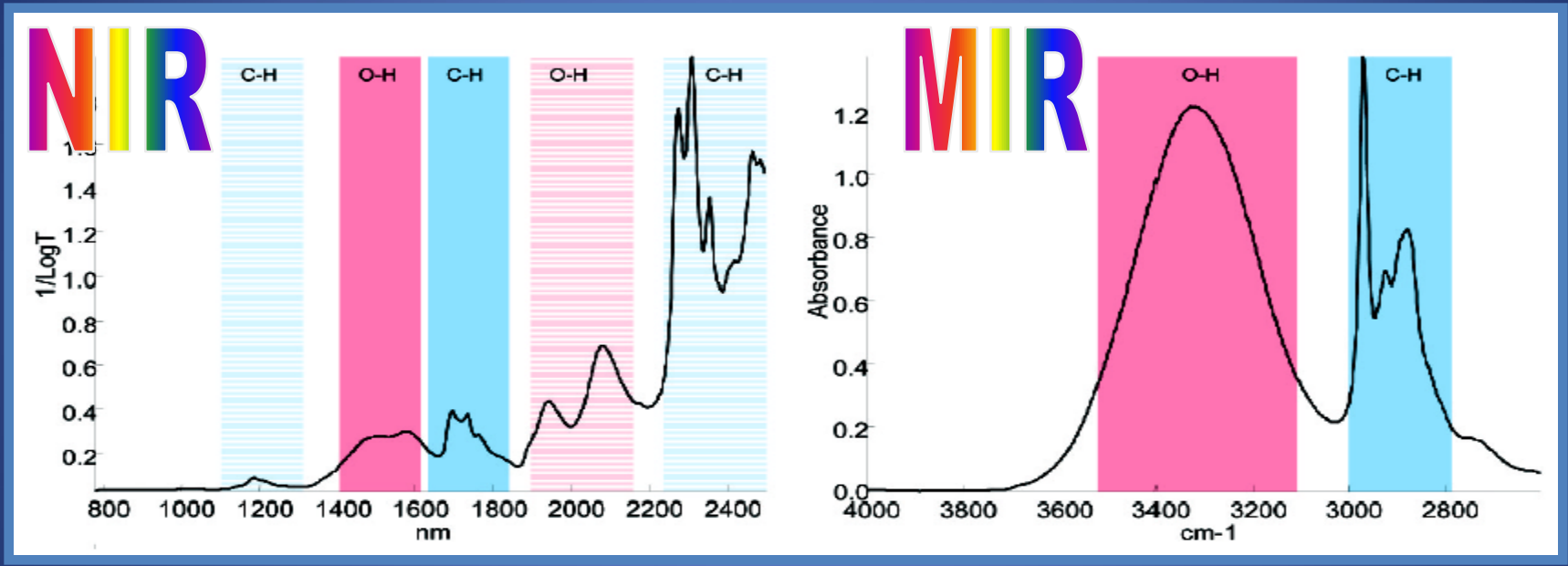
- from
  - 14 000 cm^{-1} *714 nm*
  - 12 500 cm^{-1} *800 nm*
  - 12 000 cm^{-1} *833 nm*
- to
  - 4 000 cm^{-1} *2 500 nm*

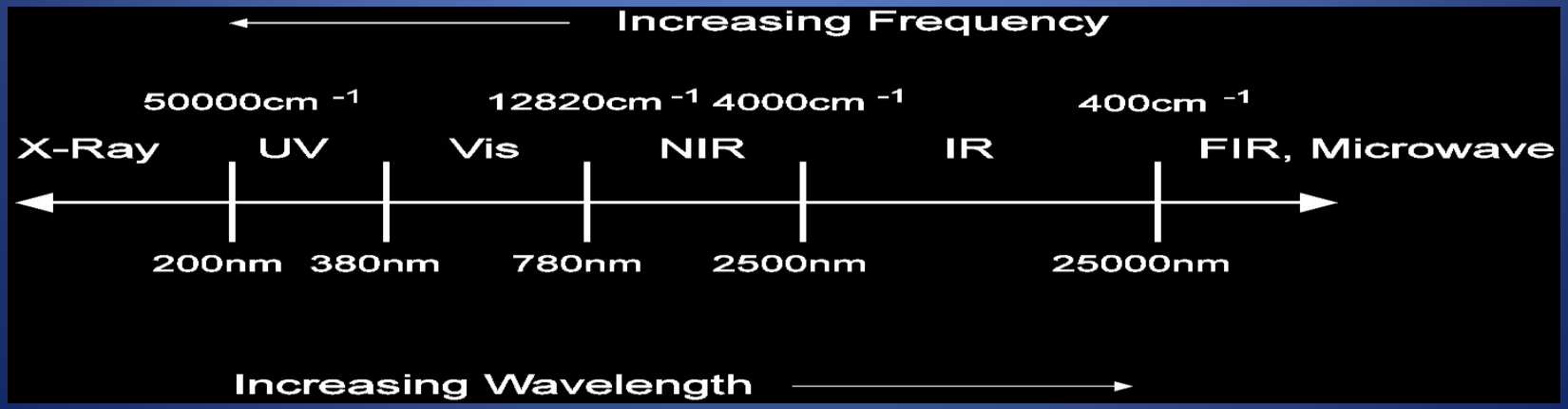
MIR

- from
  - 4 000 cm^{-1} *2 500 nm*
- to
  - 400 cm^{-1} *25 000 nm*
  - 200 cm^{-1} *50 000 nm*

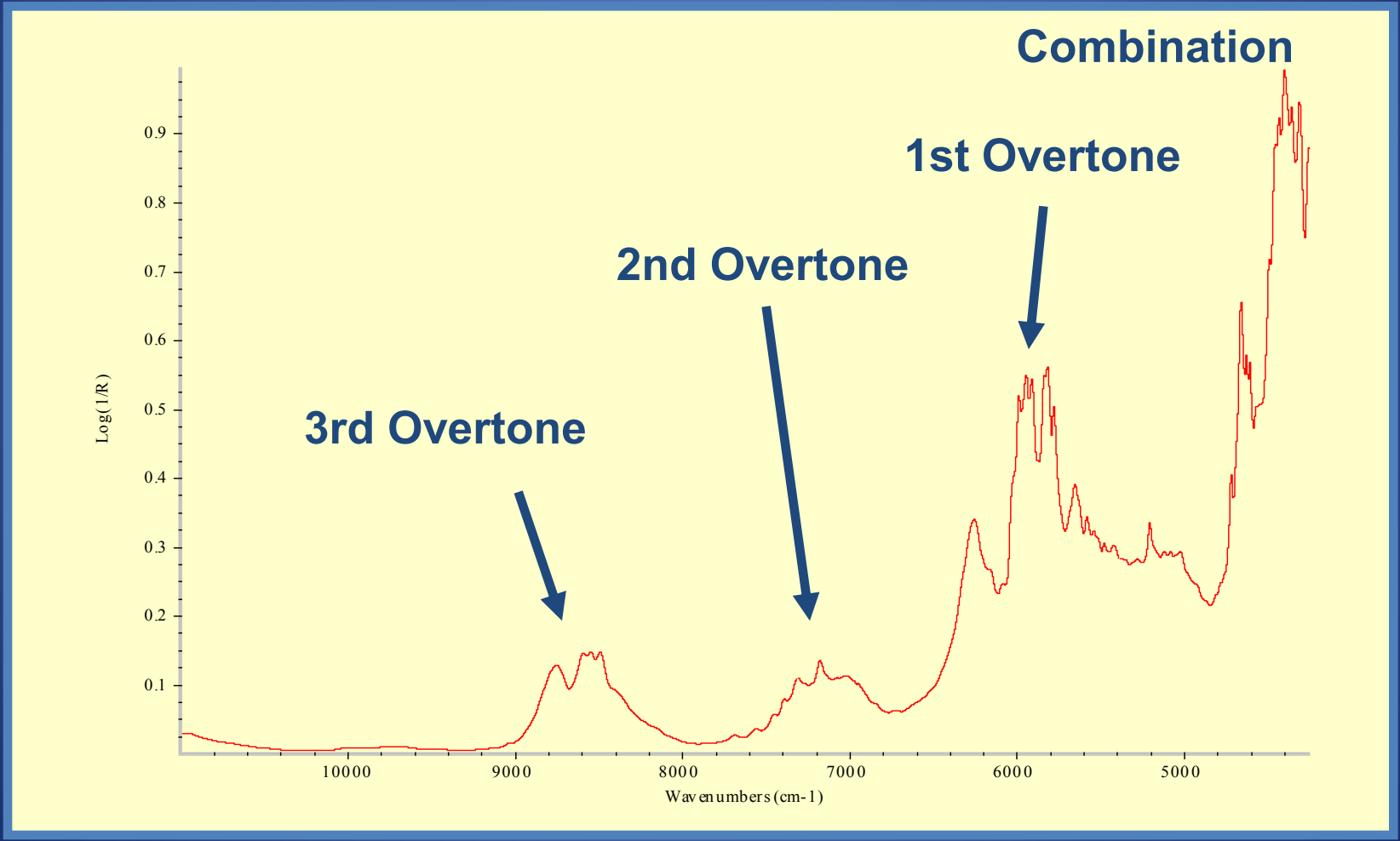
NIR spectrometry

- relatively broad bands – overtones and combination bands

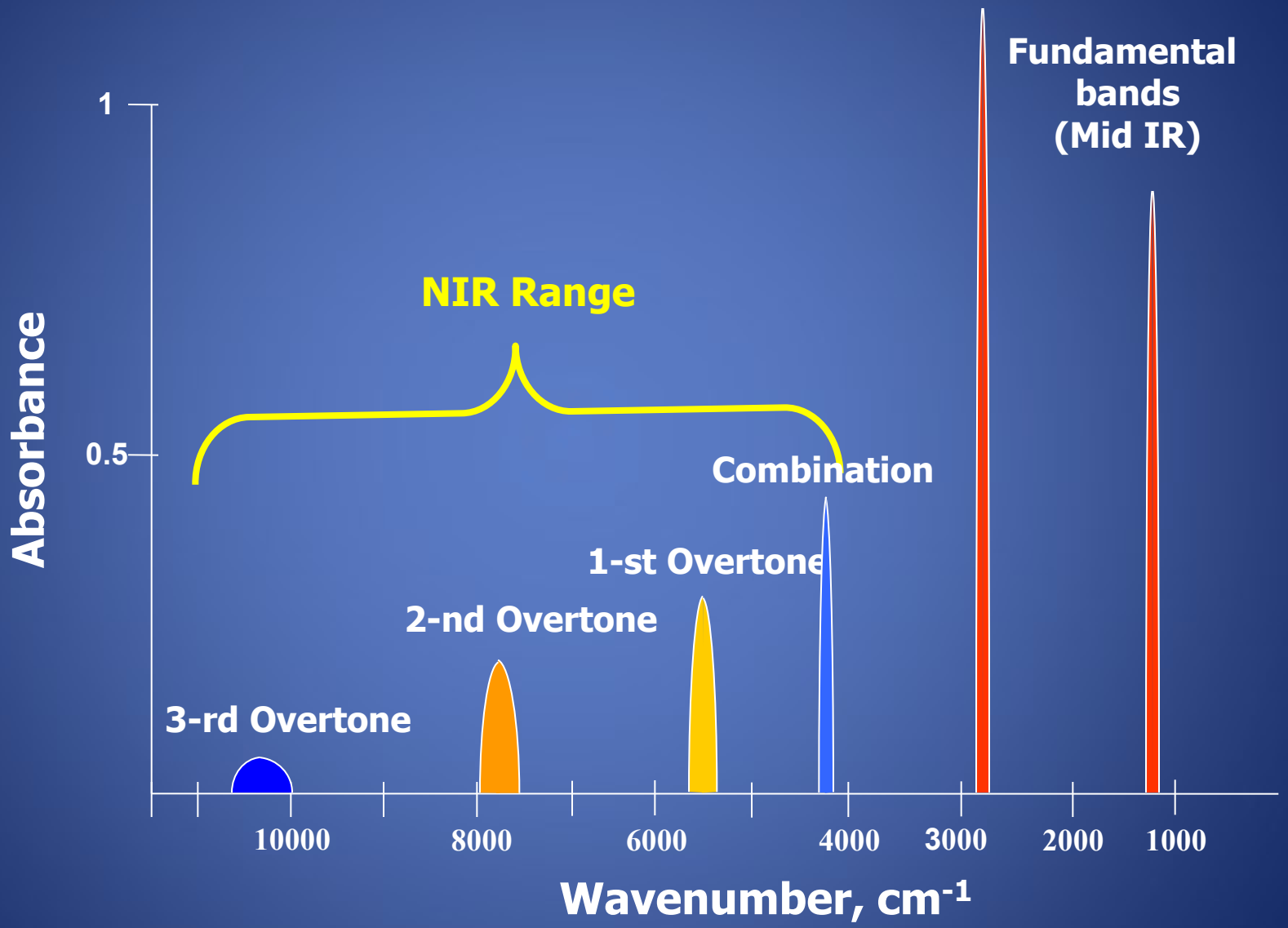


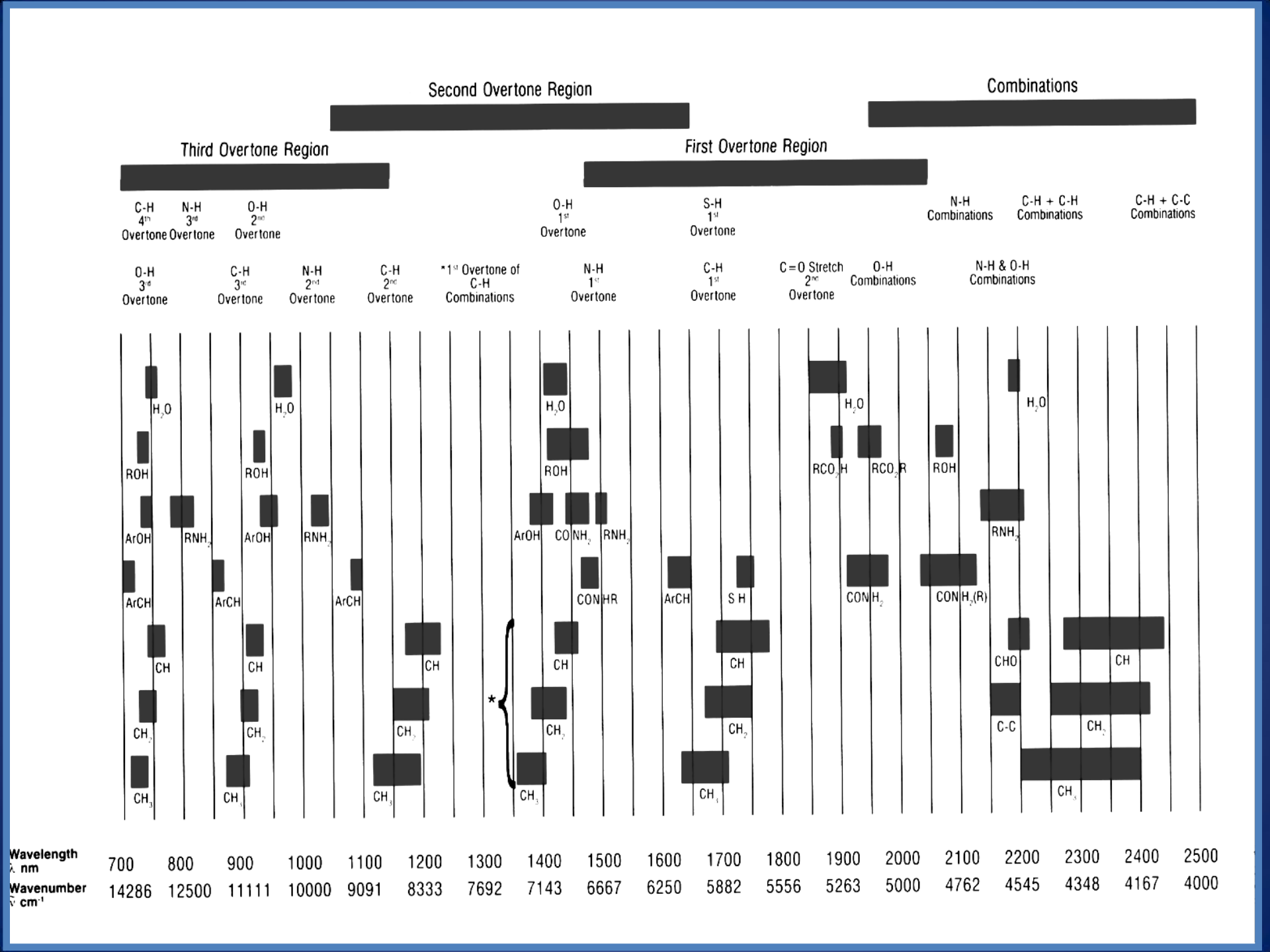


NIR spectra


Combination
1st Overtone
2nd Overtone
3rd Overtone
Log(1/R)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10000
9000
8000
7000
6000
5000
Wavenumbers (cm-1)

