



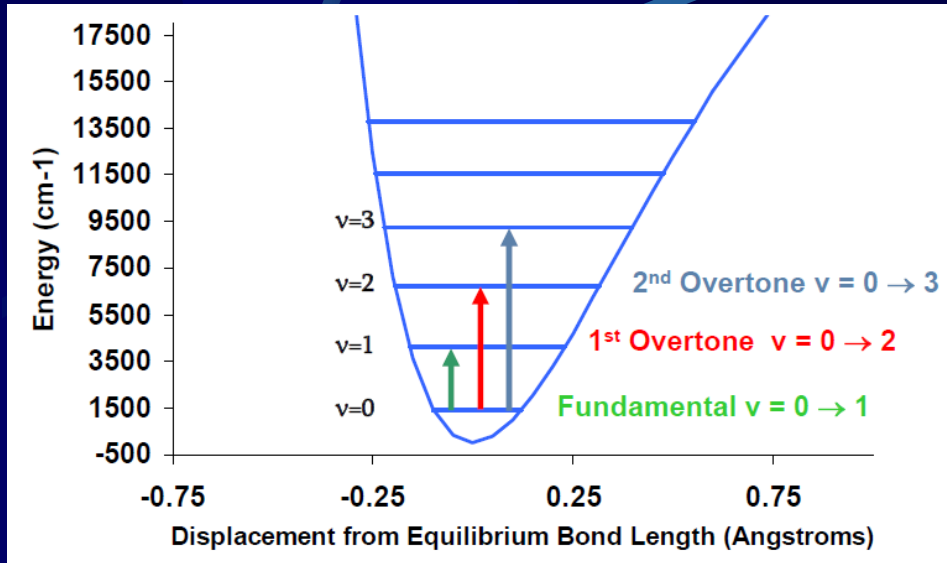
UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE



NIR spectrometry

Pavel Matějka

NIR – overtones and combinations

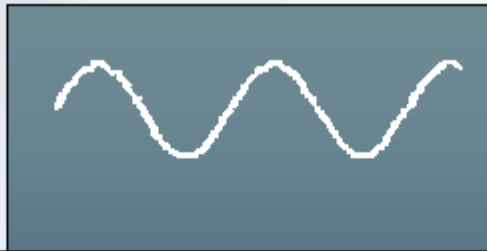


❖ **Combination** – sum of two fundamental transitions

- Str CH + Def CH
- $2960 + 1460 = 4420$ cm⁻¹

- Normal mode vibration (MIR)

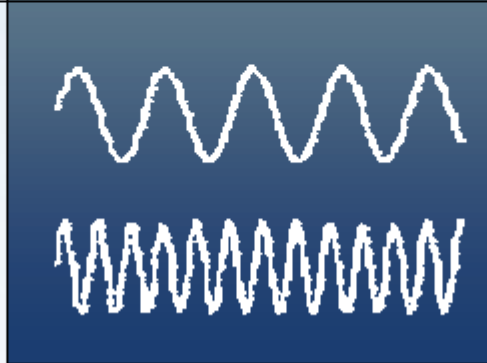
MIR



- High degree of excitation

- Combination and overtones (NIR)

NIR



- Low degree of excitation

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

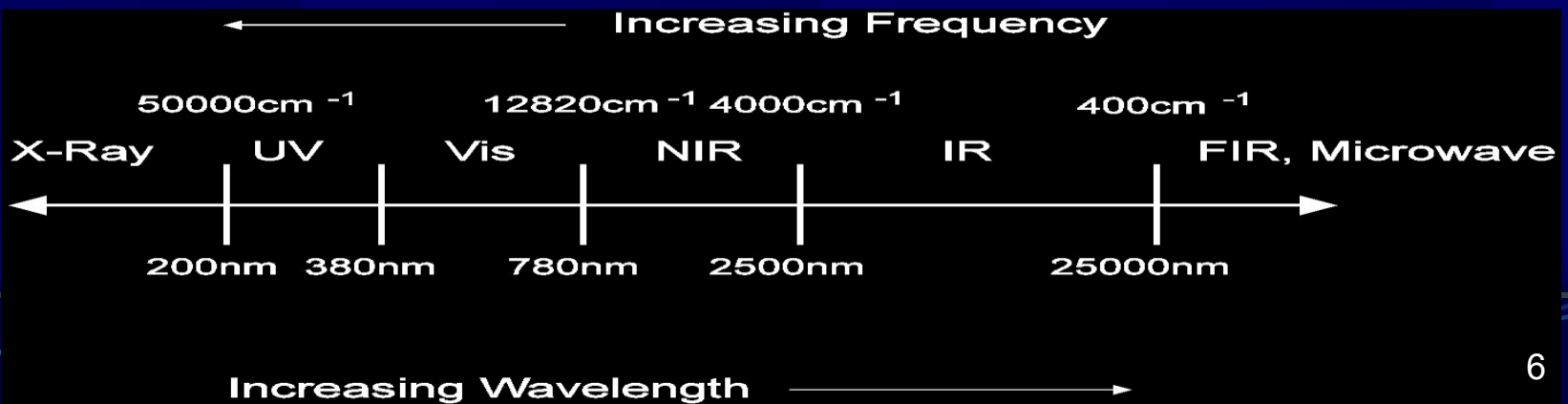
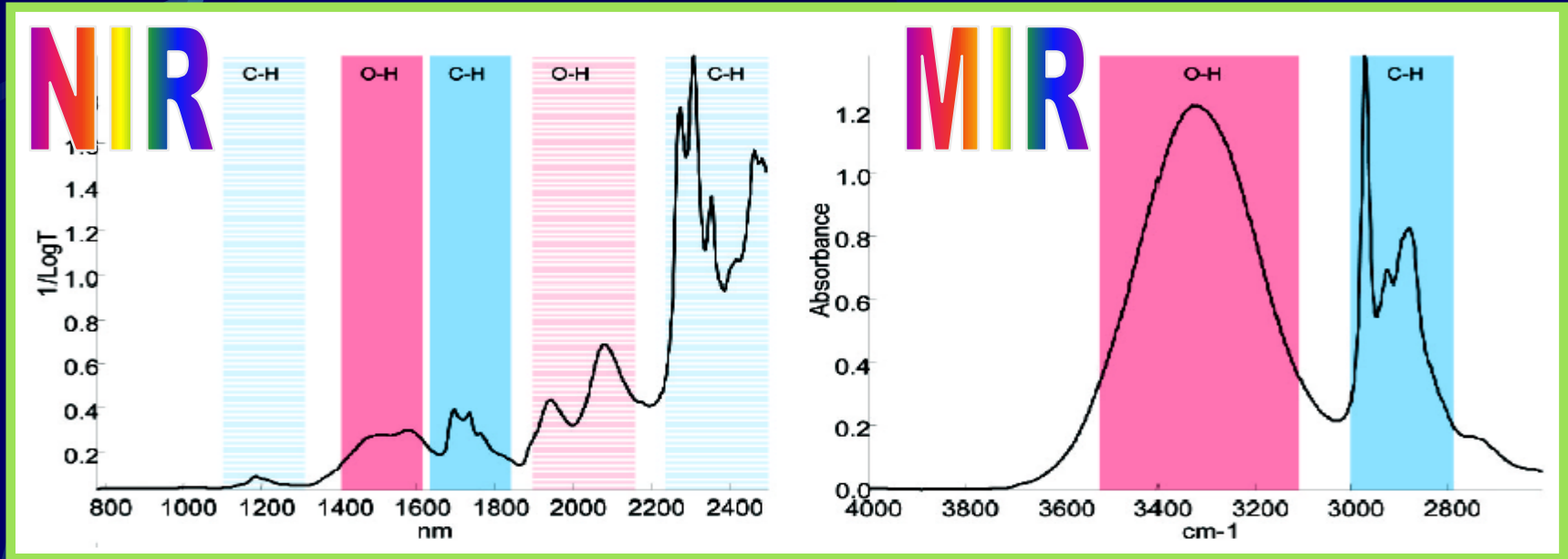
- ❖ molecular absorption/reflection spectrometry
- ❖ non-destructive method used in process analysis, QC/AC
- ❖ practical method that can replace more expensive, more time-consuming and more laboured methods – GC, HPLC, titrimetry
- ❖ relatively fast method for a routine use in technological applications

NIR spectrometry

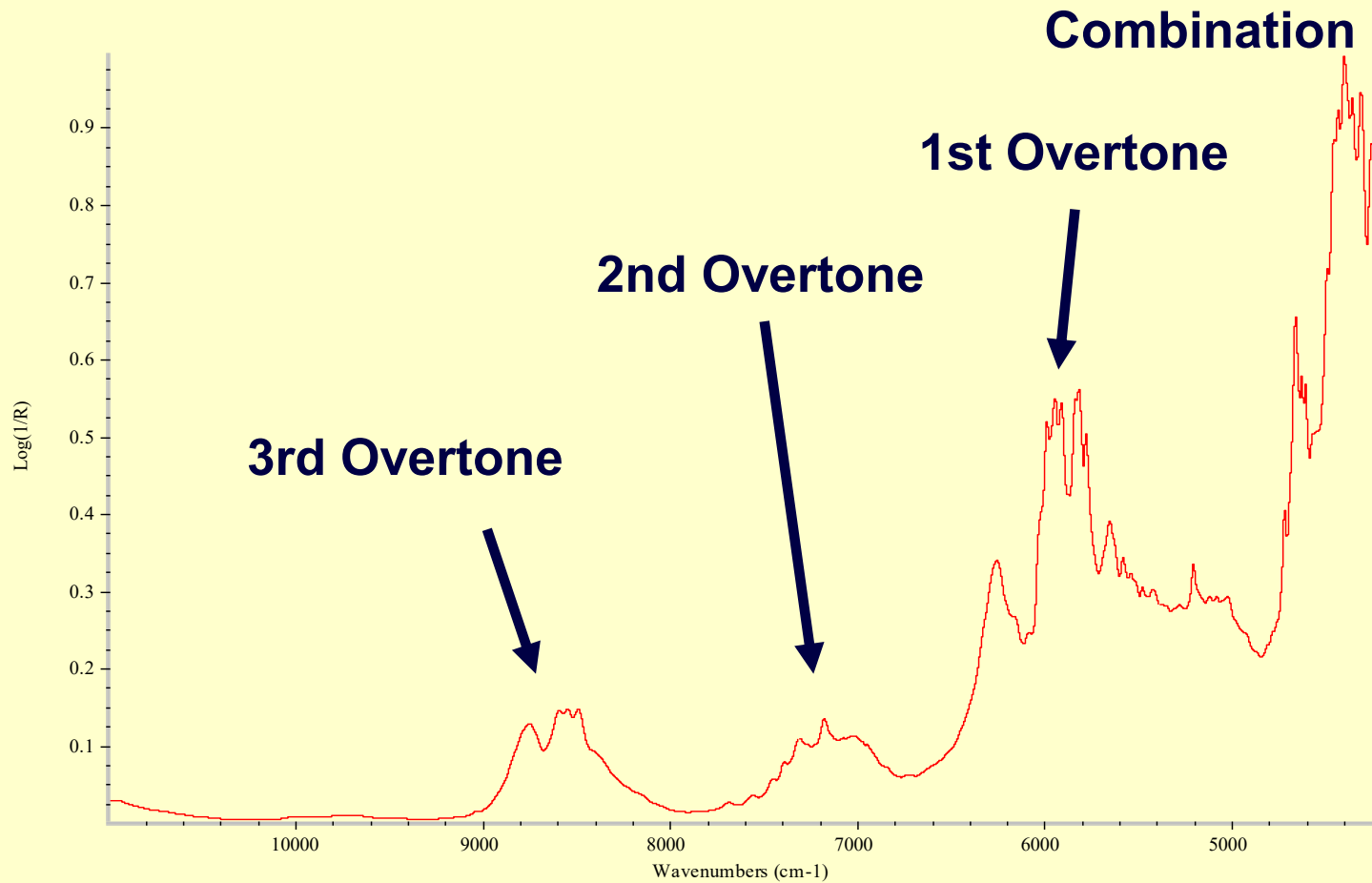
- ❖ qualitative information – **NIR libraries** – identification of pure substances and/or check of pre-defined mixtures
 - pharmaceuticals, polymers etc.
- ❖ quantitative analysis – multivariate calibration models
 - **multi-component analysis** - organic, inorganic