NIR spectra


Fundamental bands (Mid IR)
1
0.5
Absorbance
NIR Range
Combination
1-st Overtone
2-nd Overtone
3-rd Overtone
10000
8000
6000
4000
3000
2000
1000
Wavenumber, cm-1


Second Overtone Region
Combinations
Third Overtone Region
First Overtone Region
C-H 4th Overtone
N-H 3rd Overtone
O-H 2nd Overtone
O-H 1st Overtone
S-H 1st Overtone
N-H Combinations
C-H + C-H Combinations
C-H + C-C Combinations
O-H 3rd Overtone
C-H 3rd Overtone
N-H 2nd Overtone
C-H 2nd Overtone
*1st Overtone of C-H Combinations
N-H 1st Overtone
C-H 1st Overtone
C=O Stretch 2nd Overtone
O-H Combinations
N-H & O-H Combinations
H2O
ROH
ArOH
RNH2
ArCH
CH
CH2
CH3
CONH2
CONHR
RCO2H
RCO2R
SH
CONH2(R)
CHO
C-C
Wavelength λ, nm
Wavenumber ν̃, cm-1
700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500
14286 12500 11111 10000 9091 8333 7692 7143 6667 6250 5882 5556 5263 5000 4762 4545 4348 4167 4000

NIR/MIR spectra intensities

- the intensities are decreasing with increasing frequency / wavenumber

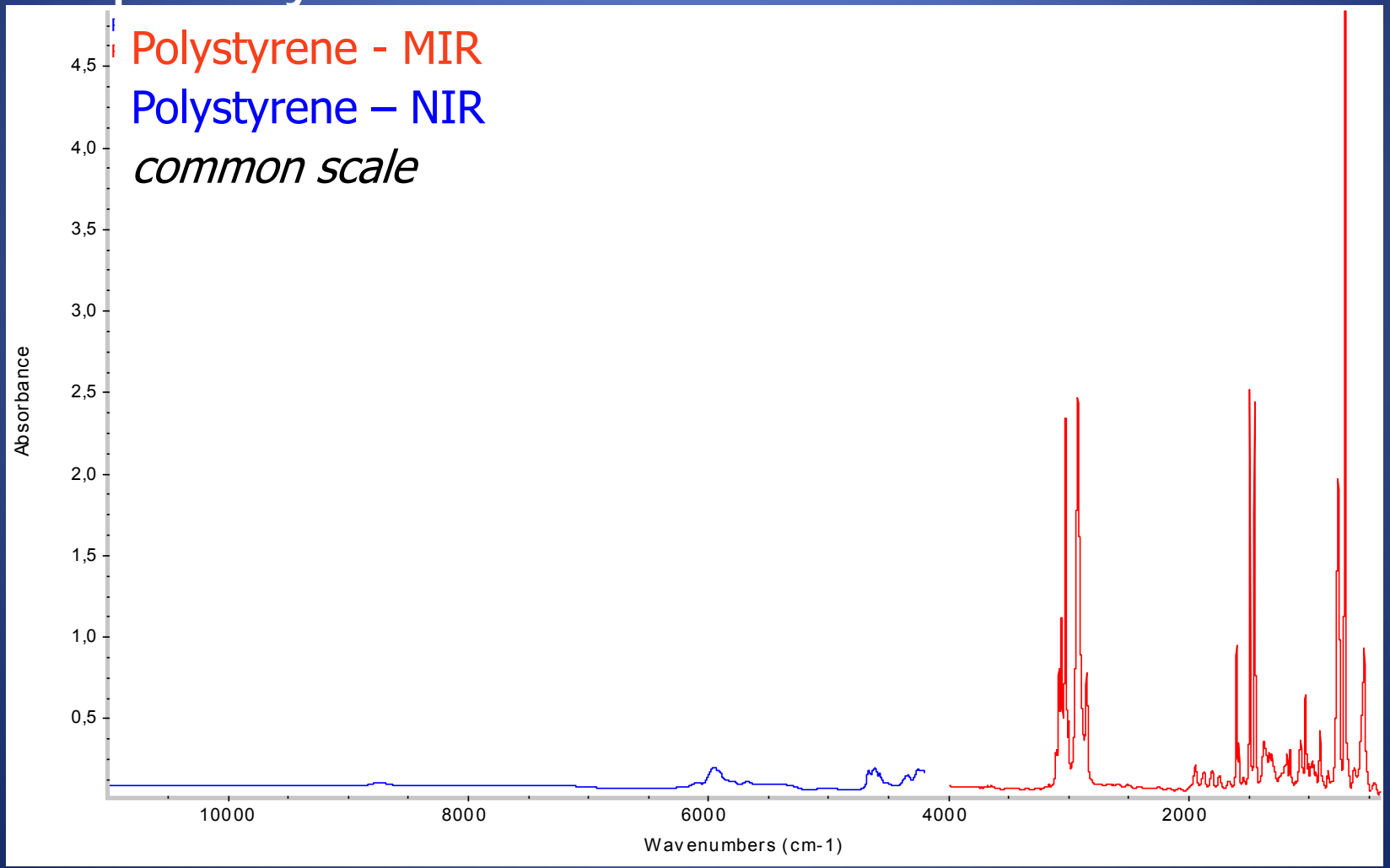
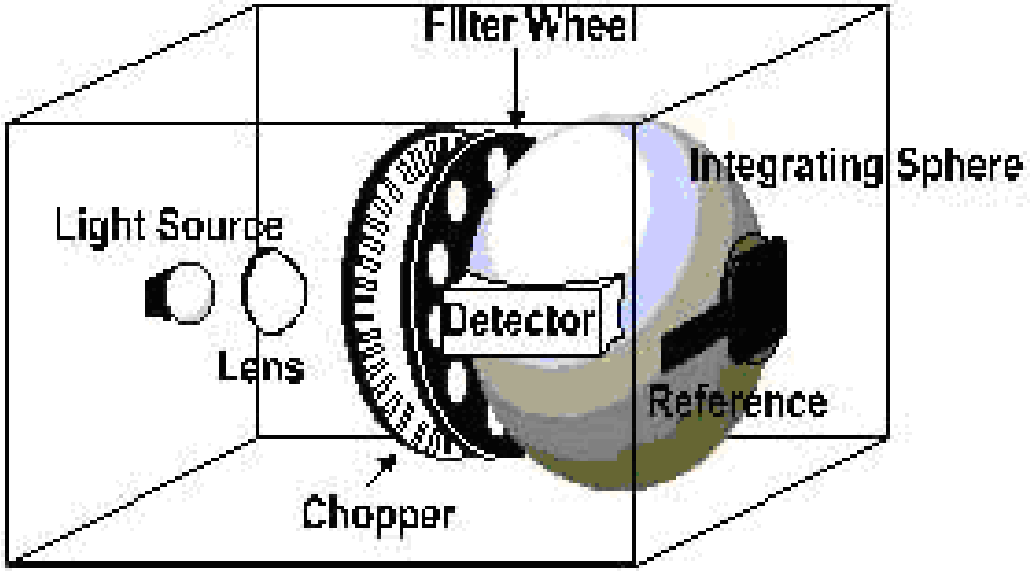


Schéma filtrového NIR spektrometru



Filtry ve filtrovém spektrometru fungují jako **selektory vlnových délek. Propouštějí pouze určité** vlnové délky ze spojitého záření zdroje. Propouštěné vlnové délky jsou vybírány experimentálně podle toho, v které oblasti spektra absorbuje např. protein. Pokud se mění matrice vzorku, je obtížné optimální sestavu filtrů experimentálně definovat.

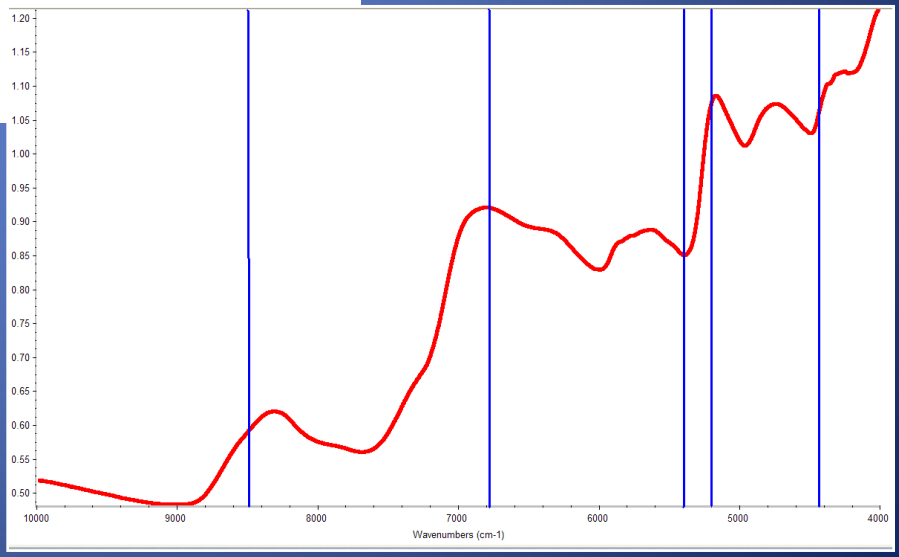
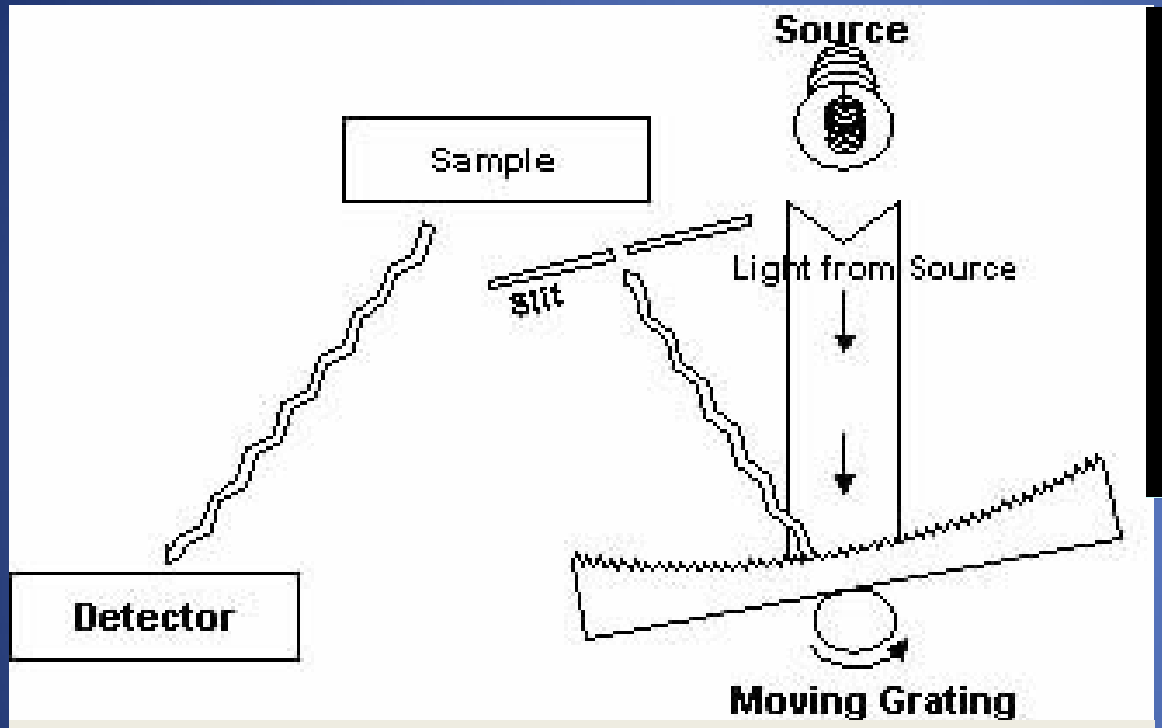
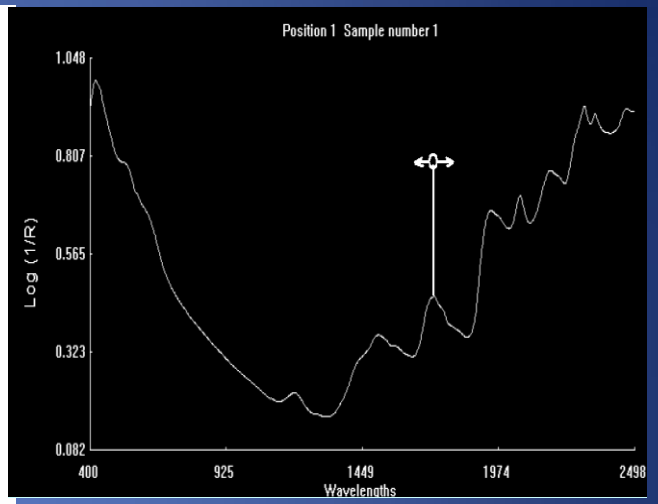


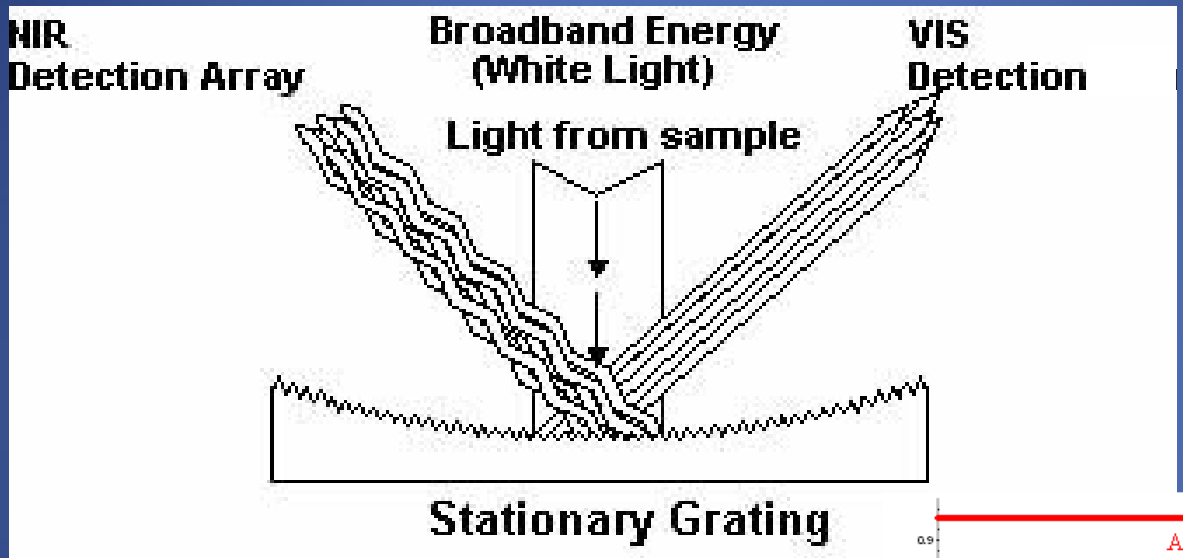
Schéma disperzního NIR spektrometru s pohyblivou mřížkou



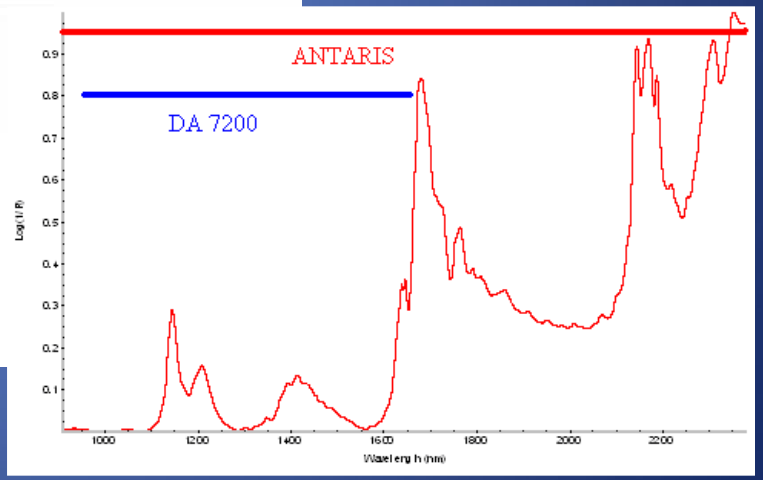


Běžné rozlišení 2 nm odpovídá přibližně vlnočtu 16 cm^{-1} (u 1650 nm je to cca 7 cm^{-1}, u 950 nm je to cca 24 cm^{-1}). Hlavní nevýhodou posuny vlnočtové osy v důsledku mechanické složitosti systémů.

Schéma disperzního NIR spektrometru s pevnou mřížkou



Diodové pole detektoru DA 7200 má 256 bodů, což při rozsahu snímání 950 – 1650 nm umožňuje nominální rozlišení 6 nm. Výše zmíněných 6 nm odpovídá přibližně 50 cm^{-1} (u 1650 nm je to cca 21 cm^{-1}, u 950 nm je to cca 72 cm^{-1}).



FT NIR spectrometry – instrumentation Nicolet

ANTARIS

FT-NIR spektrometry Antaris

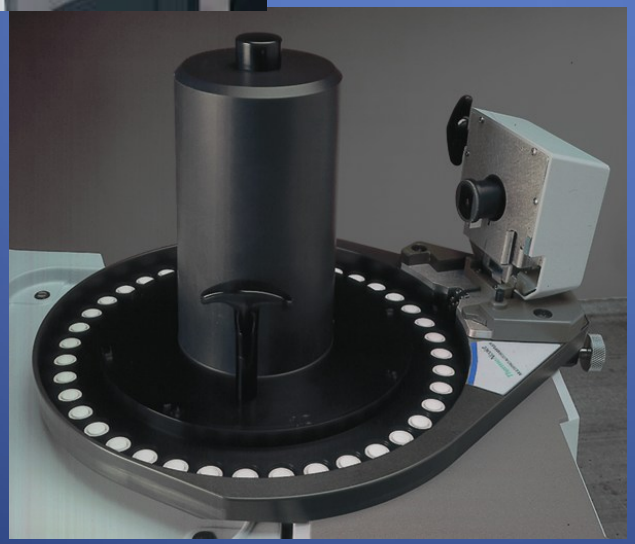
Antaris II ™

Antaris MX ™

Antaris EX ™

Antaris Target ™

Autosampler MultiPro a RS



Autosampler RS

- Příslušenství pro integrační sféru
  - Difuzní reflexe
- Práškové vzorky
- 30-60 pozicí vzorku
- Vyměnitelný karusel
- Automatická detekce chyb

Autosampler MultiPro

- Analyzátor tablet

Sample Cup Spinner

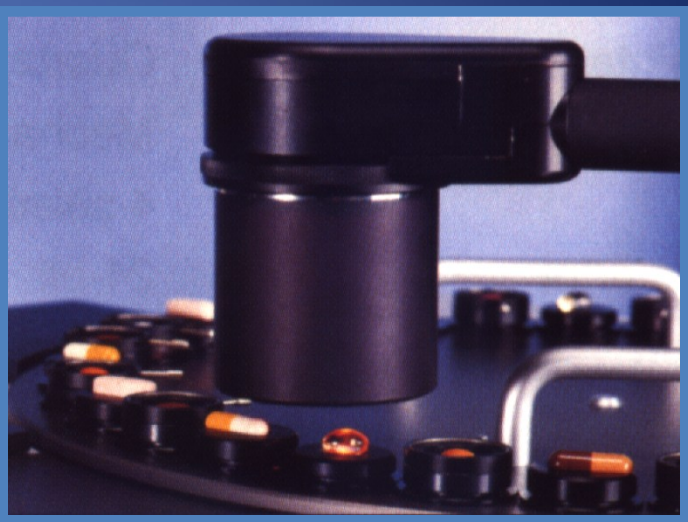
- Měření spekter heterogenních vzorků
  - Vzorky s měnící se distribucí částic
  - Hrubozrnné materiály
  - Granulované vzorky
- Eliminuje potřebu měření několika spekter za stejného vzorku

Sample Cup Spinner

- Vzorek umístěný do vzorkovací nádobky pomalu rotuje nad NIR paprskem
  - Kontinuální měření během rotace vzorku
- Doplňkové zařízení k modulu s integrační sférou
- Difúzně reflexní měření

FT NIR spectrometry – instrumentation Bruker

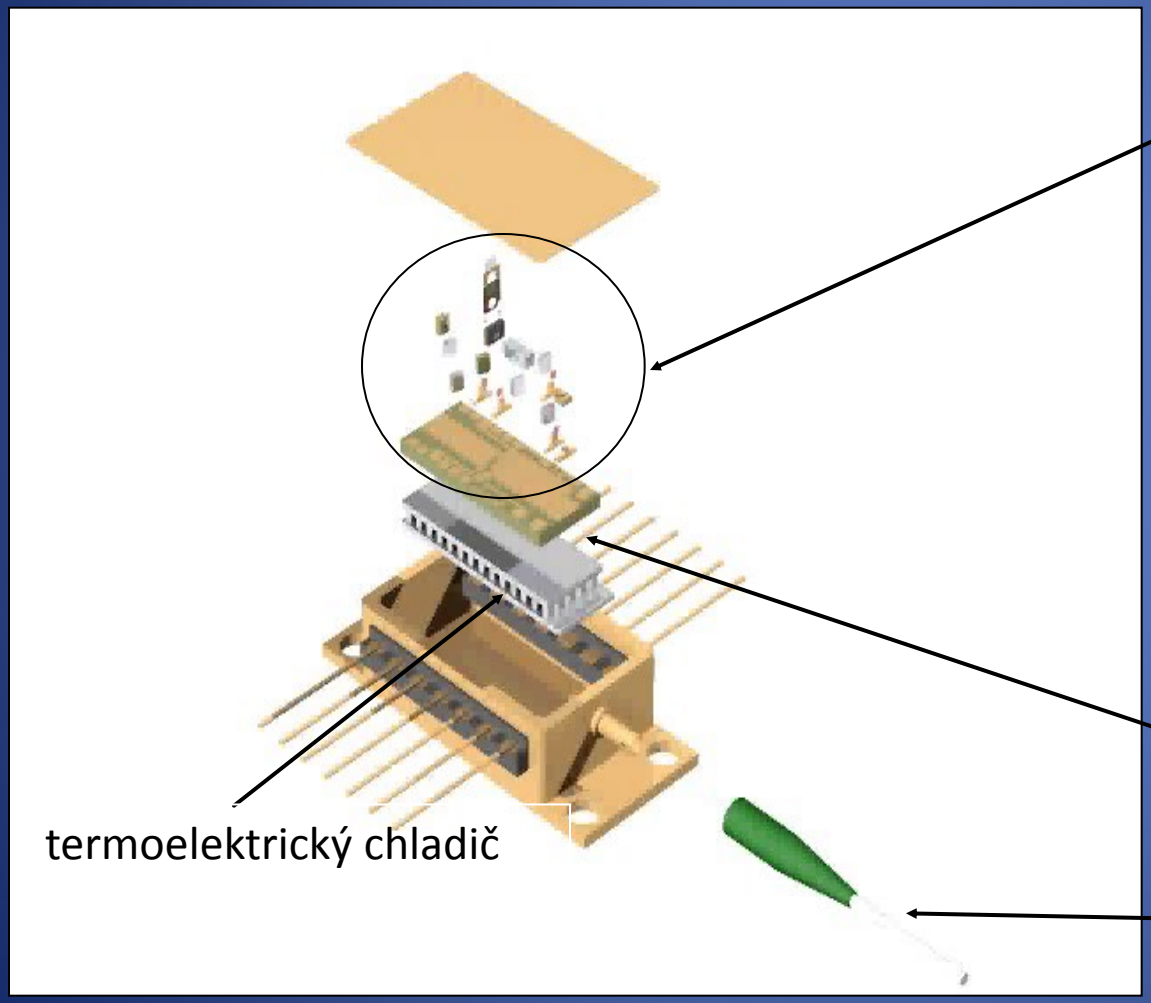
MPA - multi-purpose analyzer



NIR spectrometry – instrumentation

various probes for technologies

Schéma hlavní komponenty NIR spektrometru Antaris Target



zdroj záření,

InGaAs detektor,

Fabry-Perotův interferometr

justovatelná zlatá zrcadla a čočky

optická základna z nitridu hlinitého

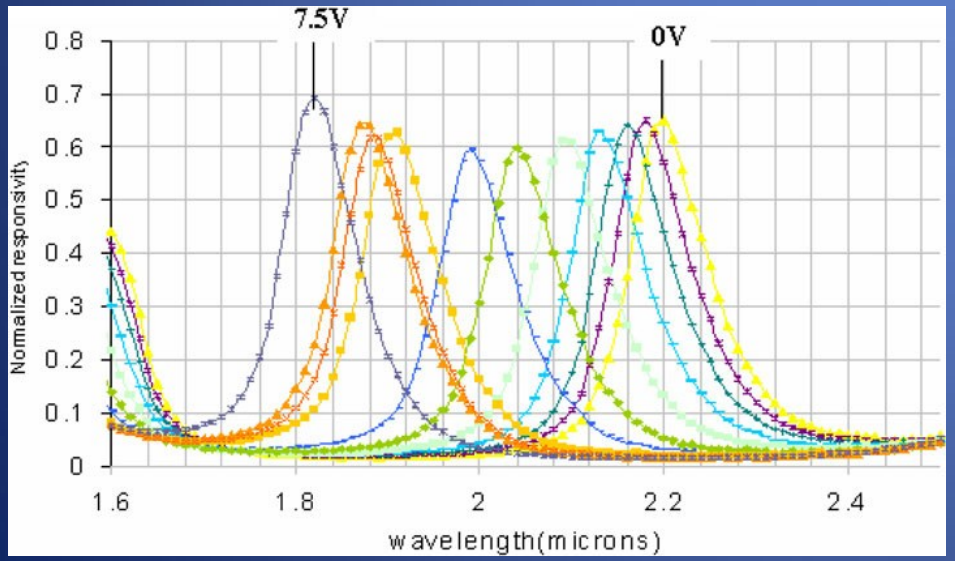
optické vlákno

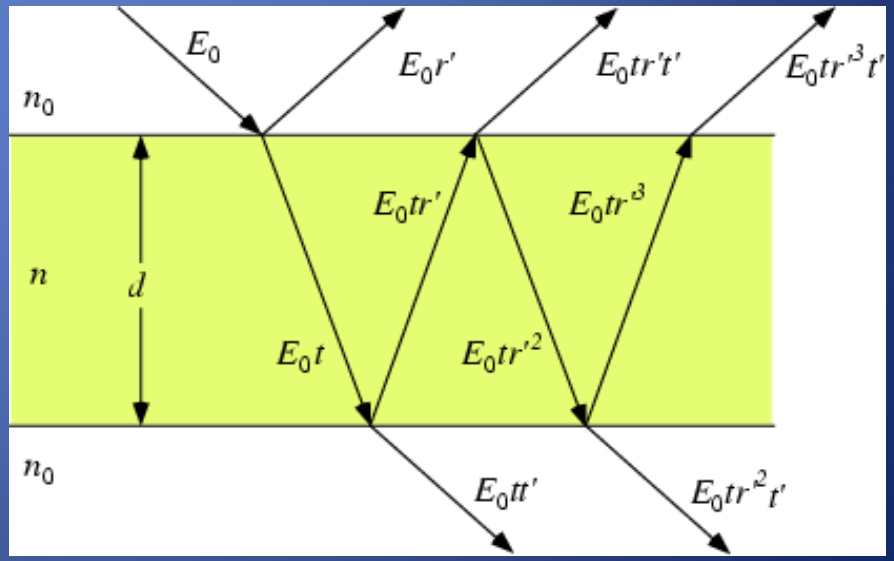
SLED a Fabry Perotův interferometr

• zdrojem je miniaturní polovodičový zdroj záření - SLED (Superluminescent Light-Emitting Diode) – předpokládaná životnost 25 let.

• Fabry Perotův interferometr byl navržený roku 1899. Skládá se ze dvou plochých nebo zakřivených zrcadel od sebe definovaně vzdálených. V případě interferometru ve spektrometru dochází ke změně této vzdálenosti v závislosti na změně napětí.

(The Fabry-Perot filter consists of a pair of vertically-distributed Bragg mirrors)





Instalace Antaris™ Target

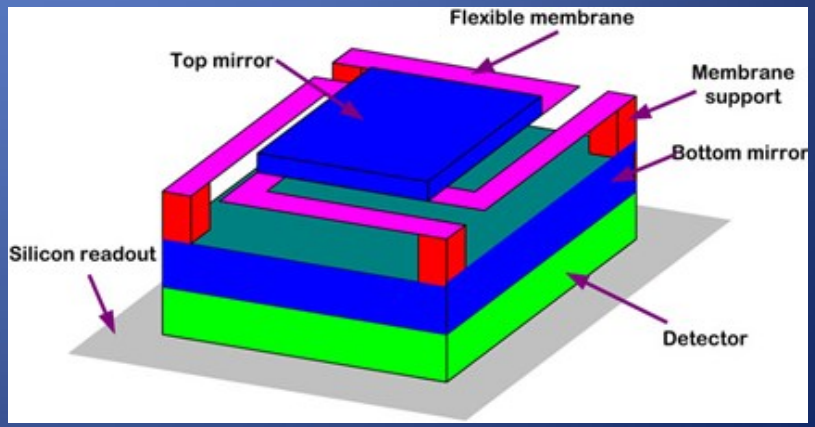
Antaris Target Blend Analyzer

Průmyslový spektrometr **Antaris Target** byl vyvinut pro farmaceutický průmysl.

- On-line kontrola uniformity práškových směsí
- Odstranění ztrát způsobených nedokonalou kontrolou výroby
- Snadná montáž na technologické zařízení
- Analytická kontrola mísení tabletoviny v reálném čase

technologie MEMS (Micro- Electro-Mechanical Systems)

Umožňuje on-line měření spekter v blízké infračervené oblasti v rozsahu 7400 – 5550 cm^{-1} (1350 – 1800 nm)
s rozlišením 3,5 cm^{-1}



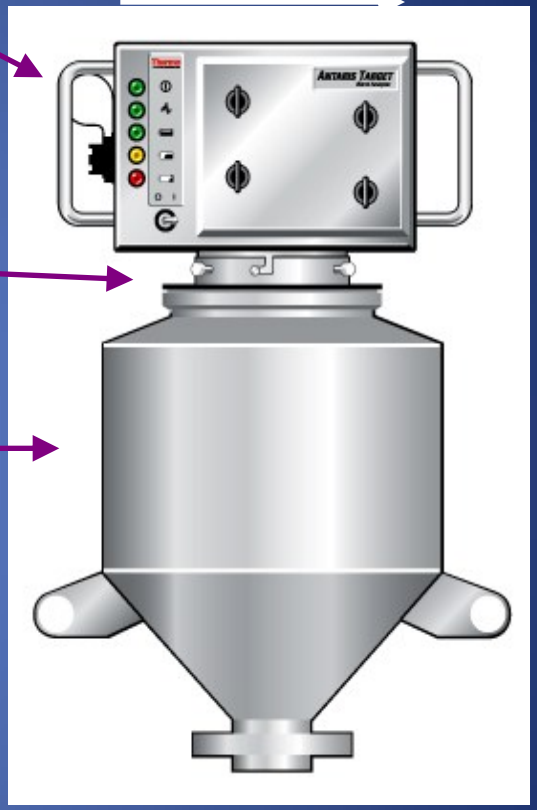
Instalace Antaris™ Target

Antaris Target Blend Analyzer

Lid Modification Kit

Existující homogenizátor

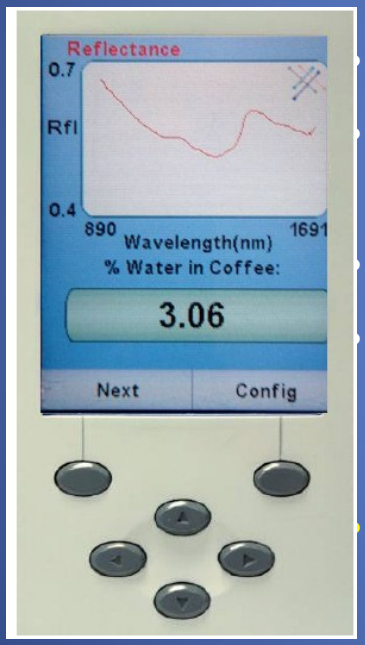
~25 cm



microPHAZIR Rx

Handheld Pharmaceutical Material Analysis

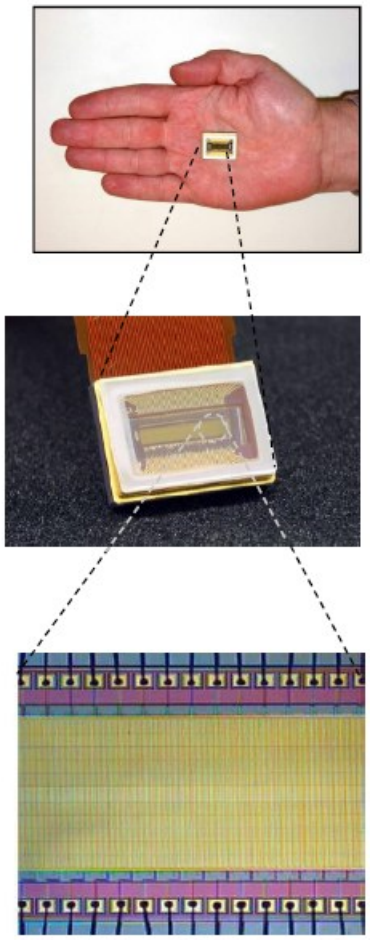
The microPHAZIRTM Rx is the world's first handheld analysis system designed for rapid on-site pharmaceutical material identification and analysis.