NIR spectrometry

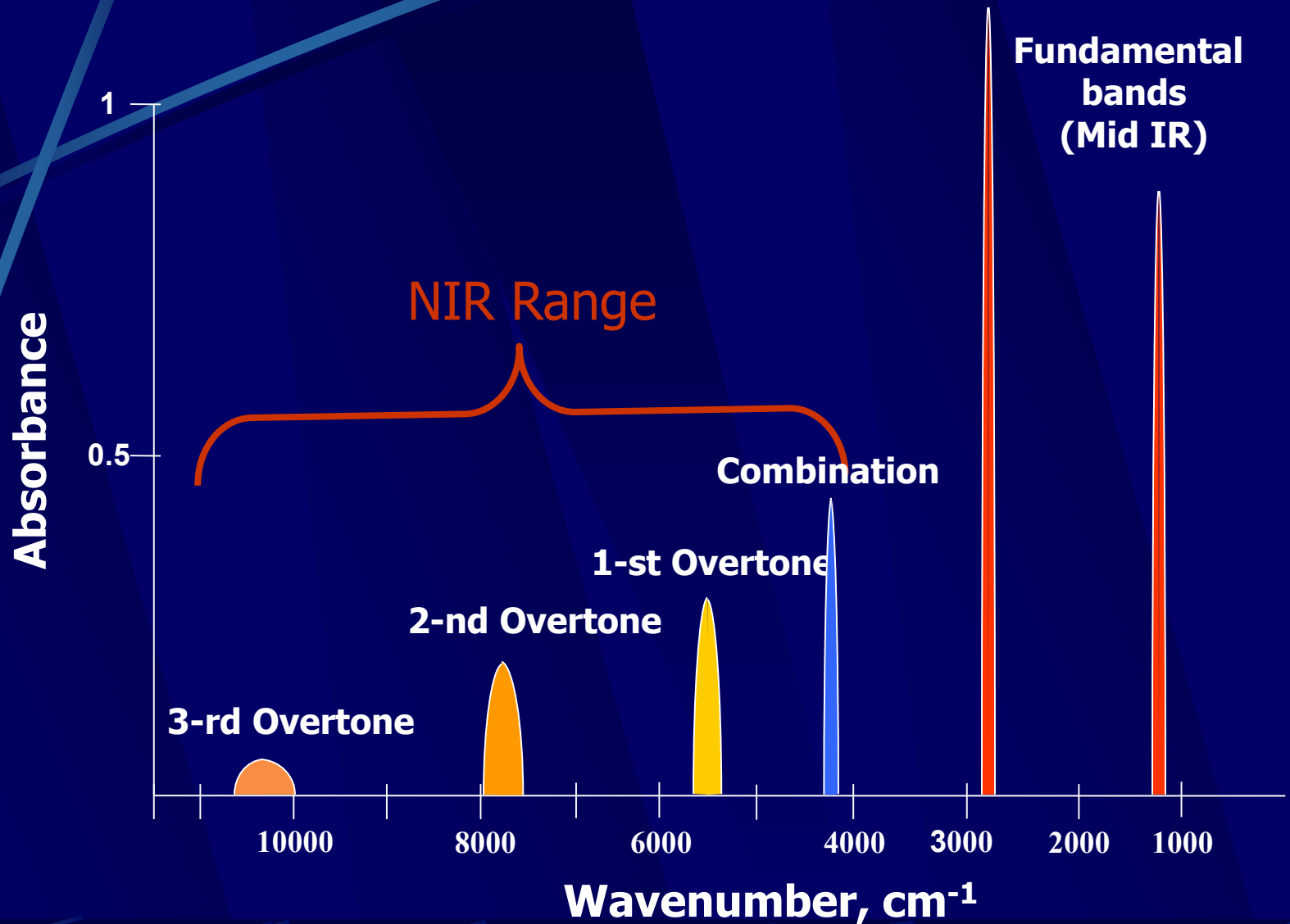
- ❖ relatively broad bands – overtones and combination bands



NIR spectra



NIR spectra



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

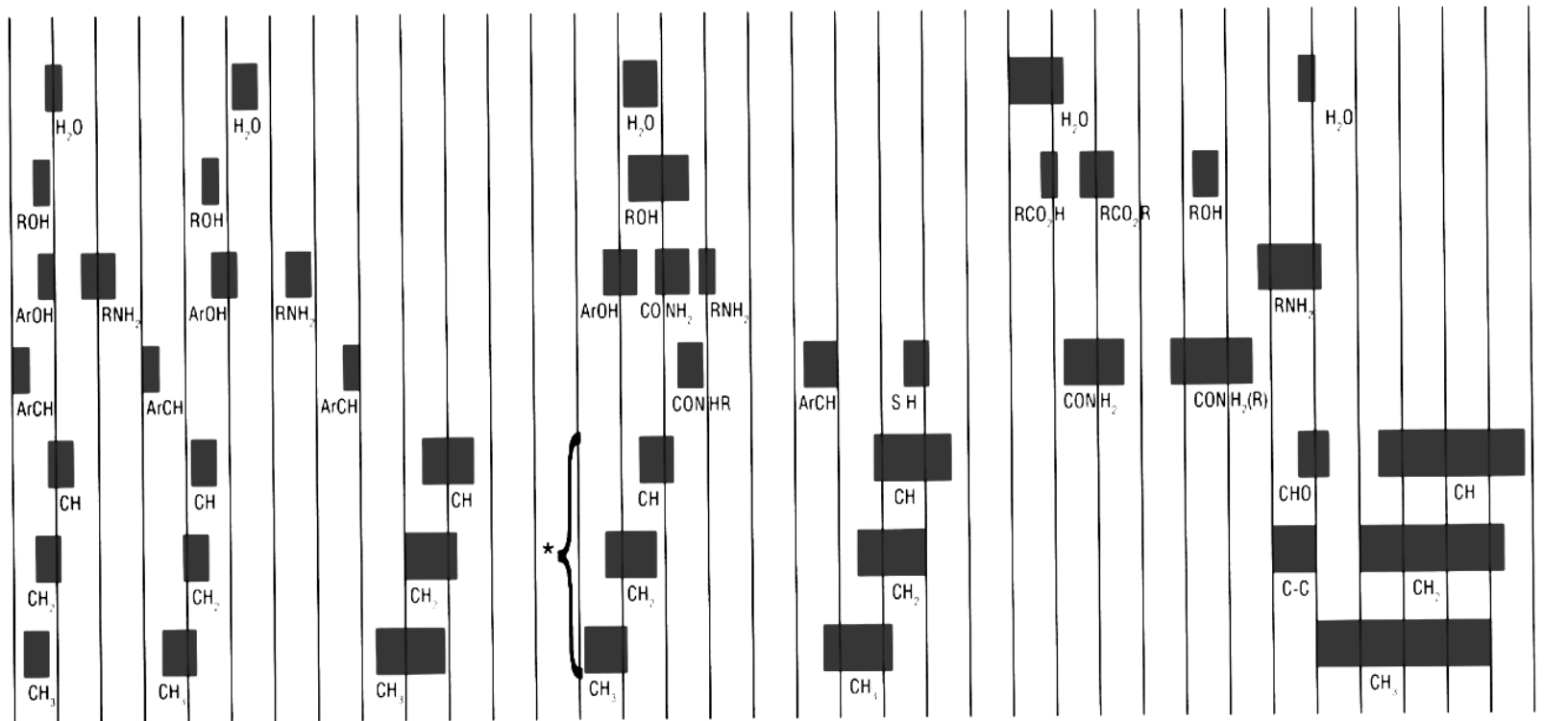
N-H 1st Overtone

C-H 1st Overtone

C=O Stretch 2nd Overtone

O-H Combinations

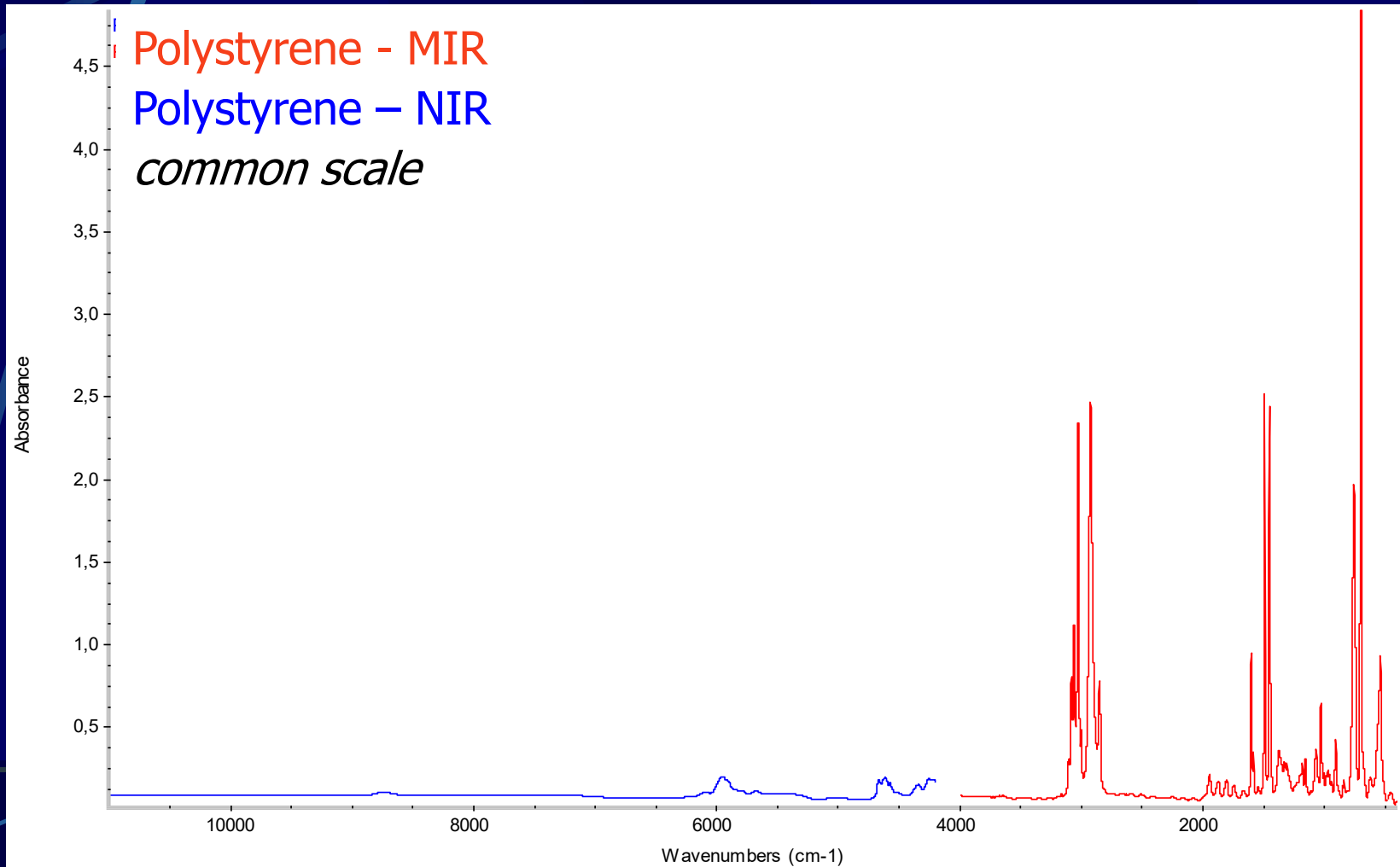
N-H & O-H Combinations



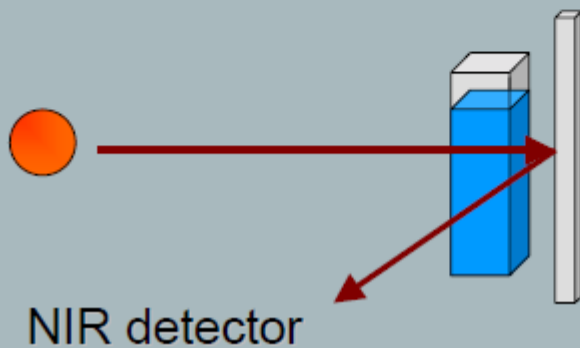
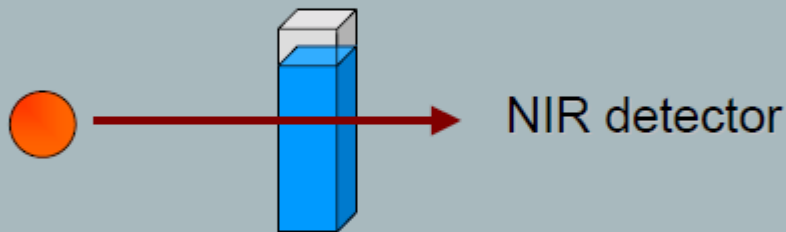
Wavelength nm	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500
Wavenumber cm ⁻¹	14286	12500	11111	10000	9091	8333	7692	7143	6667	6250	5882	5556	5263	5000	4762	4545	4348	4167	4000

NIR/MIR spectra intensities

- ❖ the intensities are decreasing with increasing frequency / wavenumber



NIR spectra experiment



❖ Reflection
(diffuse)