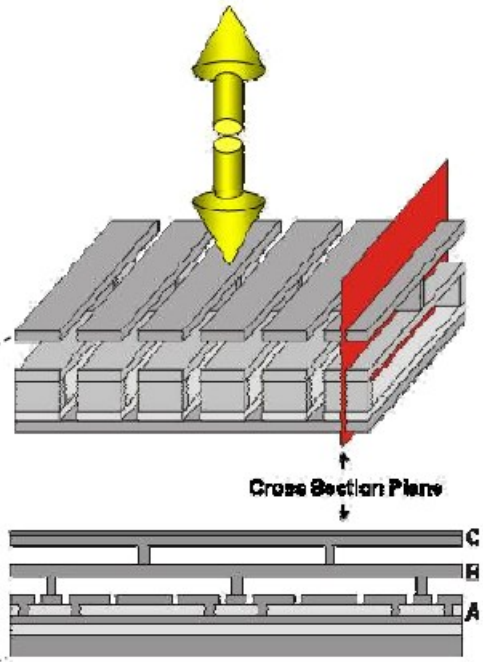
- Diffuse reflectance, optional adapters for liquids
- Tungsten light bulb, safe for operators and sample integrity
- Measurement time – several seconds
- 1600 – 2400 nm (cca 6250 – 4160 cm^{-1}) including the complete near-infrared combination region and first overtone region) – wolfram bulb – light source
- **Resolution** – 8 nm per **pixel** / 12 nm optical

microPHAZIR Rx

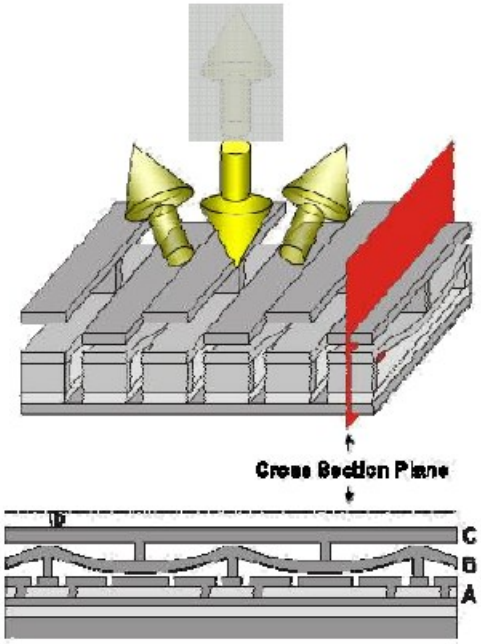
Miniature Spectrometer-on-chip spectrometers



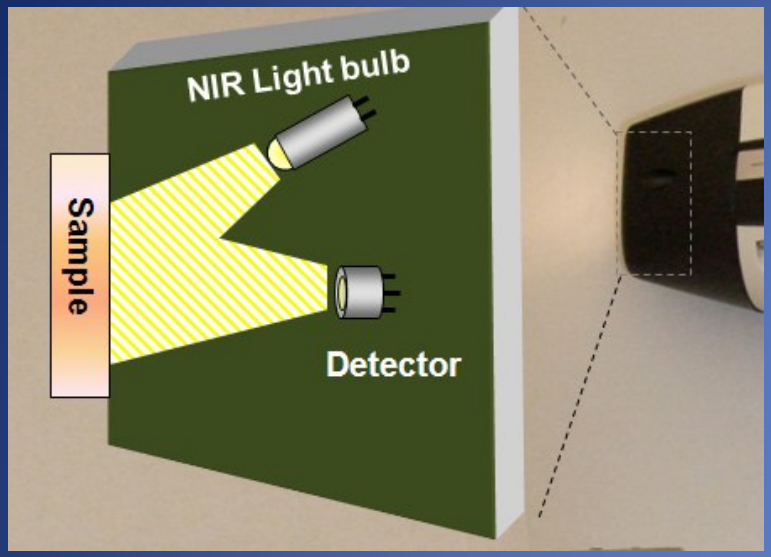
Unactuated: incident light reflected



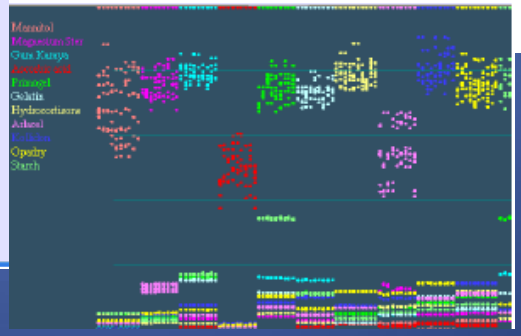
Actuated: programmable filtering at 1/4- wavelength displacement

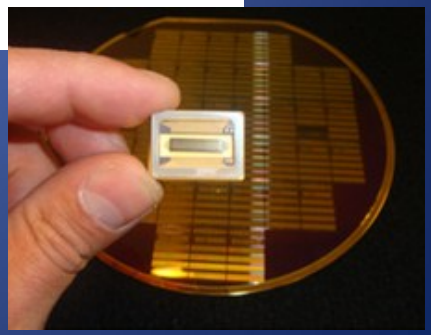


microPHAZIR Rx

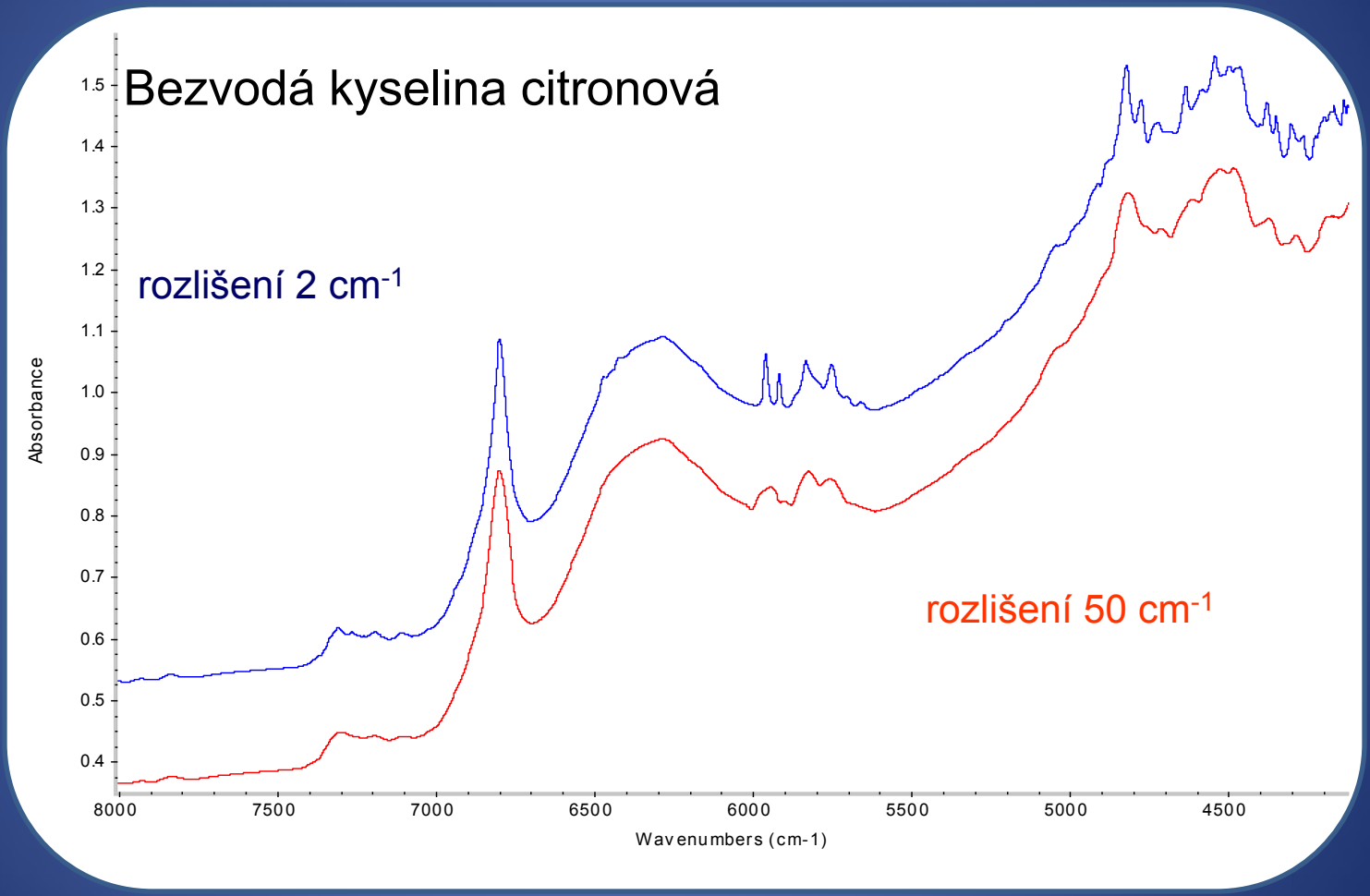


- Handheld NIR for Pharmaceutical RMID
- Used in 17 of the top 22 largest pharmaceutical manufacturing companies
- Deployed in over 25 countries
- Applications for at-line analysis
  - Blending
  - Drying
  - Coating
  - Tableting
  - Dispensing





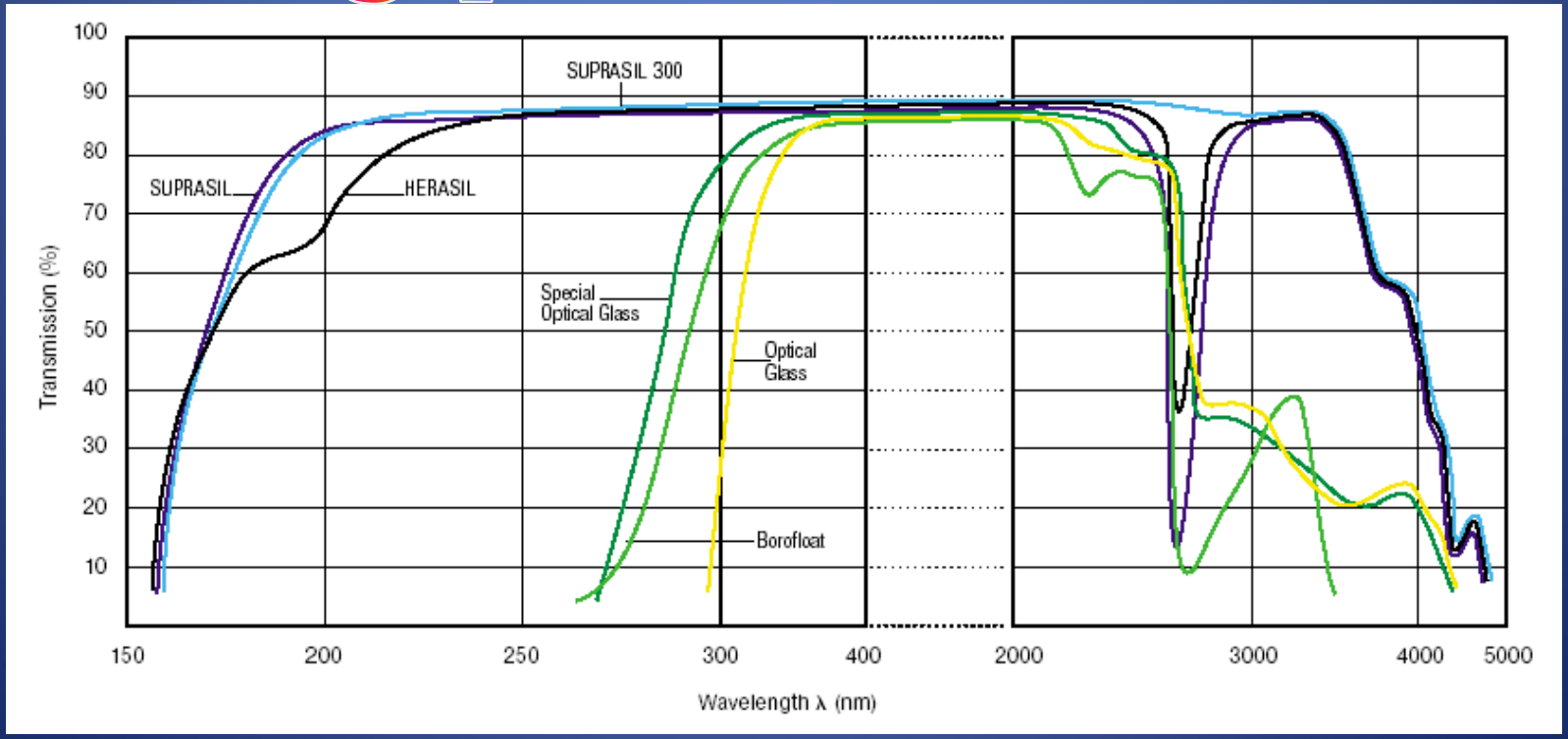
Porovnání spektra - disperzní a FT-NIR spektrometr



NIR spectrometry – transmission measurement

- cells - various types of glass
  - INFRASIL, SUPRASIL (critical part ~ 4000 cm^{-1})

UV VIS - NIR MIR

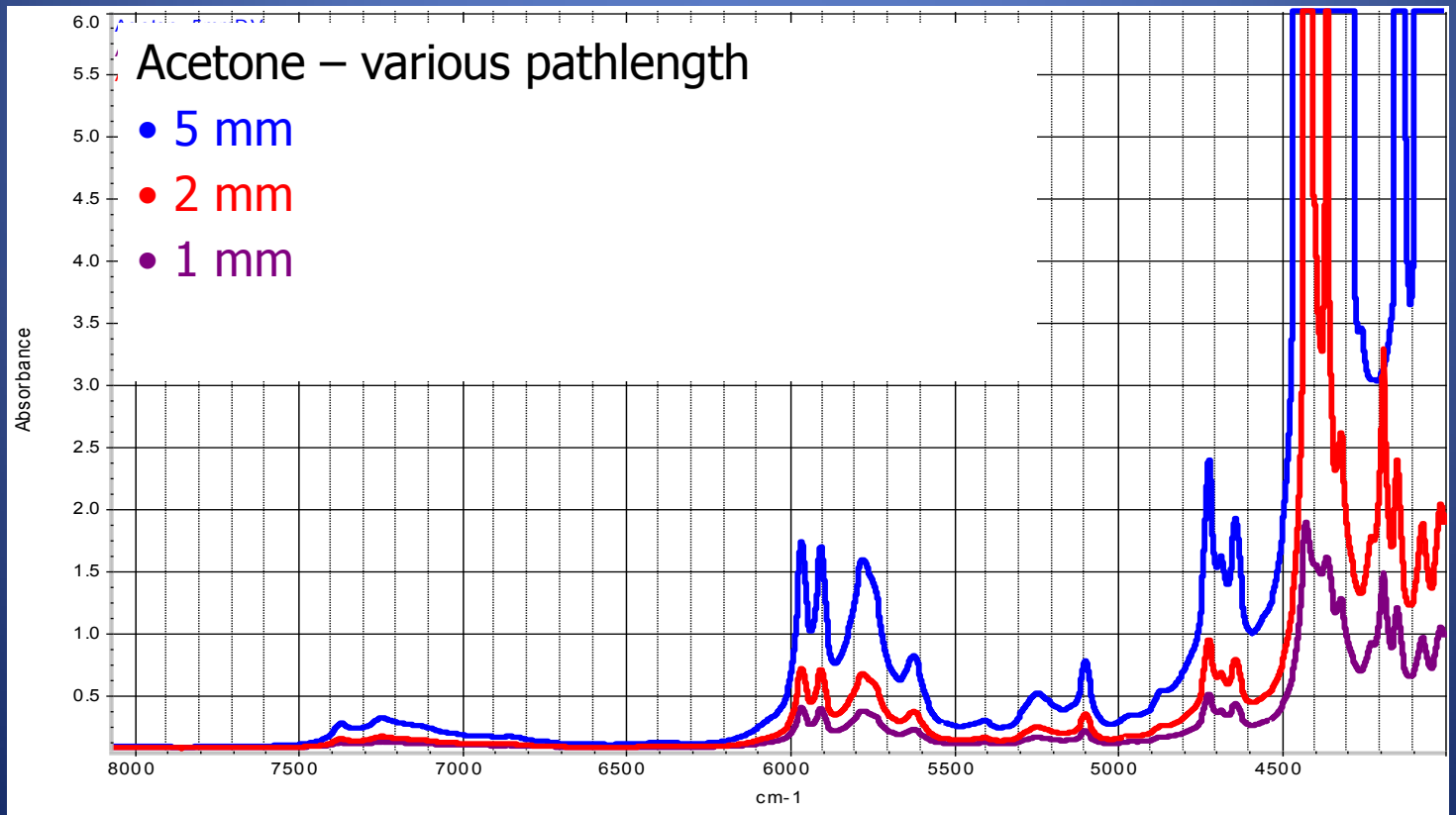


NIR spectrometry – transmission measurement

- cells - various types of glass
  - – pathlength 1 – 5 (10) mm
    - effect of solvent absorption
    - effect of selected subregion (combination bands, order of overtones)
    - effect of concentrations of analytes studied
- fiber optics probes
  - – fixed pathlength or adjustable pathlength

NIR spectrometry – transmission measurement

- cells – both polar and non-polar samples
  - organic liquids (oils, petroleum)
  - aqueous solutions (drinks – content of sugars, ethanol)



NIR spectrometry – transmission measurement

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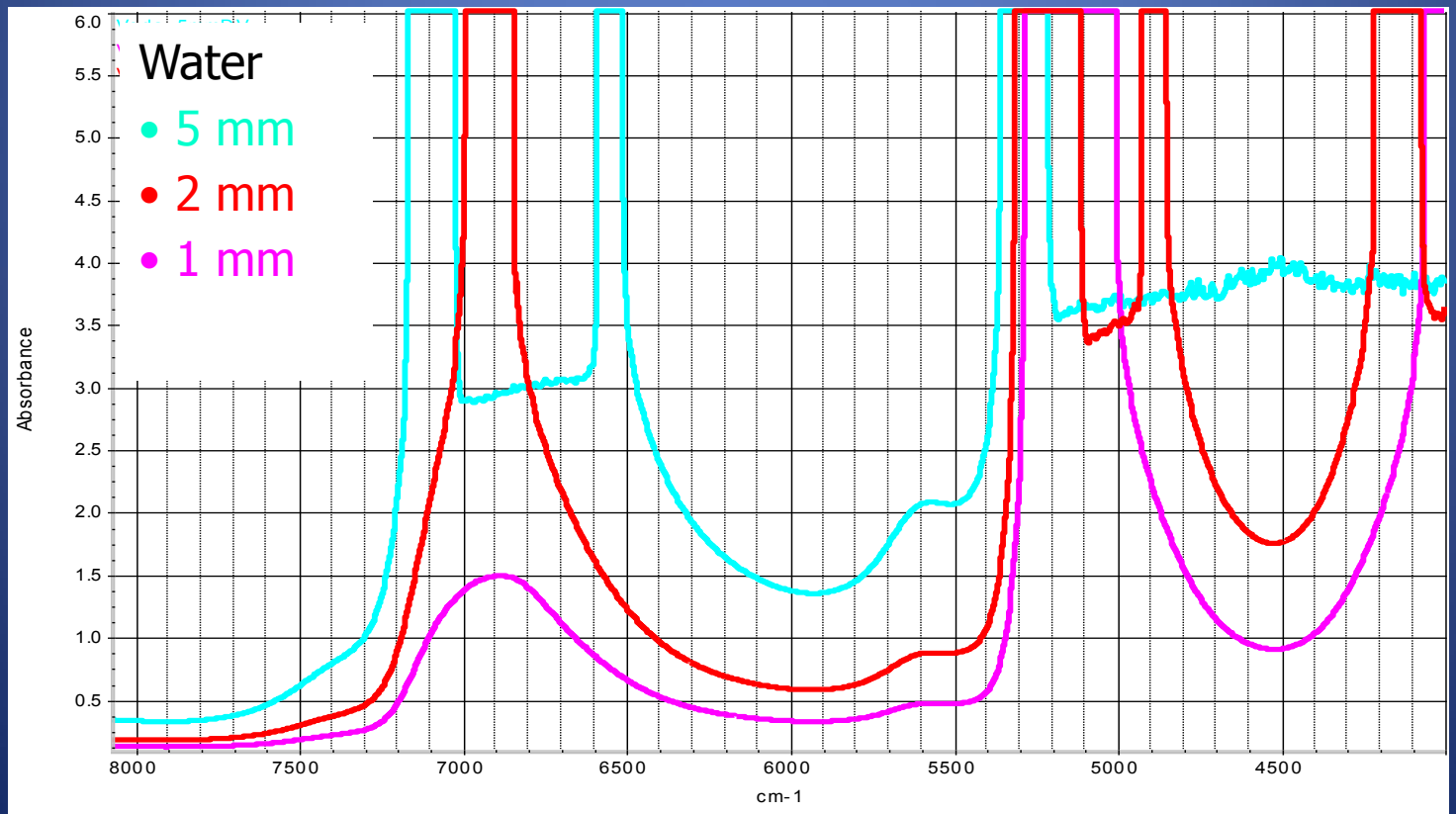
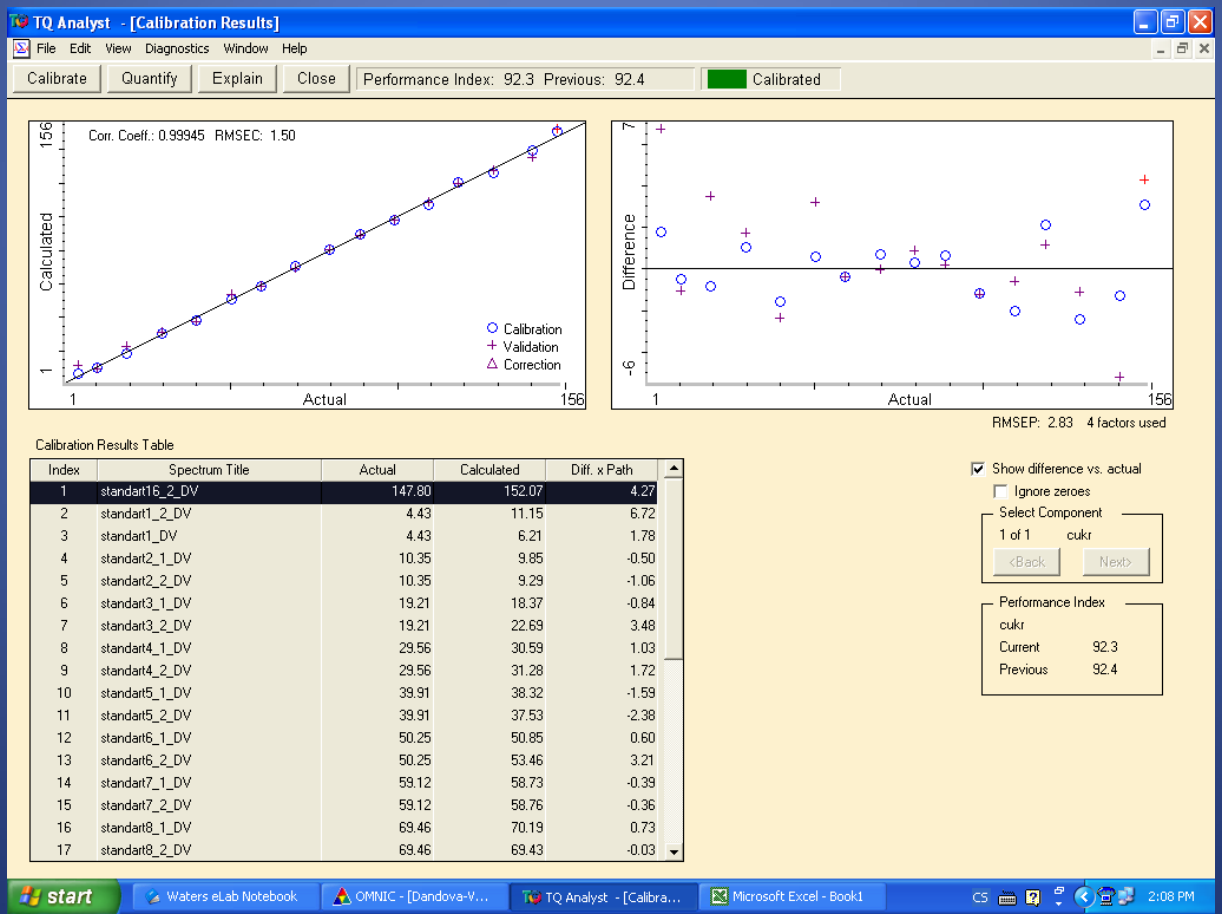


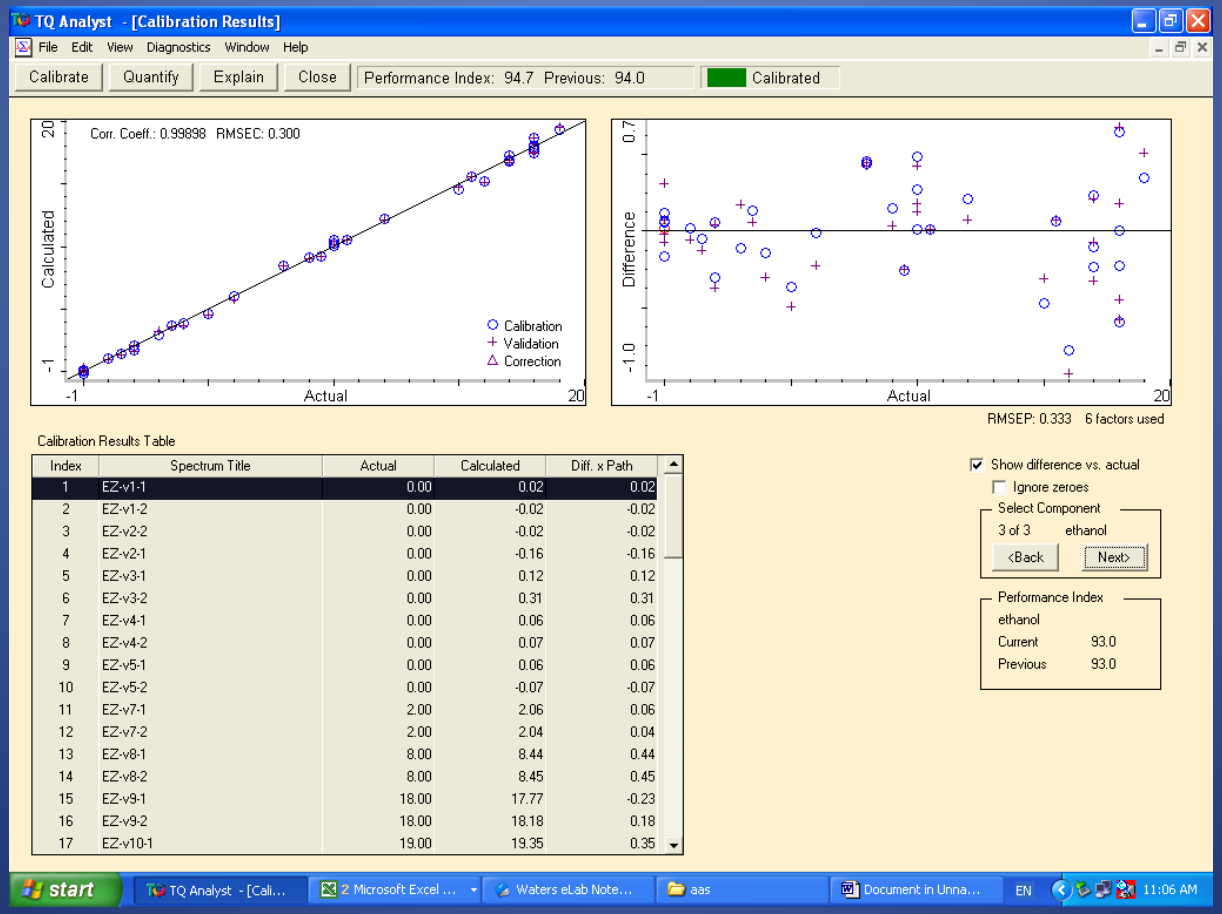
NIR spectrometry – transmission measurement

- aqueous solutions
  - calibration model for sugar content in soft drinks



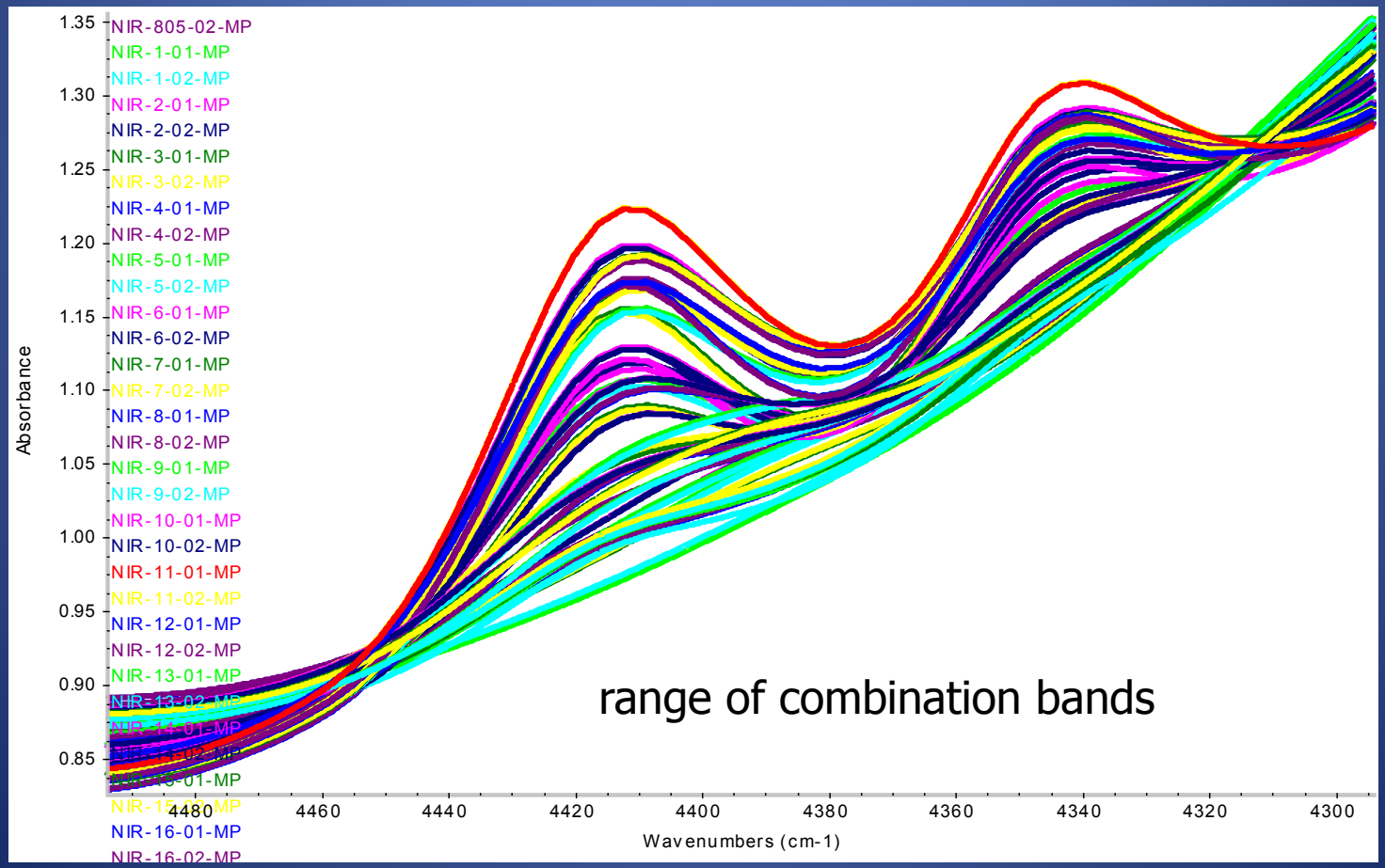
NIR spectrometry – transmission measurement