❖ Transmission

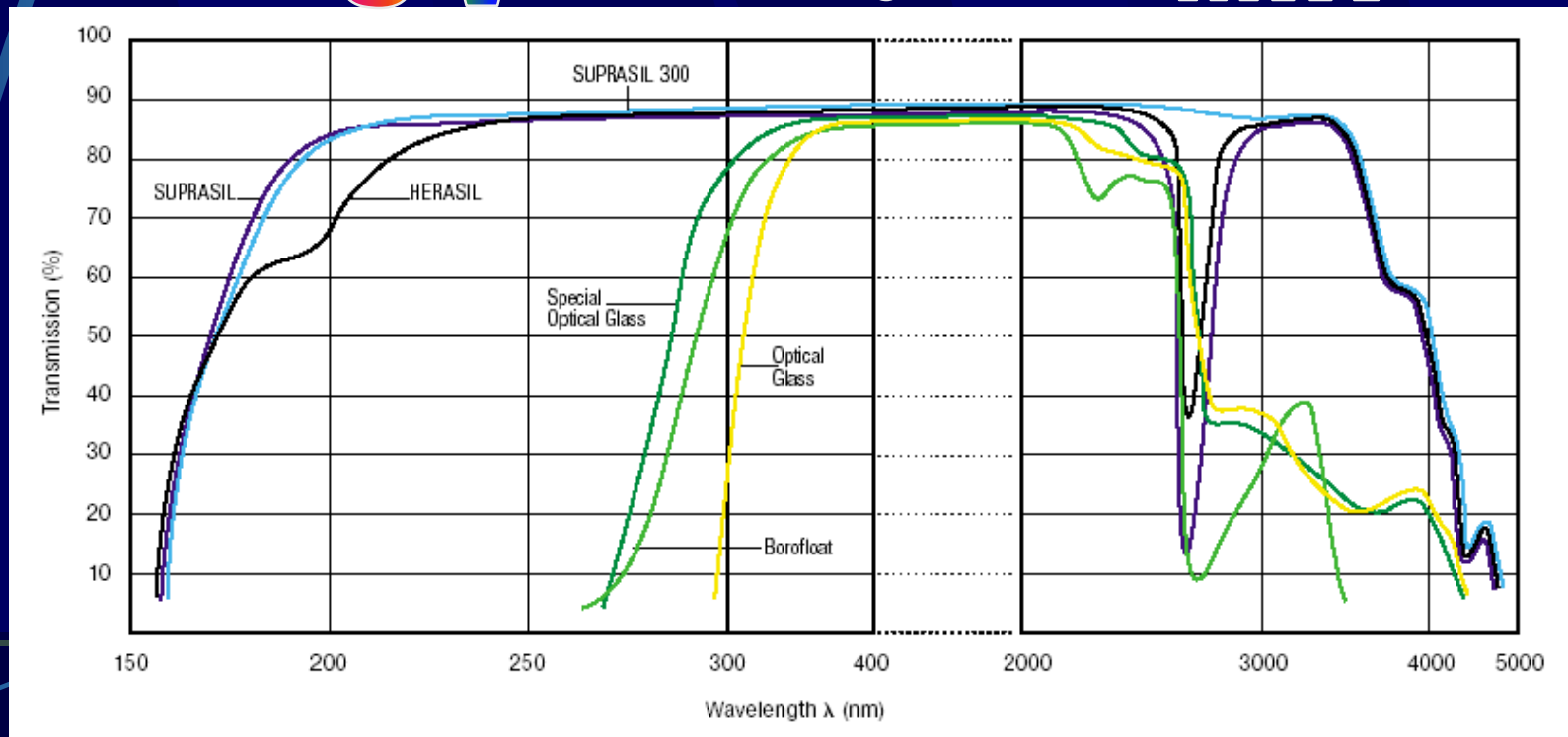
❖ Transfection

NIR spectrometry – transmission measurement

❖ cells – various types of glass

- INFRASIL, SUPRASIL (critical part $\sim 4000 \text{ cm}^{-1}$)

UV VIS - NIR MIR

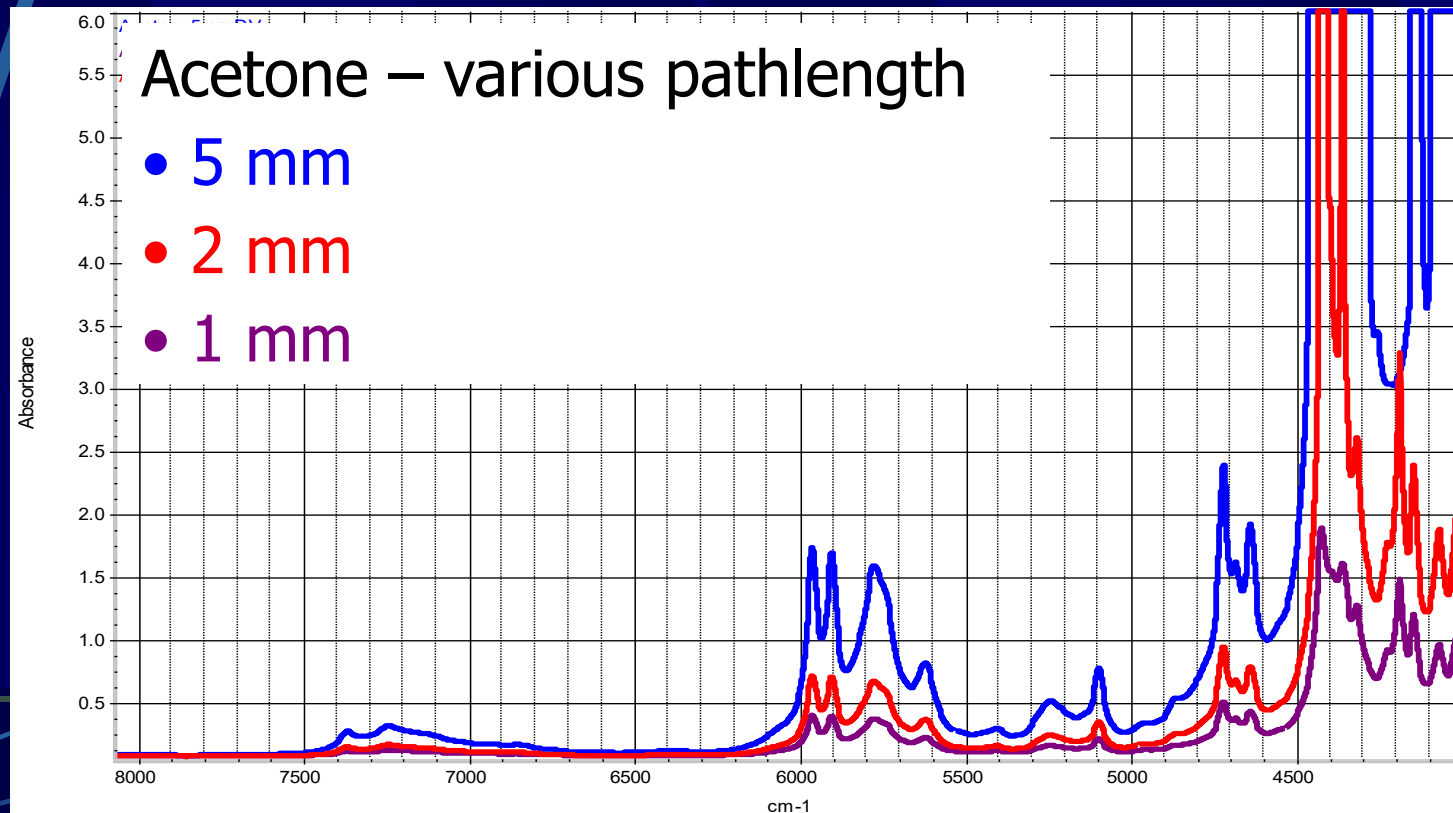


NIR spectrometry – transmission measurement

- ❖ 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

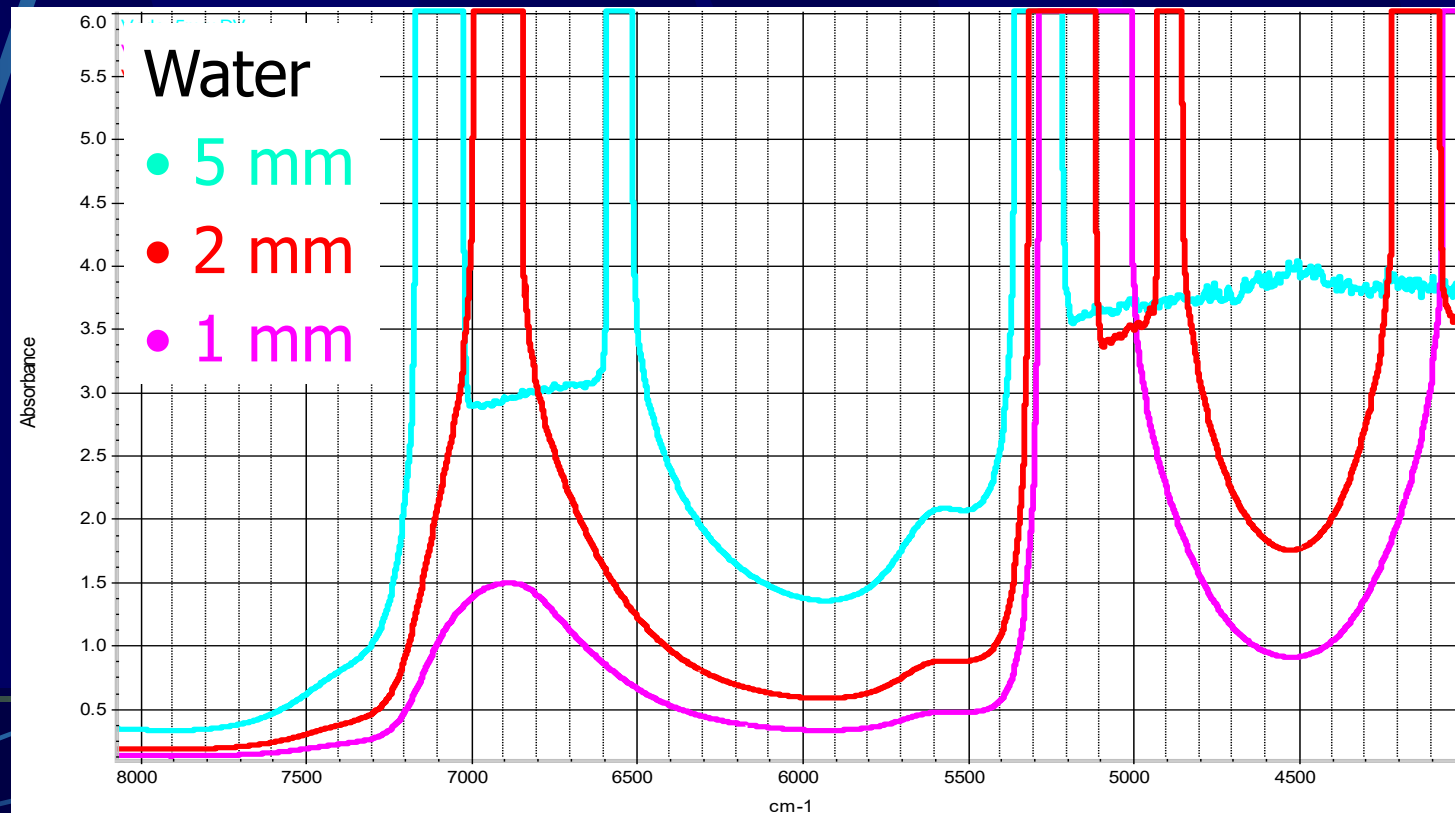
NIR spectrometry – transmission measurement

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



NIR spectrometry – transmission measurement

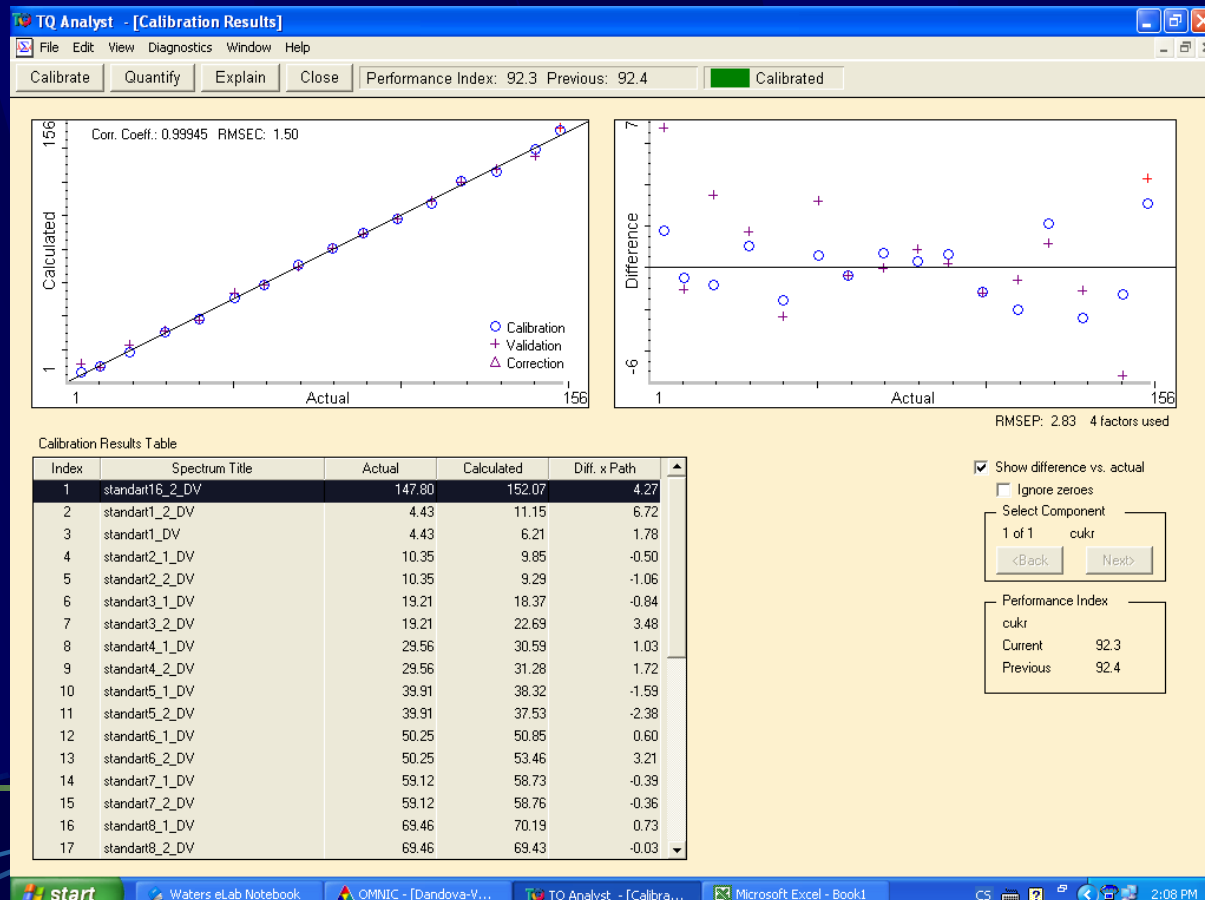
- ❖ cells – both polar and non-polar samples
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 - aqueous solutions (drinks – content of sugars, ethanol)