- aqueous solutions
  - calibration model for alcoholic drinks



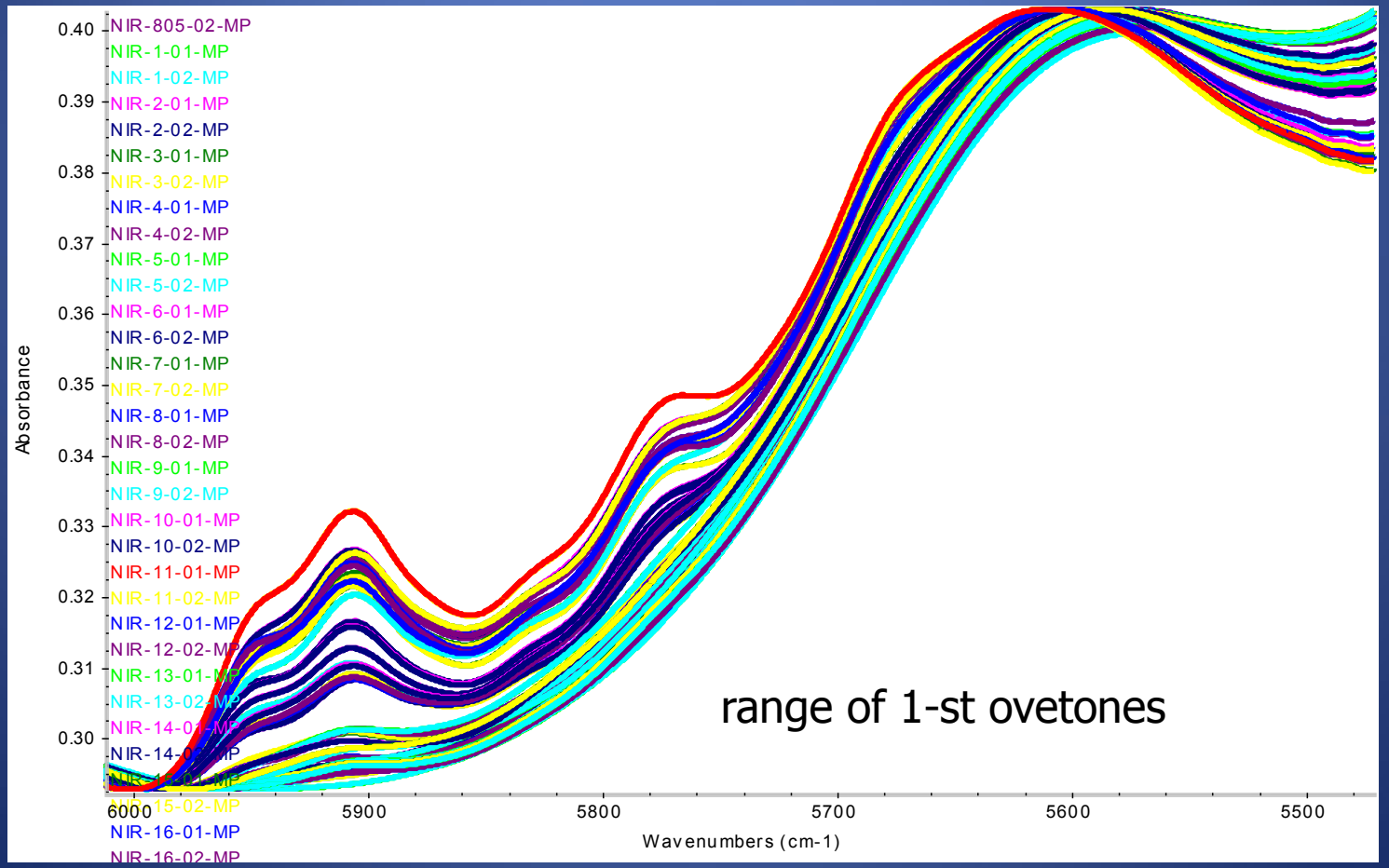
NIR spectrometry – transmission measurement

- aqueous solutions
  - calibration for alcoholic drinks - spectra



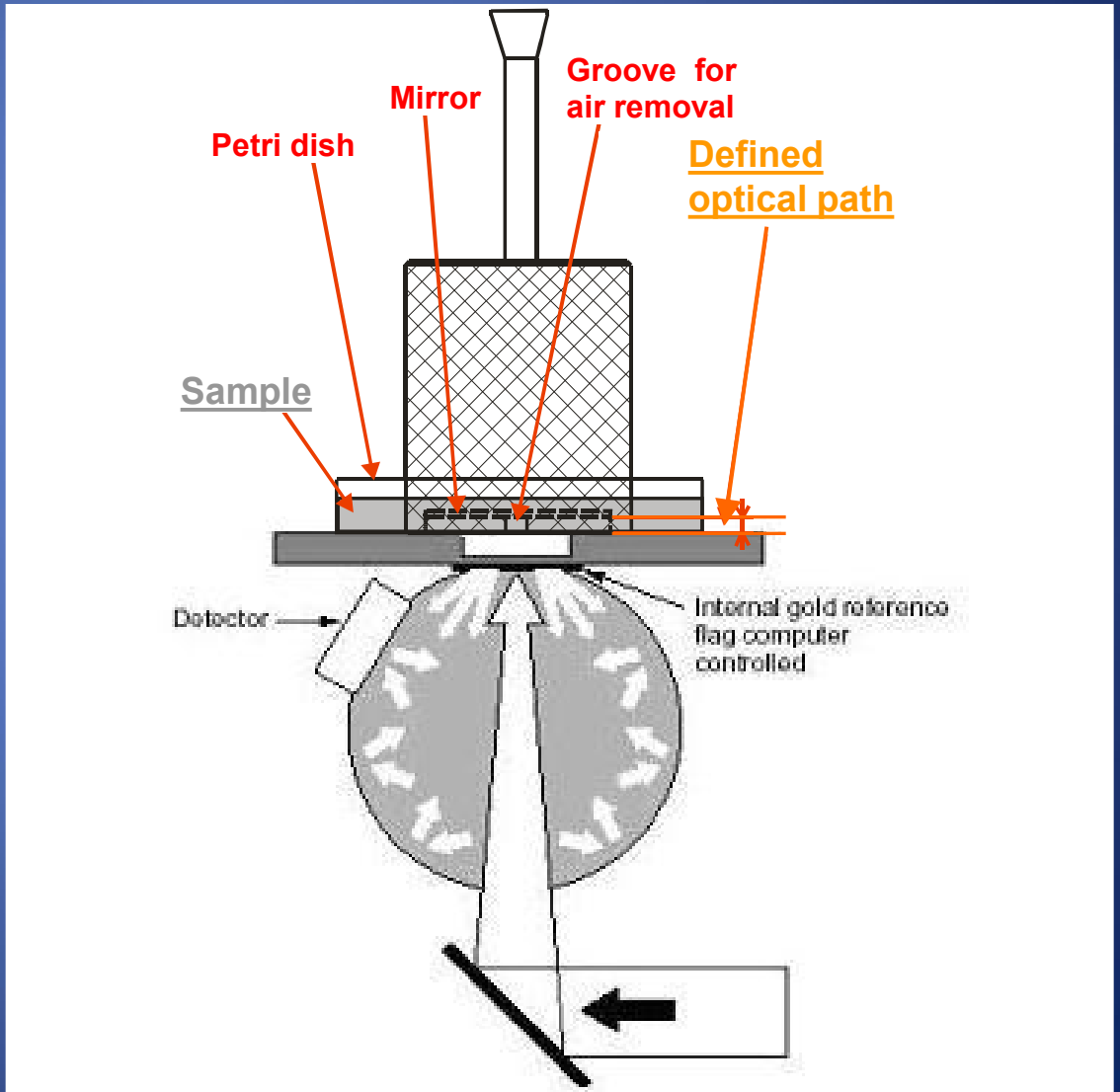
NIR spectrometry – transmission measurement

- aqueous solutions
  - calibration for alcoholic drinks - spectra



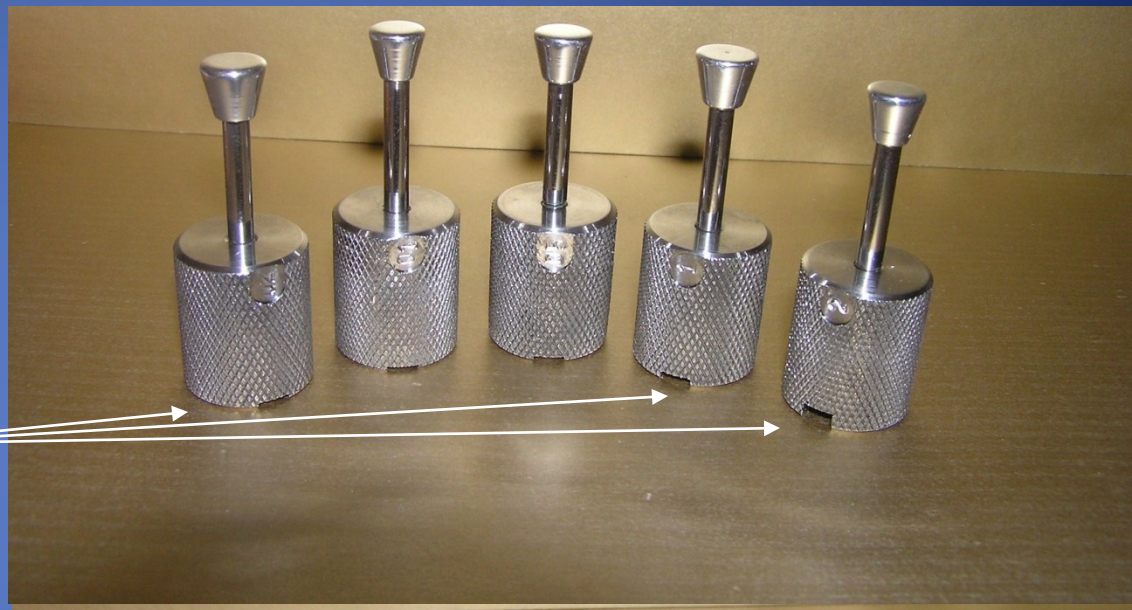
NIR spectrometry – transflectance measurement

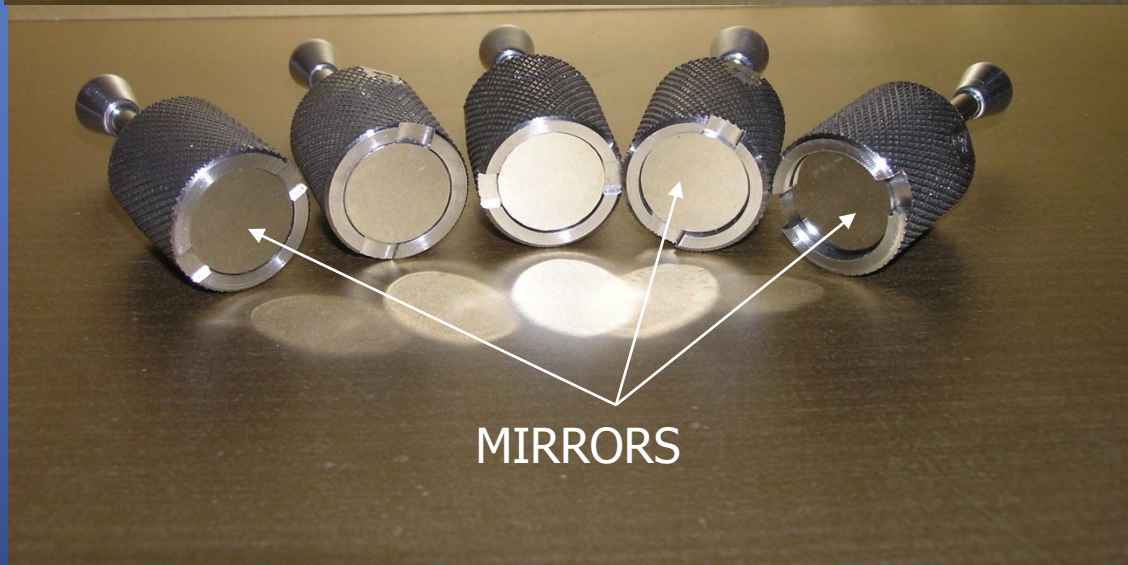
- transflectance cells
  - defined pathlength
  - transmission/ reflection
  - viscous liquids, pastes



NIR spectrometry – transflectance measurement

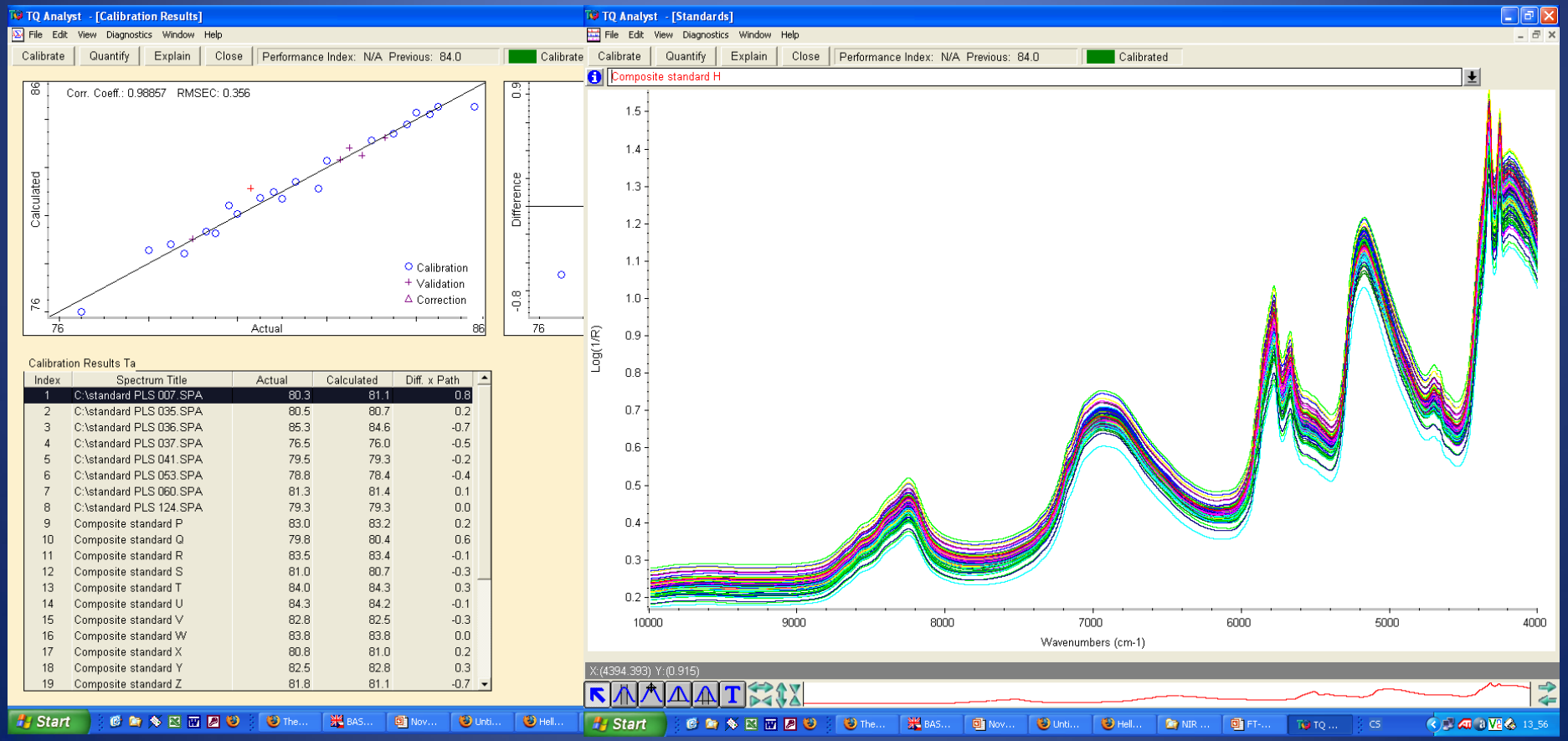
- transflectance cells
  - various pathlengths
  - transmission/ reflection
  - viscous liquids, pastes