NIR spectrometry – transmission measurement

❖ aqueous solutions

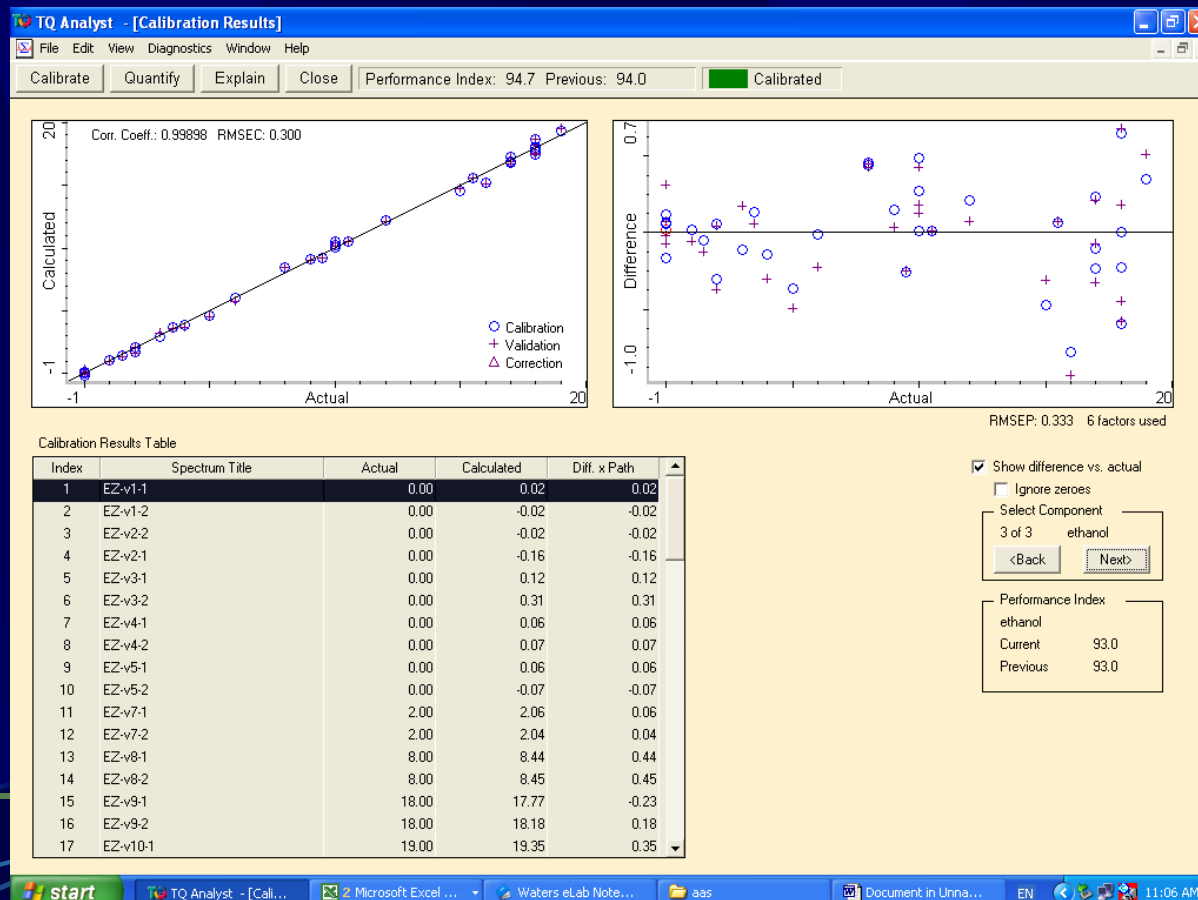
- calibration model for sugar content in soft drinks



NIR spectrometry – transmission measurement

❖ aqueous solutions

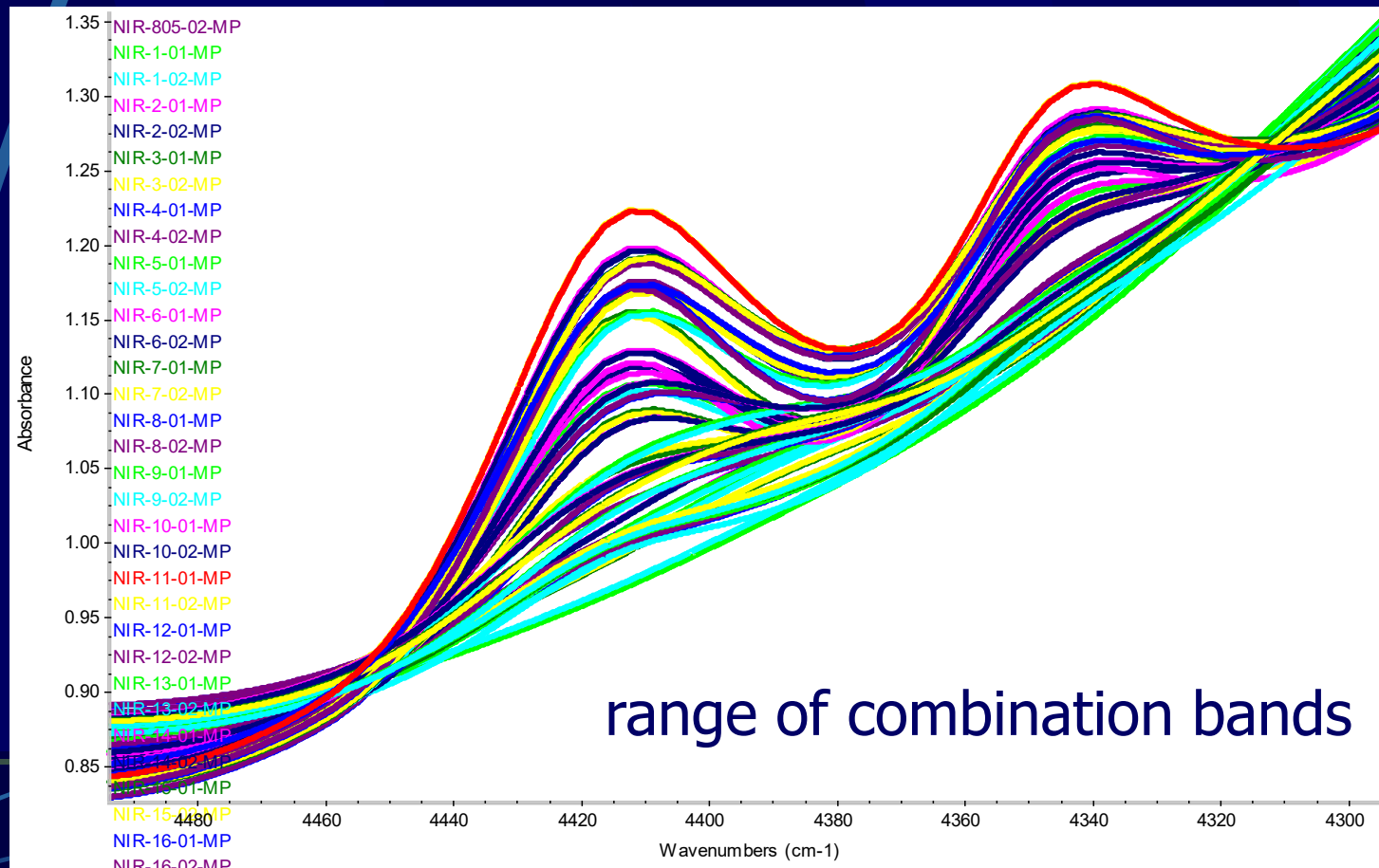
- calibration model for alcoholic drinks



NIR spectrometry – transmission measurement

❖ aqueous solutions

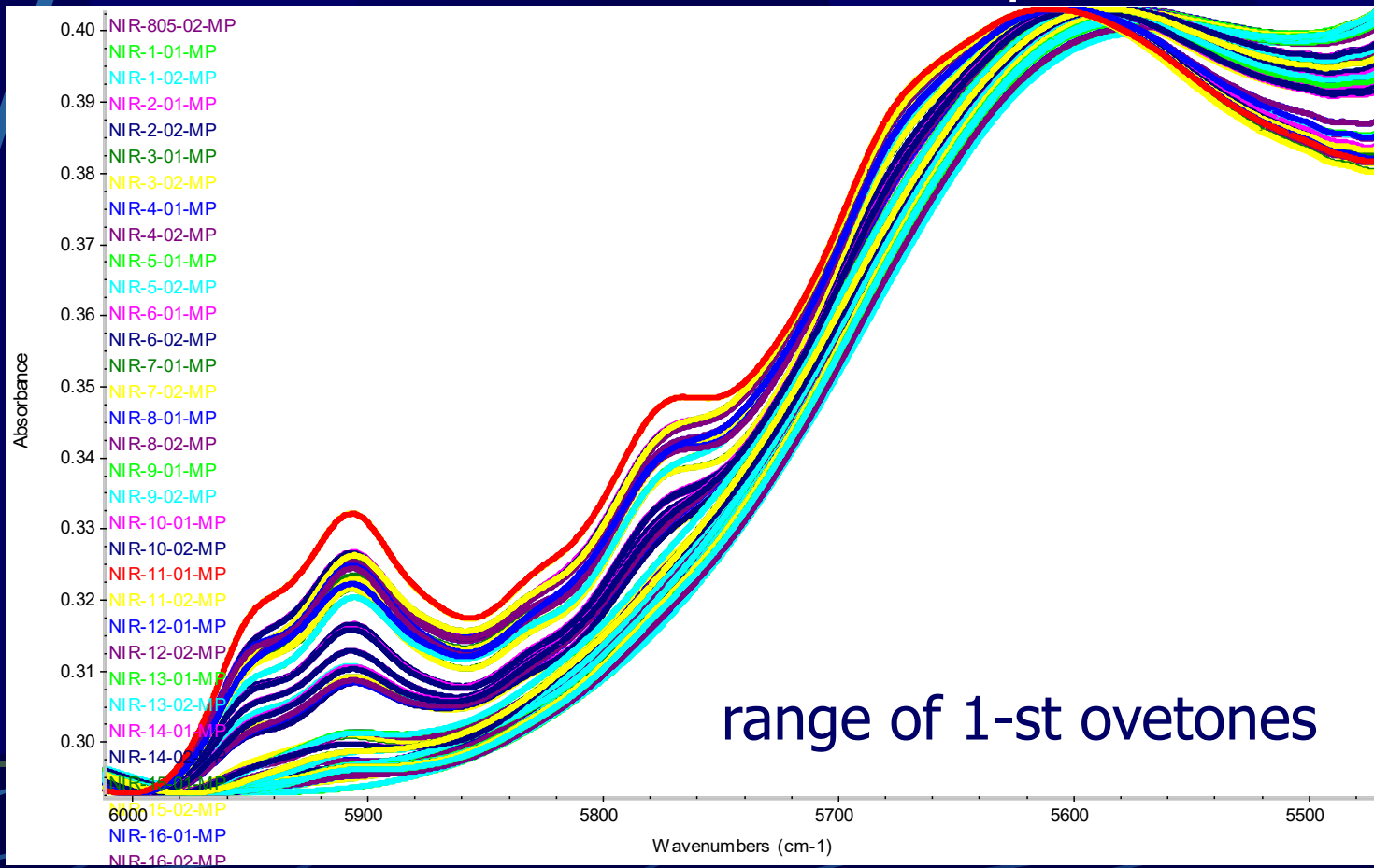
- calibration for alcoholic drinks - spectra



NIR spectrometry – transmission measurement

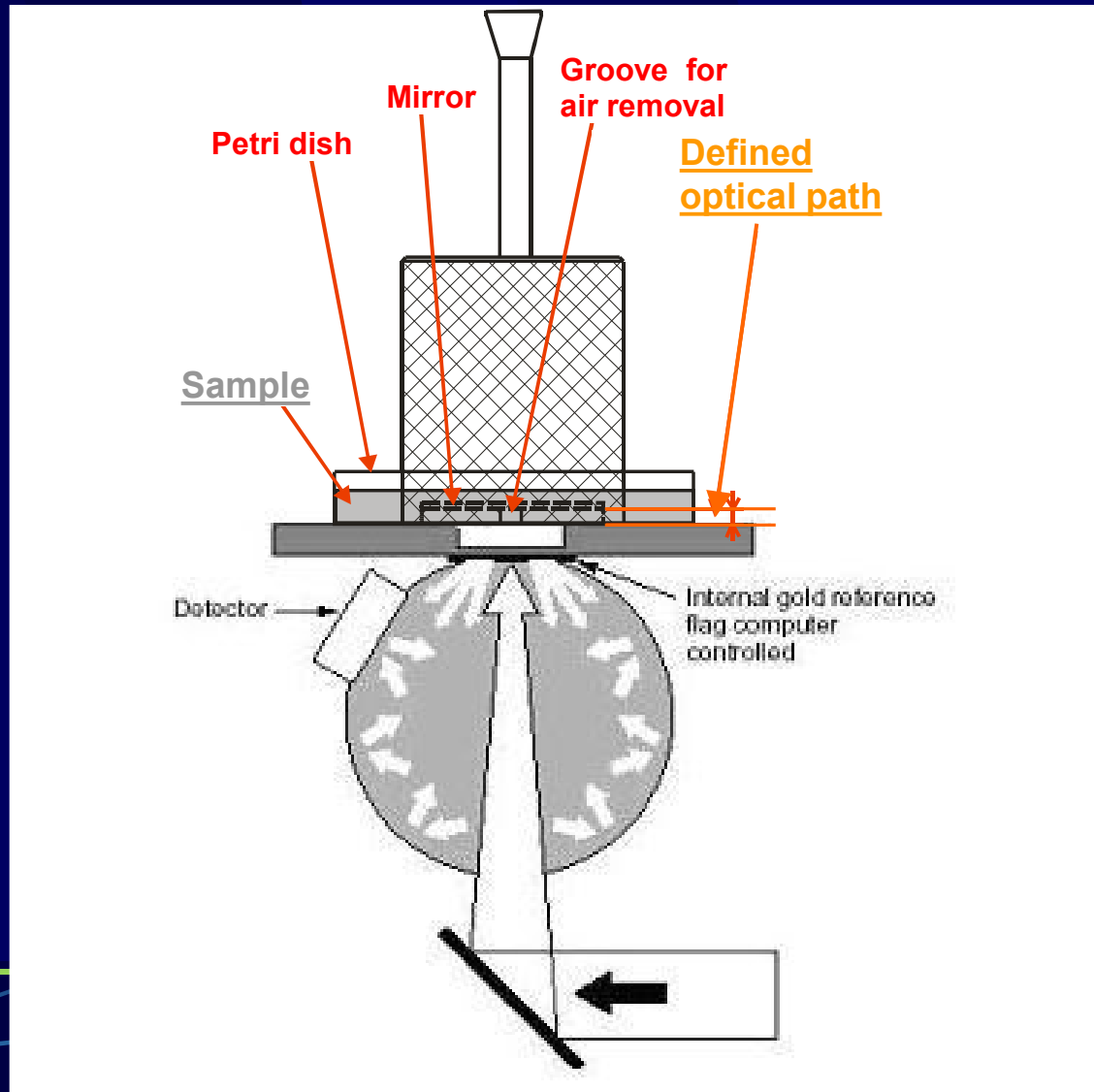
❖ aqueous solutions

- calibration for alcoholic drinks - spectra



NIR spectrometry – transflectance measurement

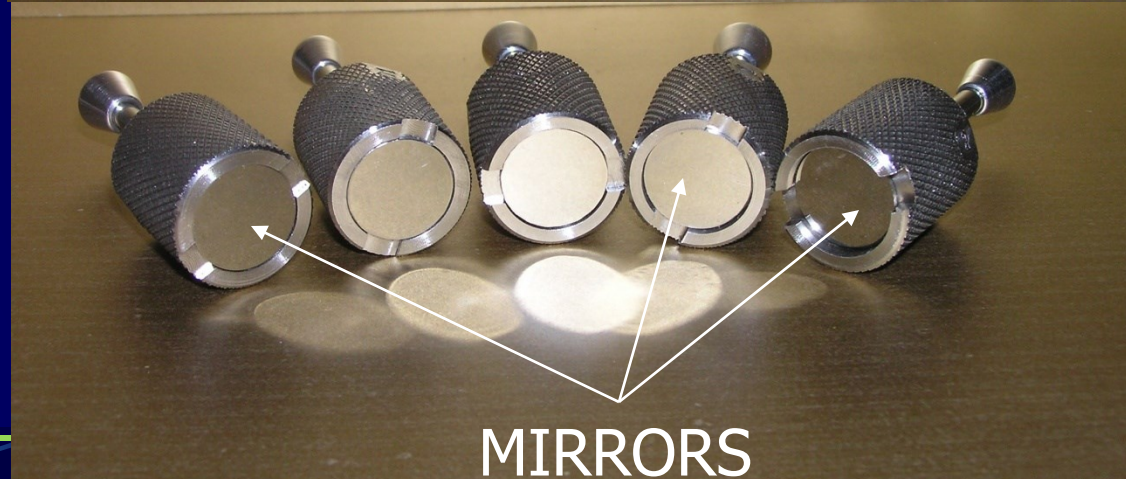
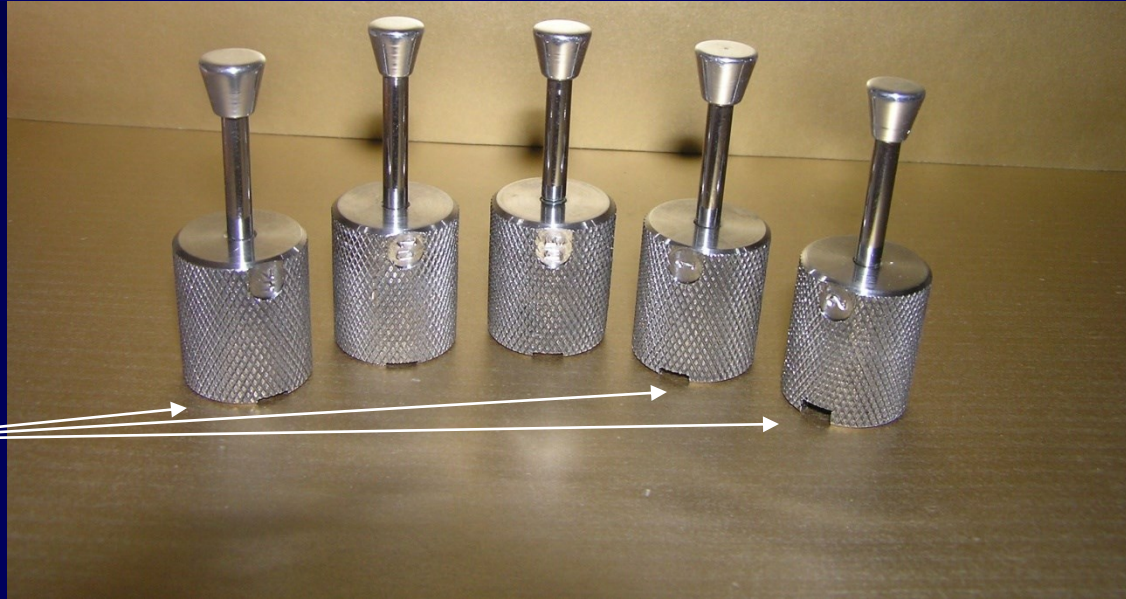
- ❖ transflectance cells
 - defined pathlength
 - transmission/reflection
 - viscous liquids, pastes