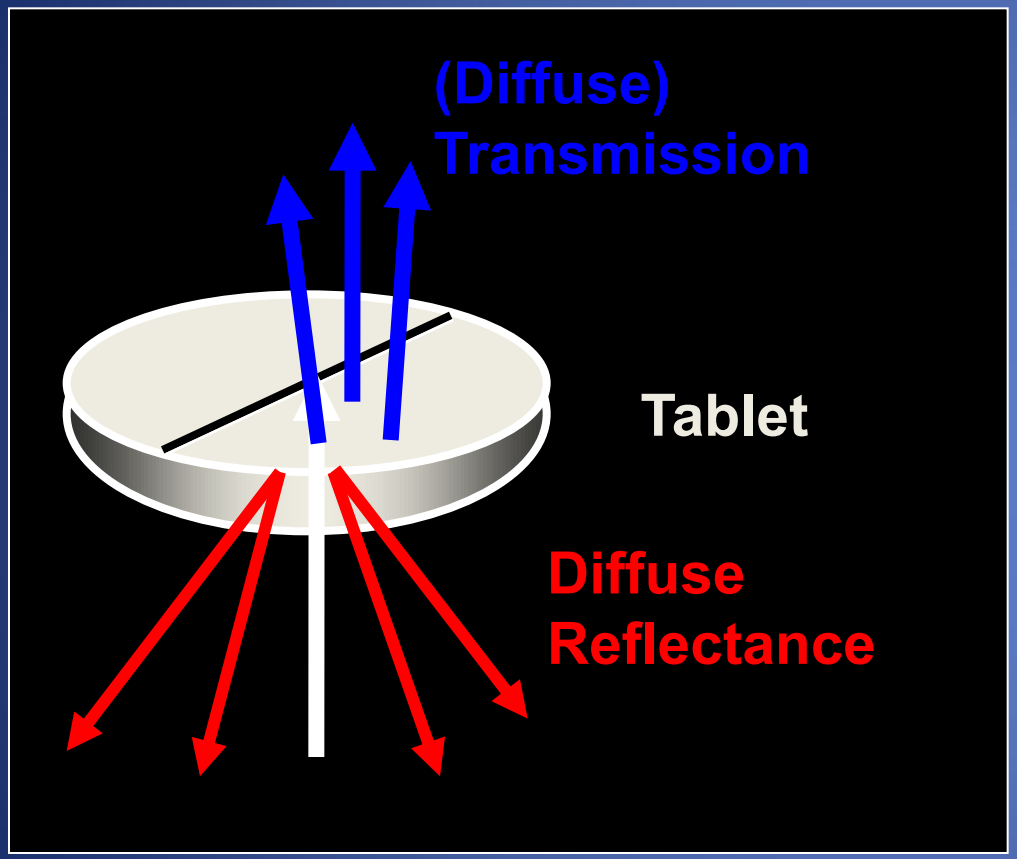


NIR spectrometry – transflectance measurement

- transflectance cells
  - fat in the butter

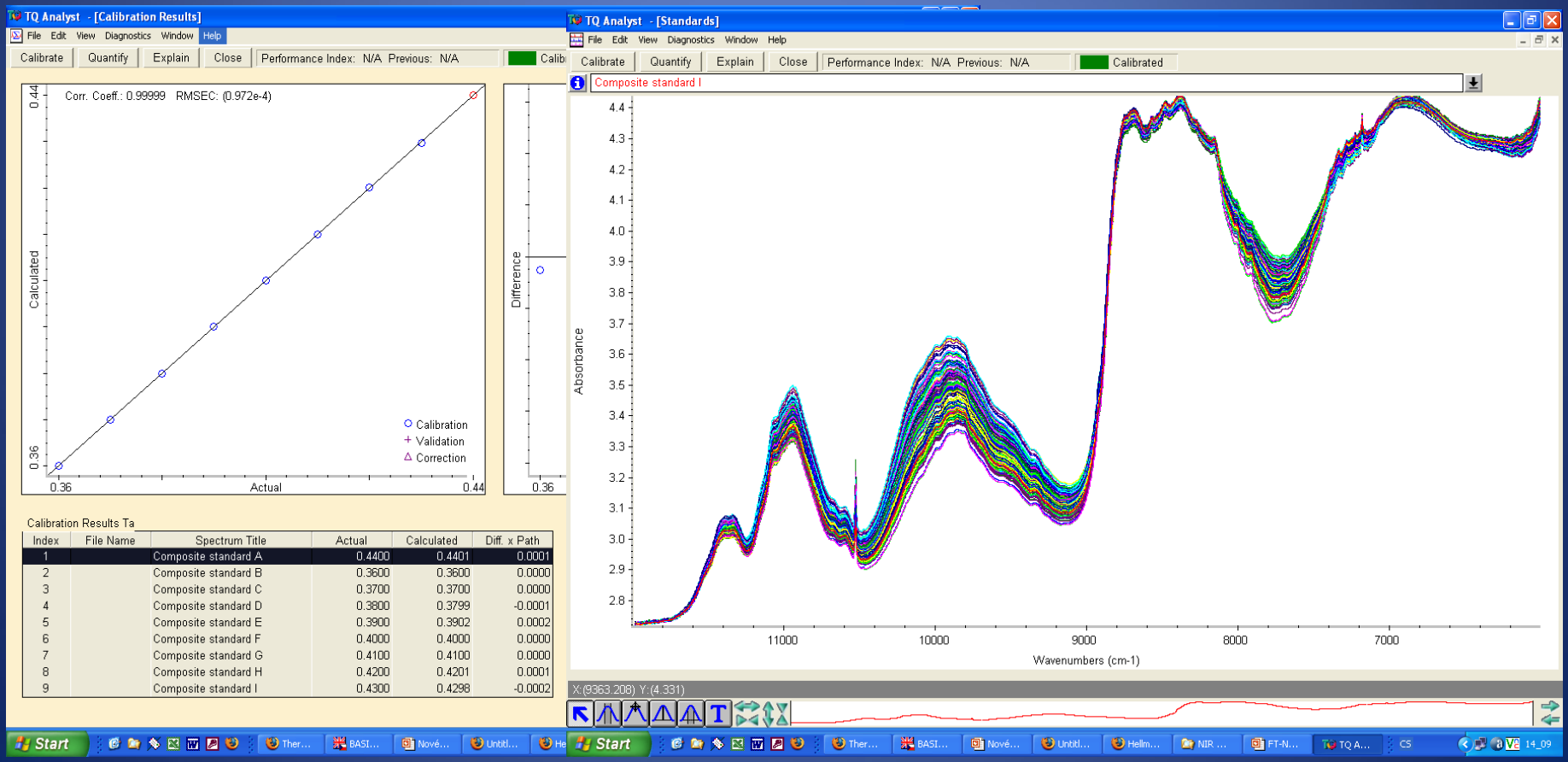


NIR spectrometry –
TABLET Analyzer



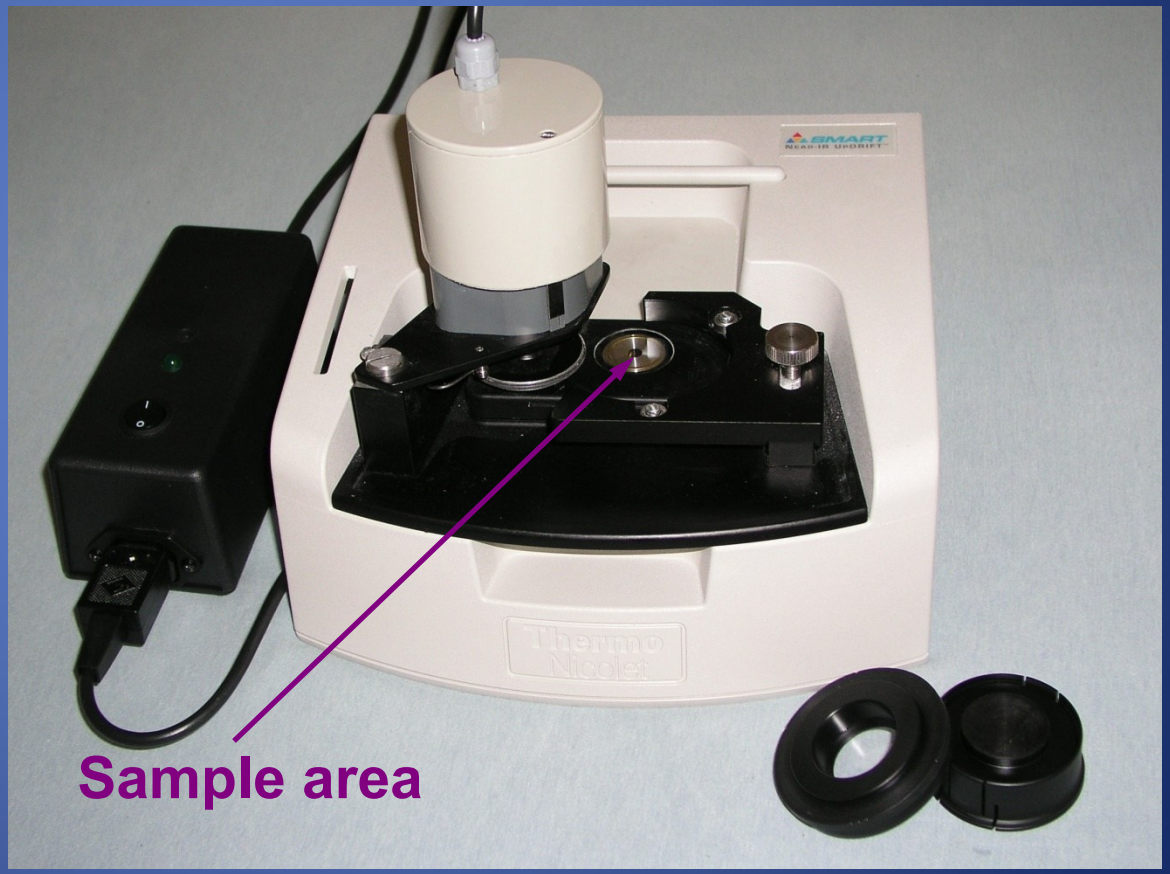
NIR spectrometry – TABLET Analyzer

- tablet analyzer
  - – determination of active substance in a capsule



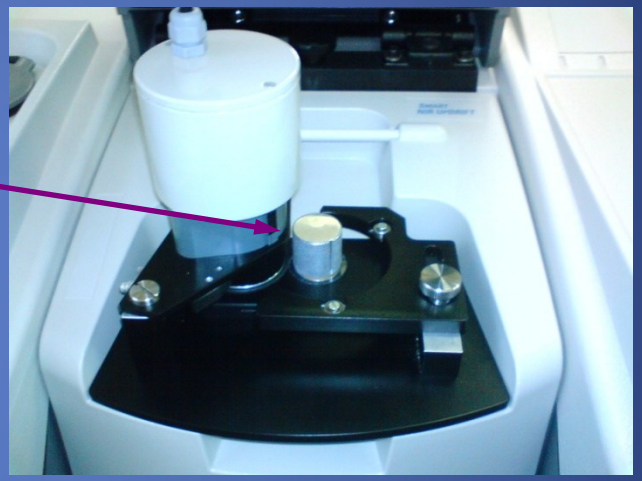
NIR spectrometry – diffuse reflectance measurement

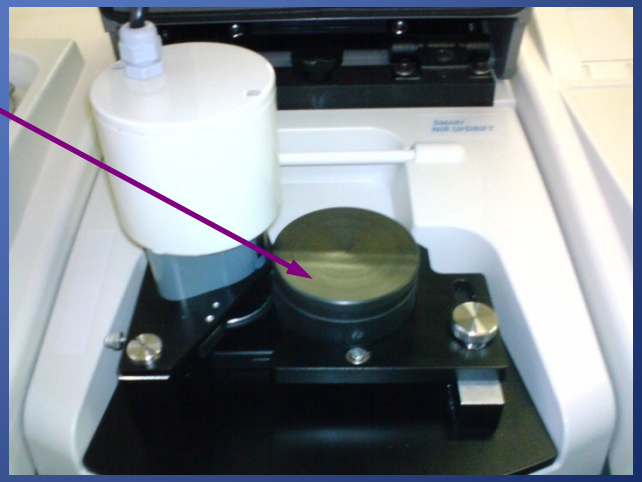
- UpDRIFT
- absorption and reflections on irregular particles
  - reflected radiation collected



NIR spectrometry – diffuse reflectance measurement

- UpDRIFT
  - background measurement with Spectralon (ceramics)
  - direct measurement of pellets, powders …
  - measurement in rotational cell (glass bottom) – powders, granular materials, pulps …



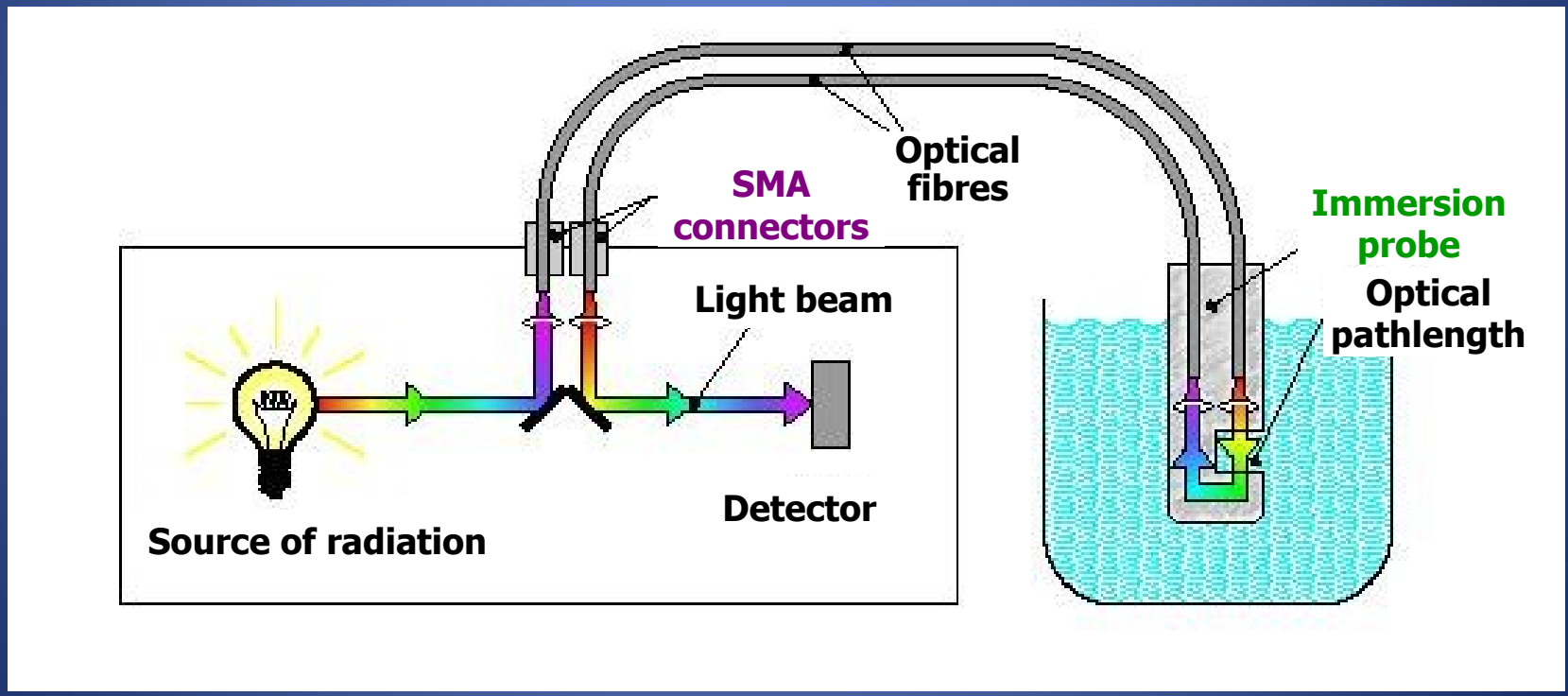


NIR spectrometry – fibre optics probes

- remote sensing

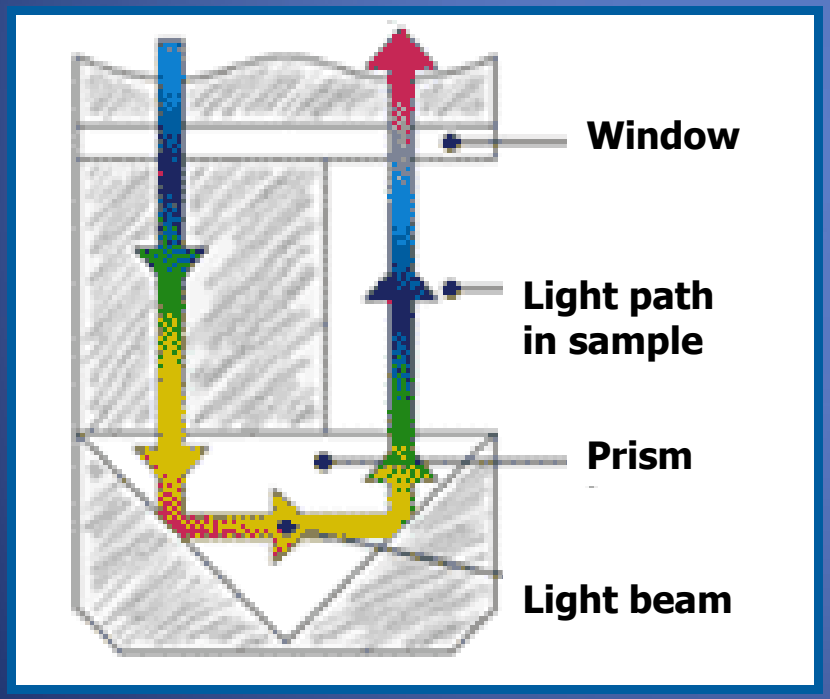
NIR spectrometry – fibre optics probes

- remote
  sensing



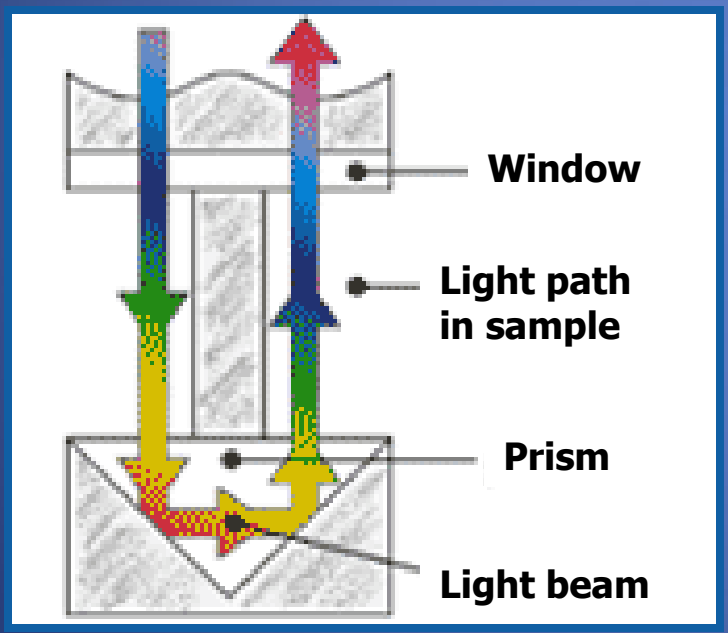
NIR spectrometry – fibre optics probes

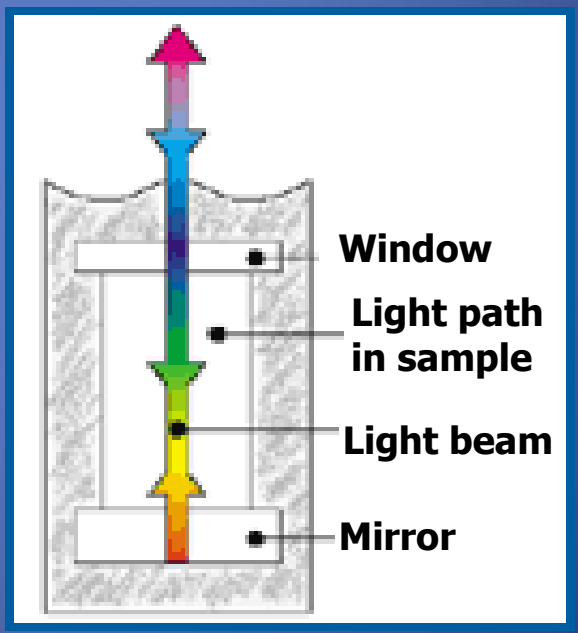
- IMMERSION PROBES
  – standard type



NIR spectrometry – fibre optics probes

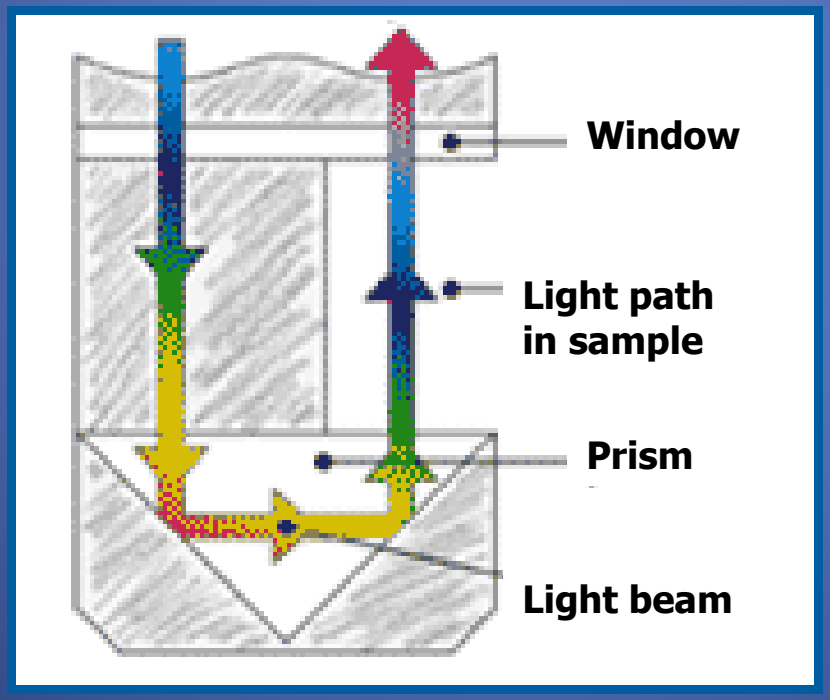
- IMMERSION PROBES
  - types for small sampling volumes





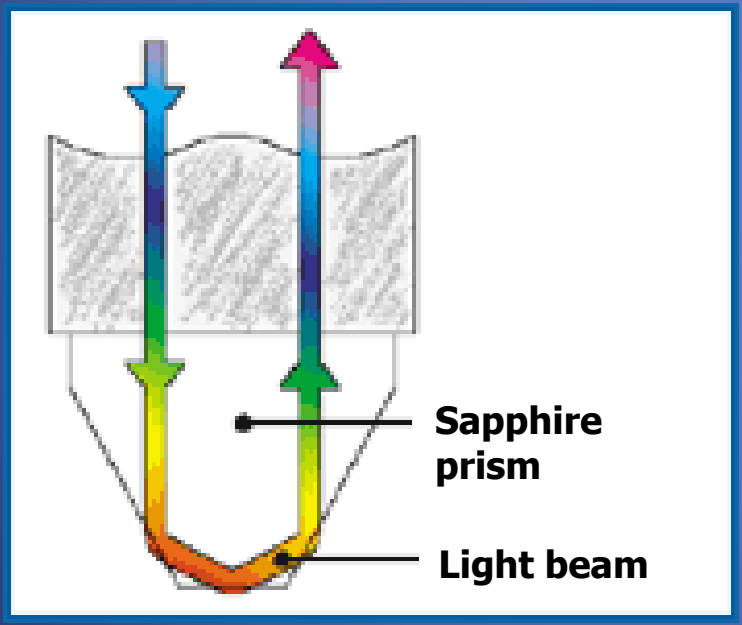
NIR spectrometry – fibre optics probes

- IMMERSION PROBES
  - types for process analysis



NIR spectrometry – fibre optics probes

- IMMERSION PROBES
  - ATR probe



NIR spectrometry – fibre optics probes

- Multiplexer System

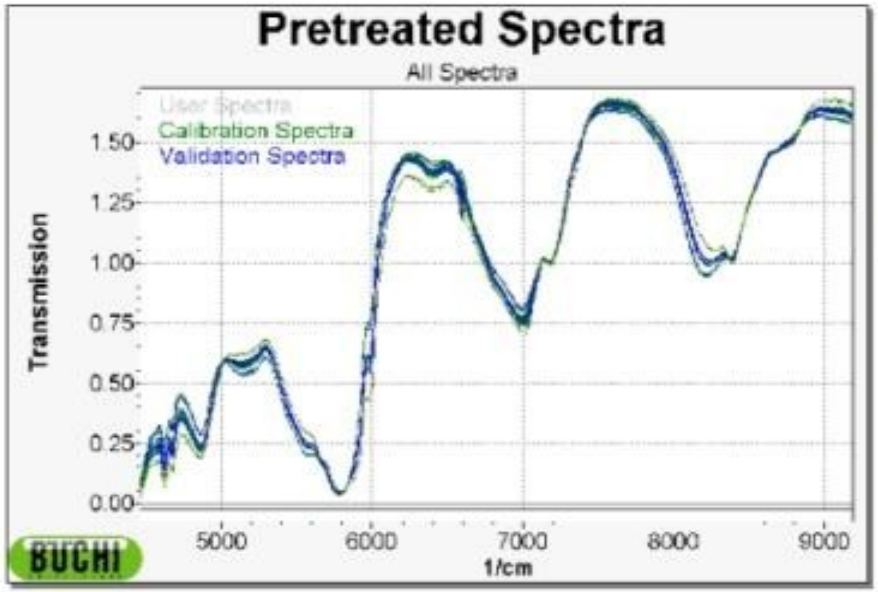
NIR spectrometry – some practical applications

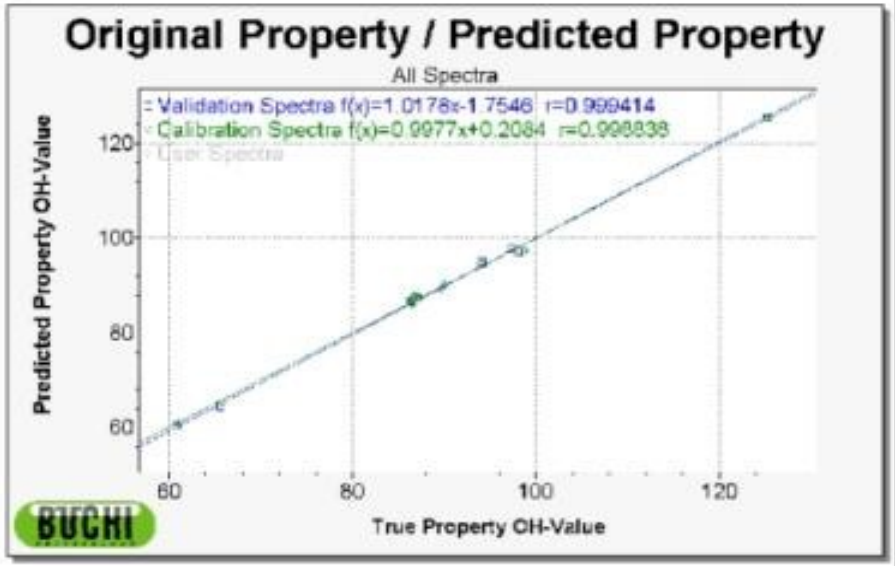
- ANALYSIS OF FOODS
  - MILK, CHEESES, SOFTDRINKS, WINES etc.
- ANALYSIS OF MEDICAMENTS
  - active substances in tablets, plant extracts etc.
- ANALYSIS OF POLYMERS
  - quality control of products, additives etc.
- ANALYSIS OF PETROCHEMICAL PRODUCTS
  - content of aromates, octane number etc.

NIR spectrometry – practical examples

Determination of the OH value of Petrochemicals

Task:
Determination of the OH value in petrochemical products.





Result
Application works with SEP of 0.79

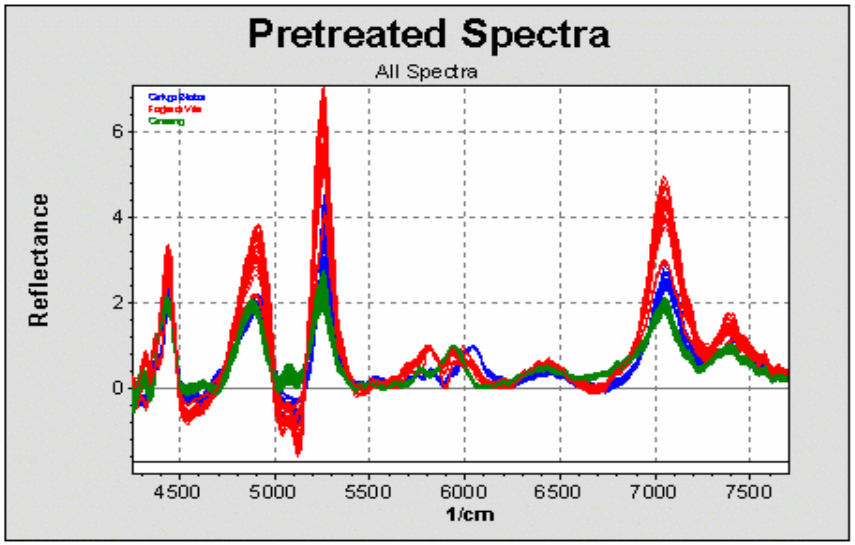
Measurement Technique
Transmittance: GC vials in the kuvette channel, 3 Scans.

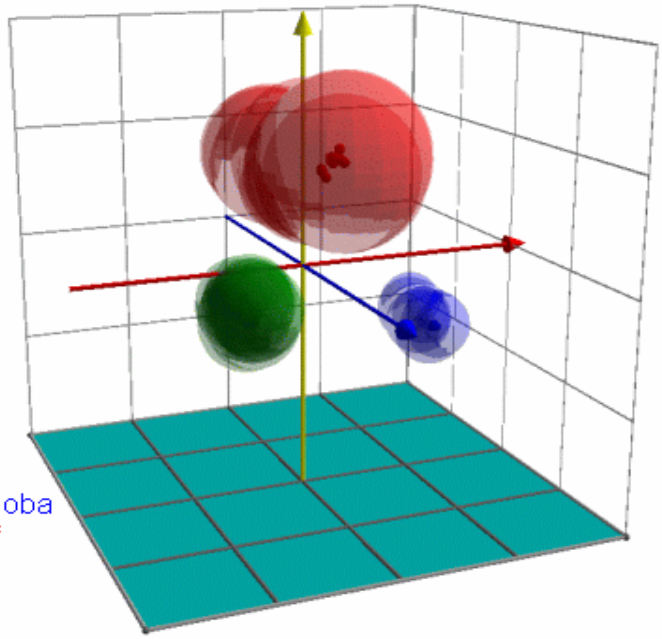
NIR spectrometry – practical examples

Raw Material Testing: Plant Extracts

NIRFlex N-400

Task
Plant Extracts are used as ingredients in natural care products. For QC purposes it is necessary to identify the incoming dried plant extracts of Gingko Biloba, Ginseng and Wine Leaf.
One of the expected difficulties is to identify products from different harvests as one property.





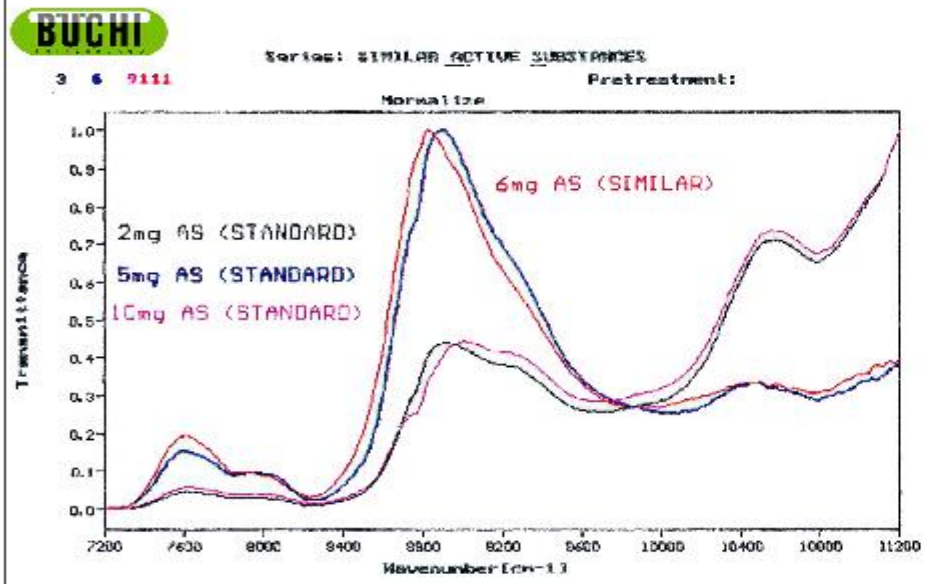
Result
Reliable identification of plant extracts possible. Even the products coming from a broad variety of different harvests and regions can be projected into one cluster that is well distinguished from the other products. Therefore NIR can be used to perform a quick QC of Plant Extracts in the warehouse.

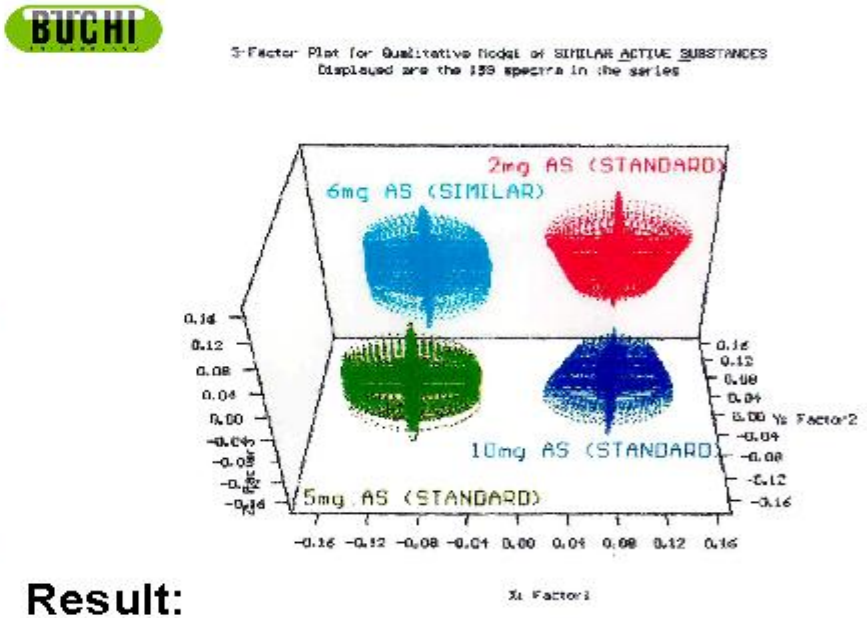
Measuring principle
Diffuse Reflectance, 6 Scans

NIR spectrometry – practical examples

Tablets: active substance — NIRTAB

Task:
Distinction of tablets with different contents of active substance.





Result:
The distinction is possible.

Measuring principle:
Diffuse transmission (20 scans).