NIR spectrometry – transflectance measurement

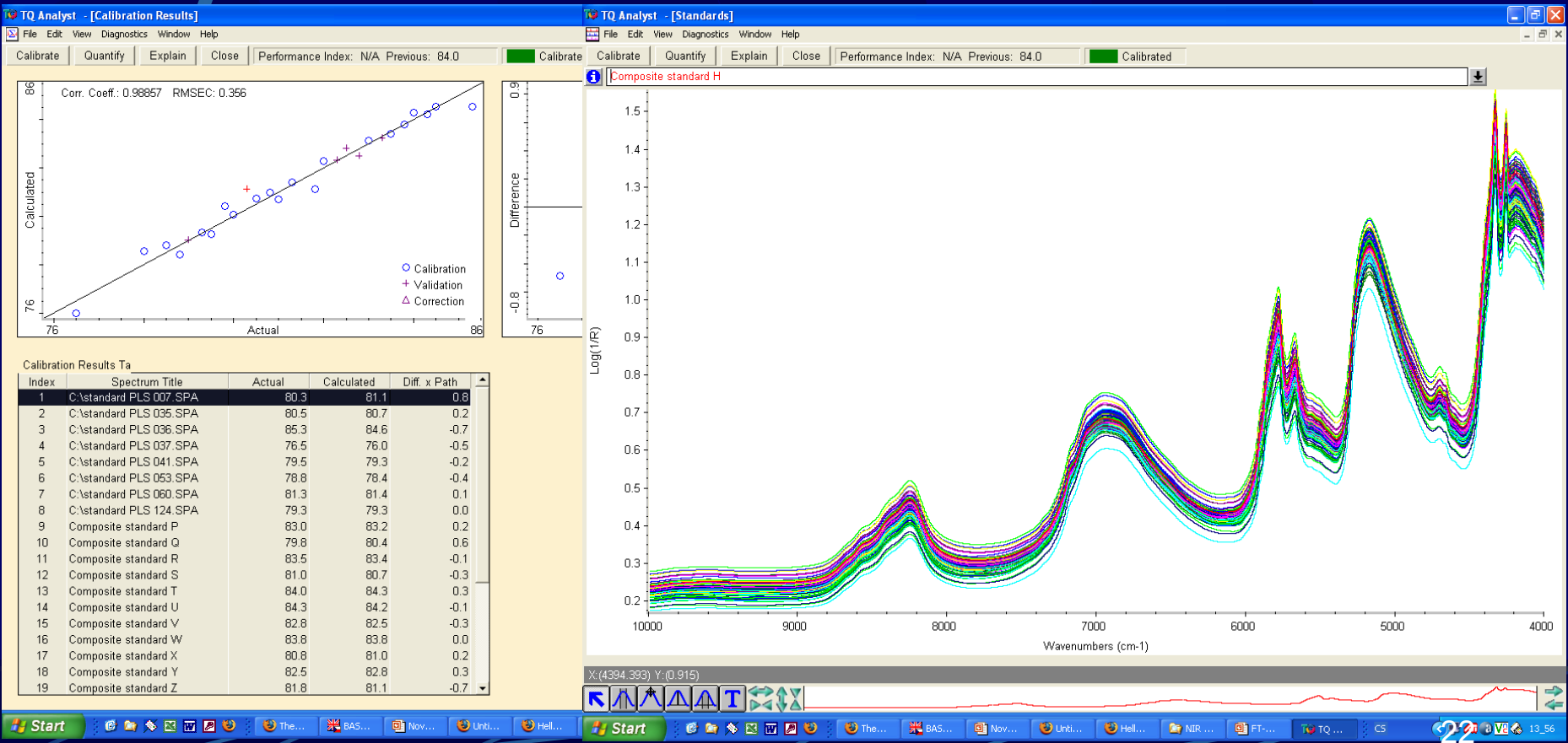
❖ transflectance cells

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

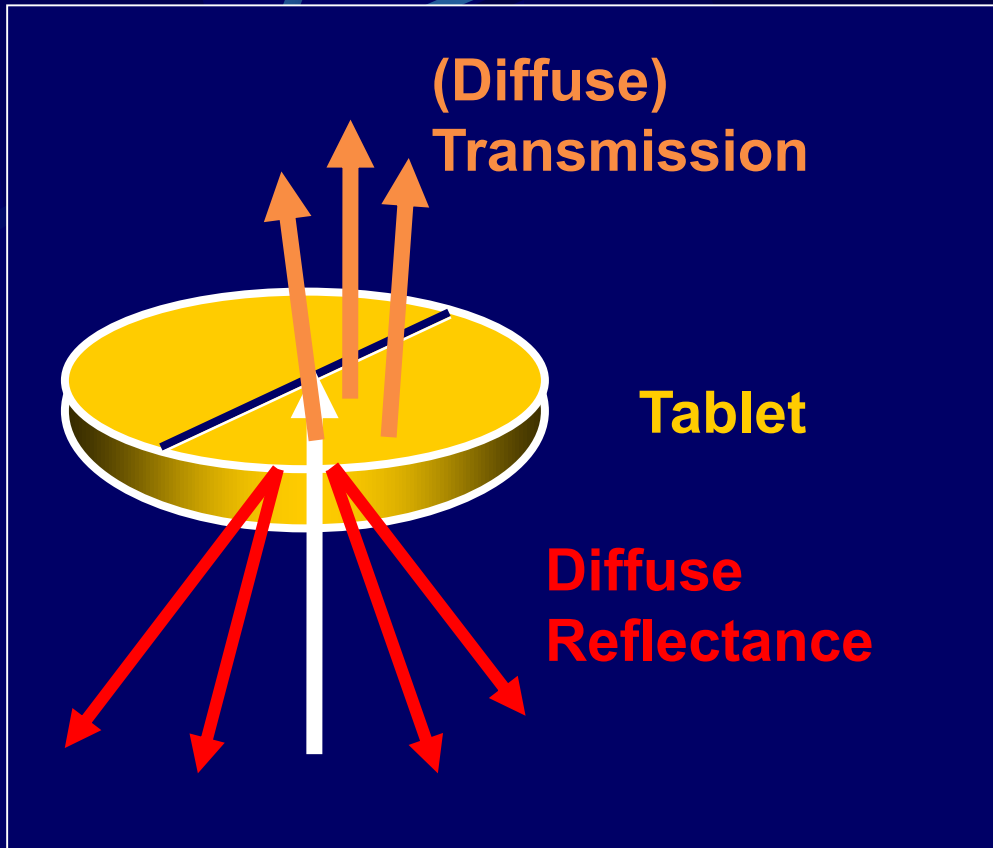


NIR spectrometry – transflectance measurement

- ❖ transflectance cells
 - fat in the butter



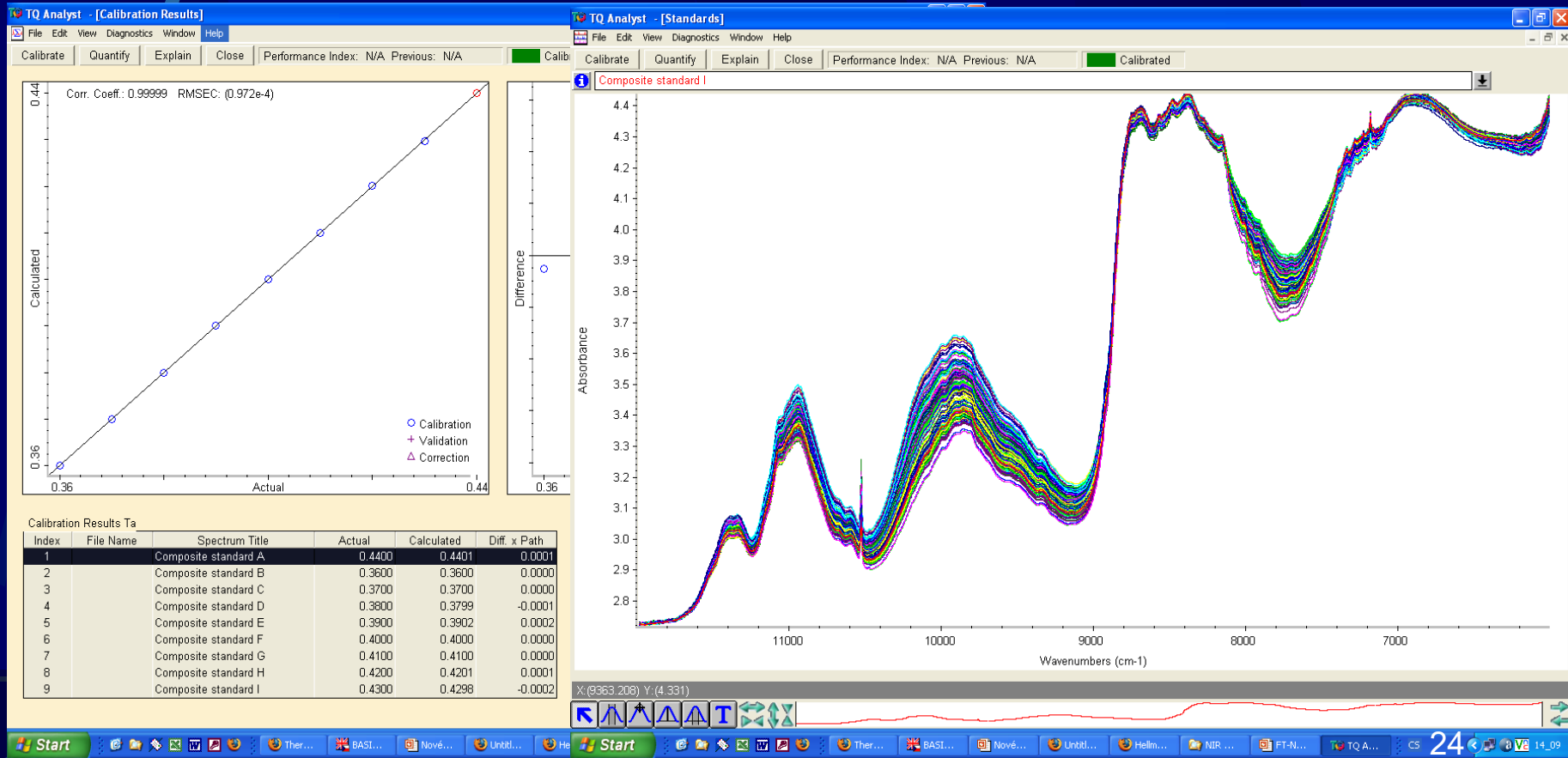
NIR spectrometry – TABLET Analyzer



NIR spectrometry – TABLET Analyzer

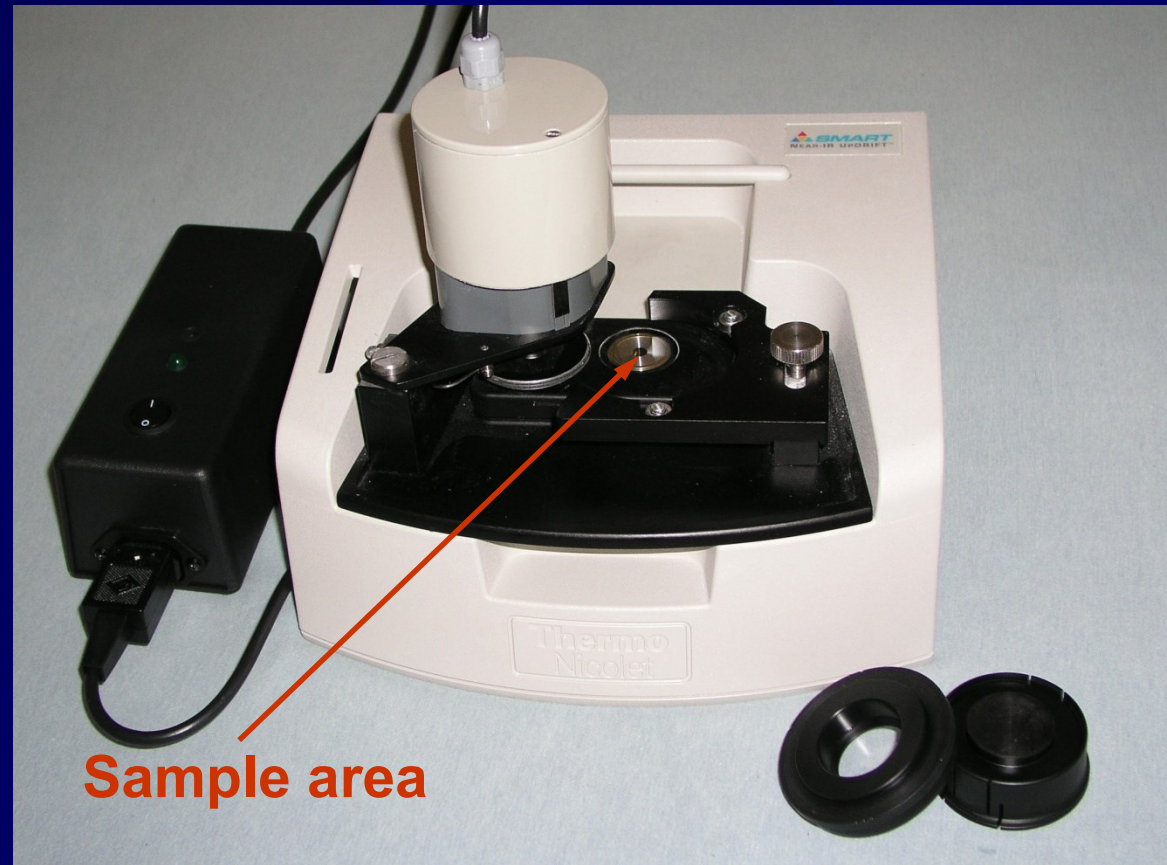
❖ tablet analyzer

- determination of active substance in a capsule



NIR spectrometry – diffuse reflectance measurement

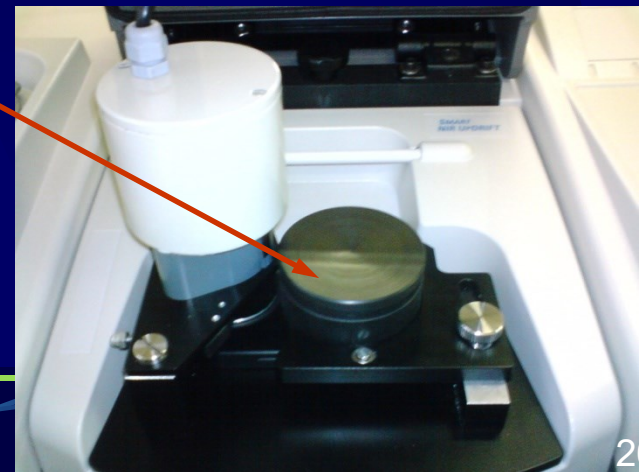
- ❖ UpDRIFT
- ❖ absorption and reflections on irregular particles
 - reflected radiation collected



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 ...



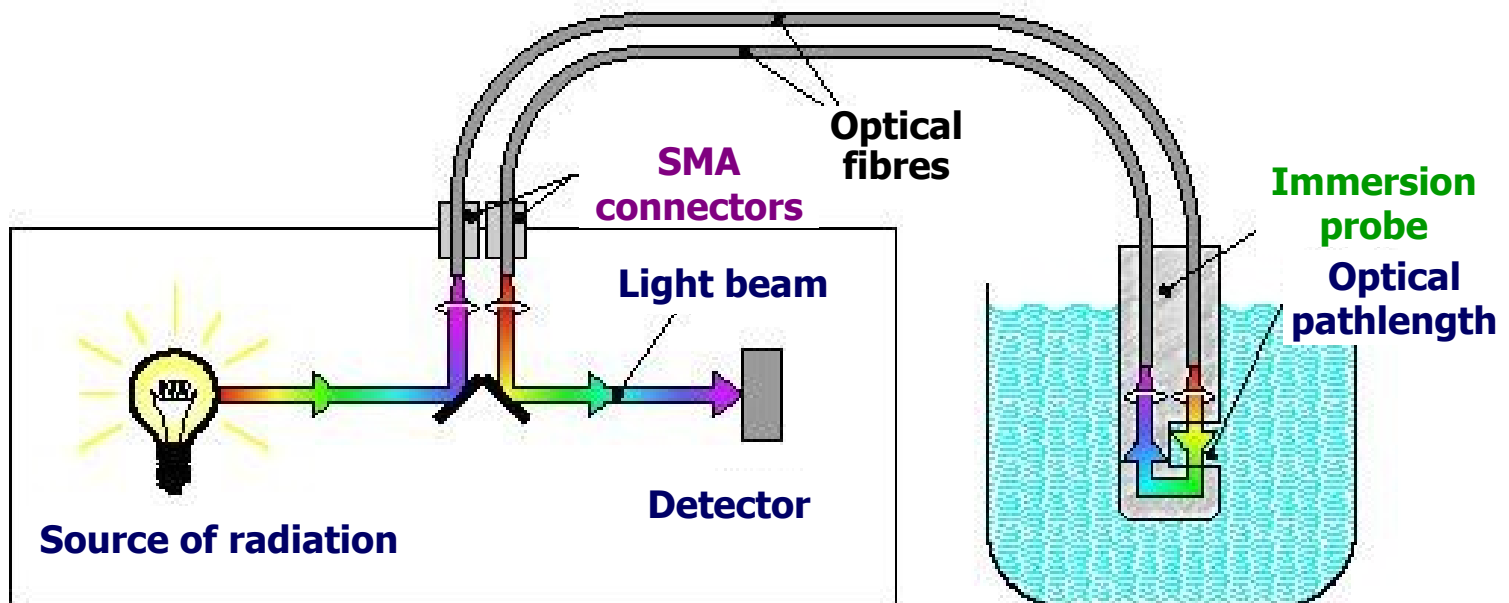
NIR spectrometry – fibre optics probes

❖ remote sensing



NIR spectrometry – fibre optics probes

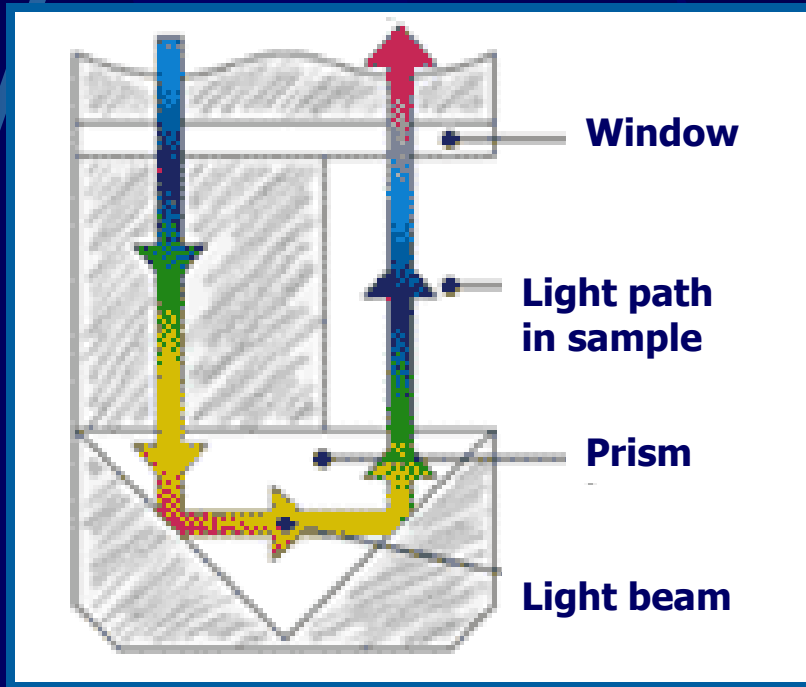
- ❖ remote sensing



NIR spectrometry – fibre optics probes

❖ IMMERSION PROBES

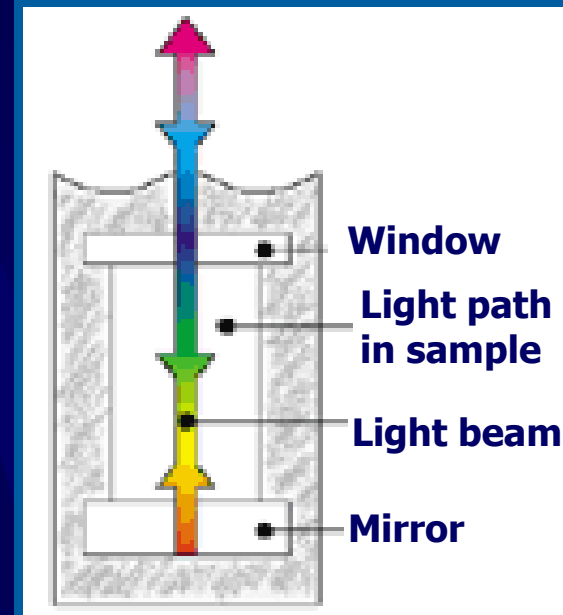
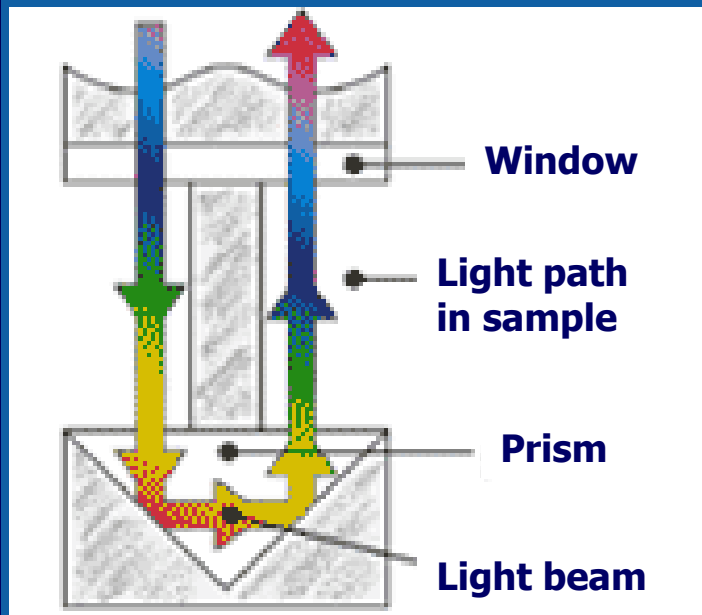
- standard type



NIR spectrometry – fibre optics probes

❖ IMMERSION PROBES

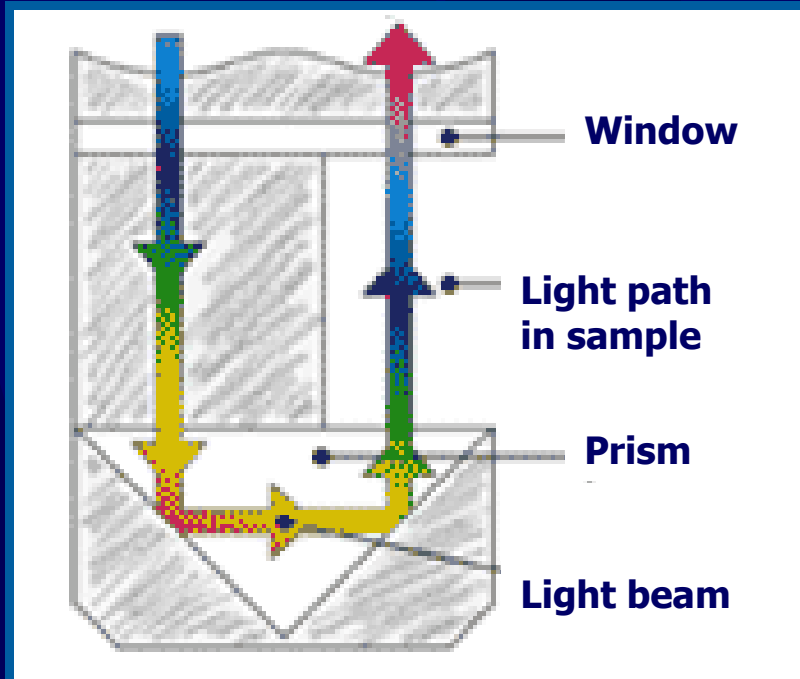
- types for small sampling volumes



NIR spectrometry – fibre optics probes

❖ IMMERSION PROBES

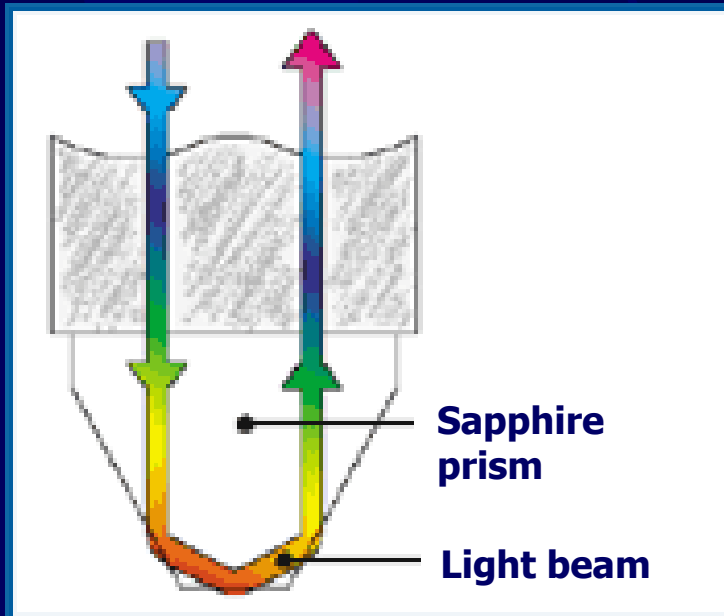
- types for process analysis



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

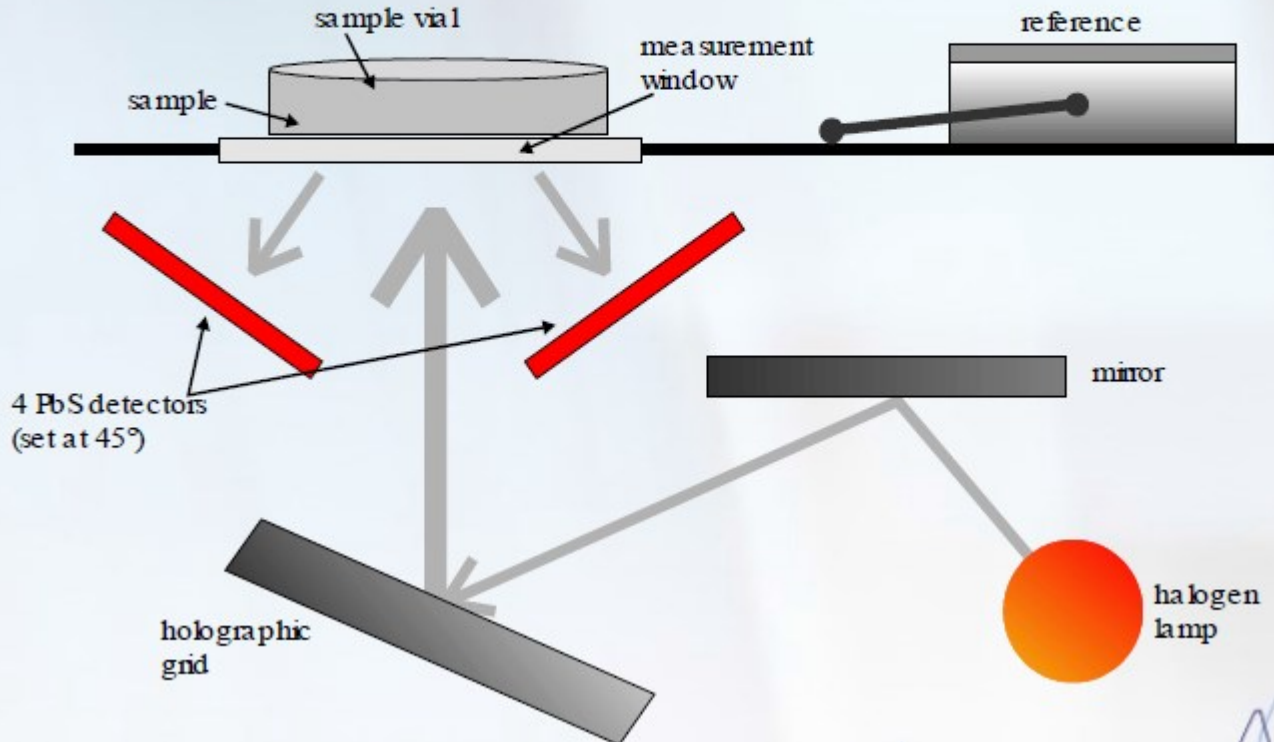
- quality control of products, additives etc.

❖ ANALYSIS OF PETROCHEMICAL PRODUCTS

- content of aromates, octane number etc.

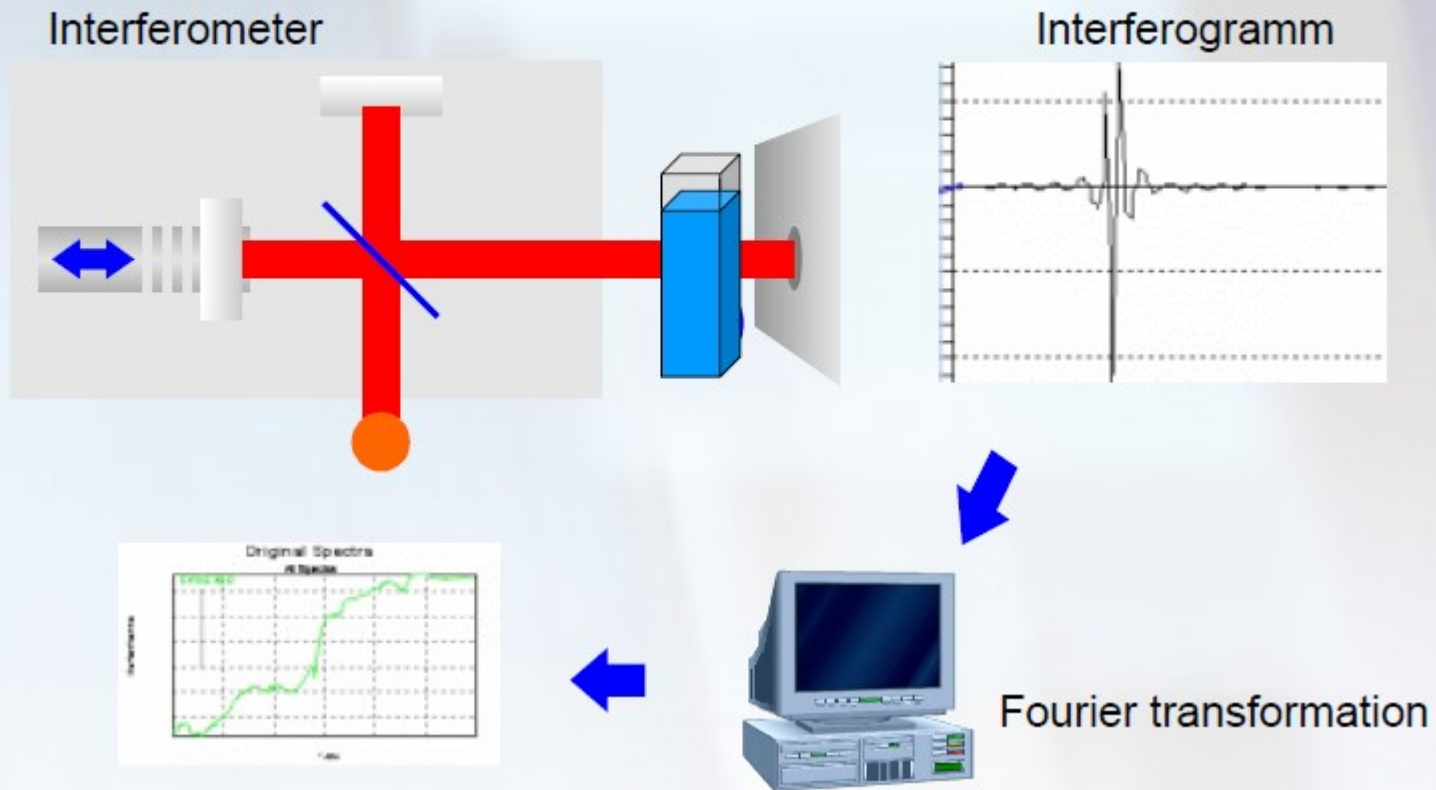
NIR spectrometry – instrumentation

- Dispersive spectrometer (e.g. Foss NIRSystems 5000):



NIR spectrometry – instrumentation

- Fourier transform spectrometer (e.g. Büchi NIRflex)



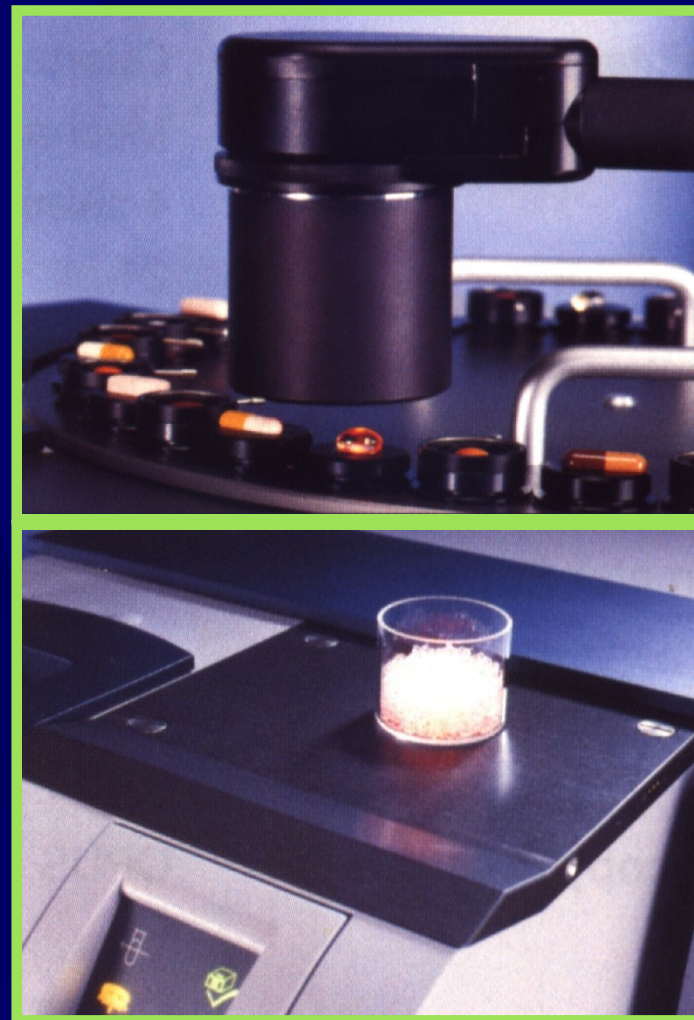
NIR spectrometry – instrumentation Nicolet



ANTARIS

NIR spectrometry – instrumentation Bruker

MPA - multi-purpose analyzer



NIR spectrometry – instrumentation

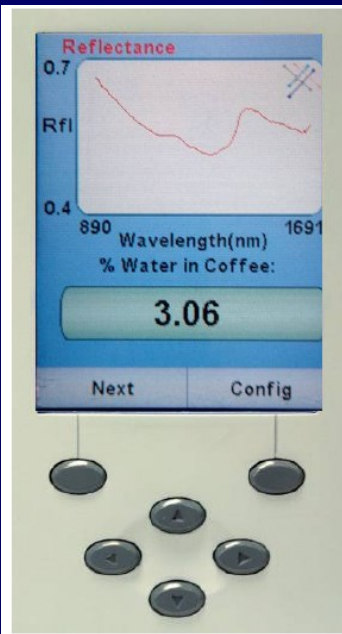
various probes for technologies



microPHAZIR Rx

Handheld Pharmaceutical Material Analysis

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

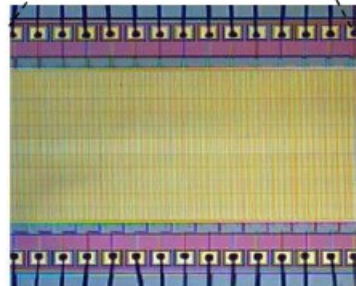
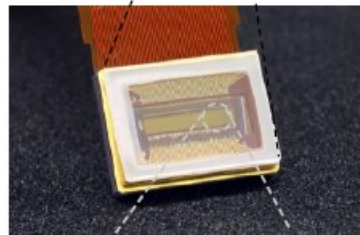
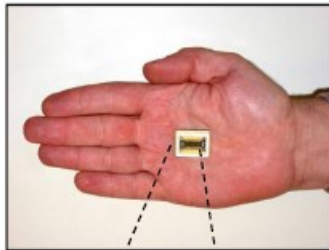


- Diffuse reflectance, optional adapters for liquids
- Tungsten light bulb, safe for operators and sample integrity
- Measurement time – several seconds
- 1600 – 2400 nm (cca 6250 – 4160 cm^{-1}) including the complete near-infrared combination region and first overtone region) – wolfram bulb – light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

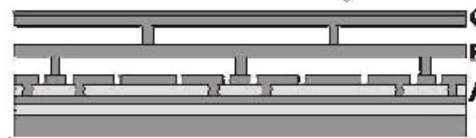
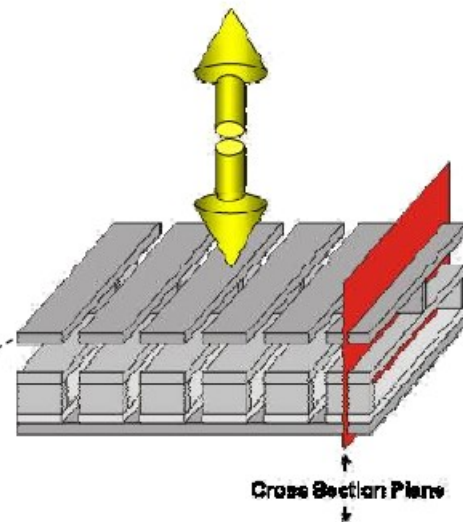


microPHAZIR Rx

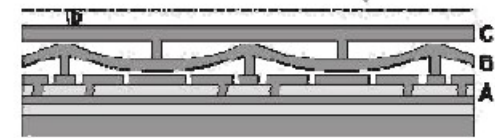
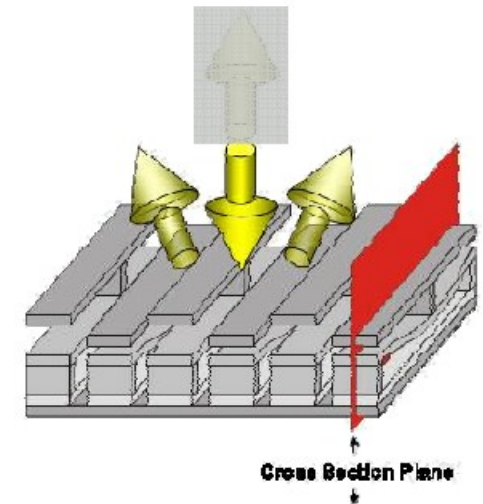
Miniature Spectrometer-on-chip spectrometers



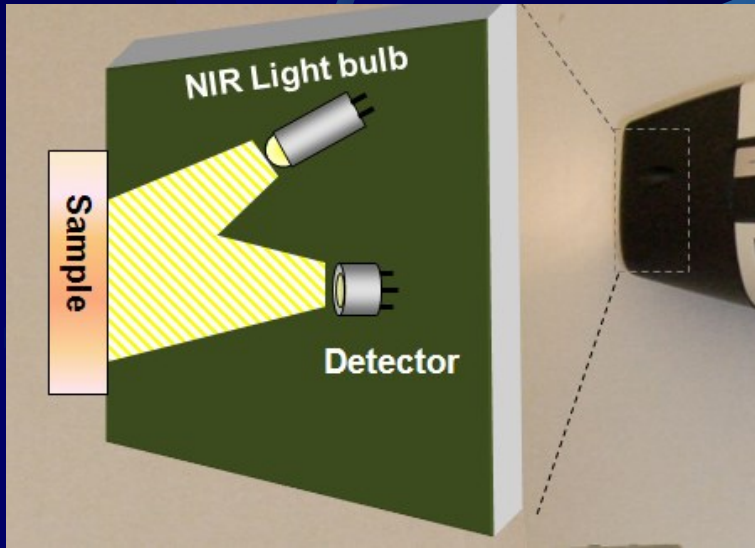
Unactuated: incident light reflected



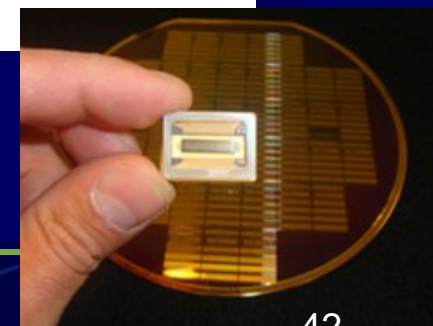
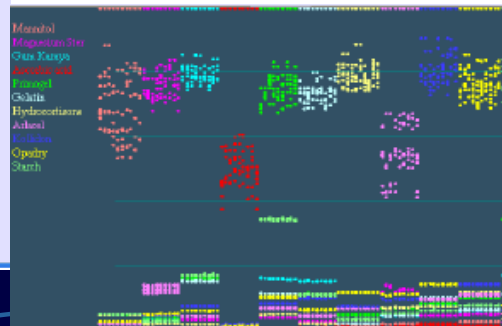
Actuated: programmable filtering at 1/4-wavelength displacement



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

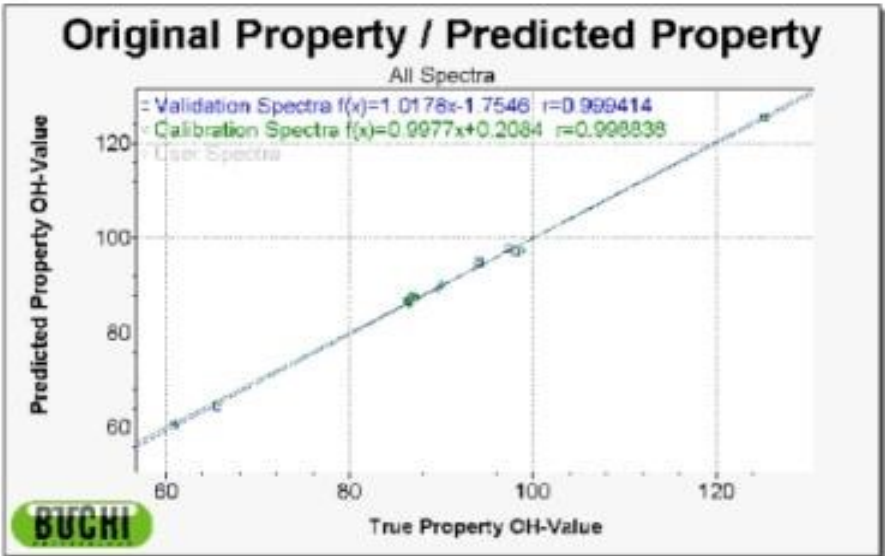
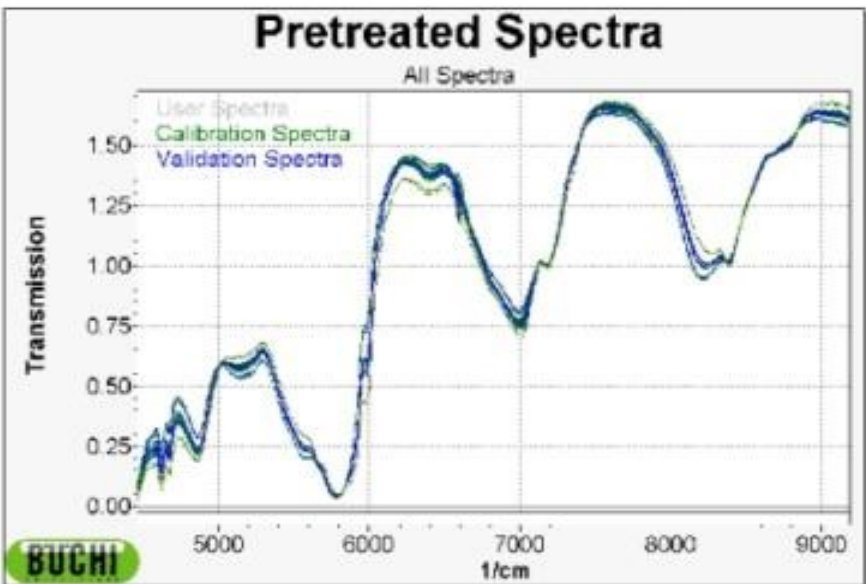


NIR spectrometry – practical examples

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.



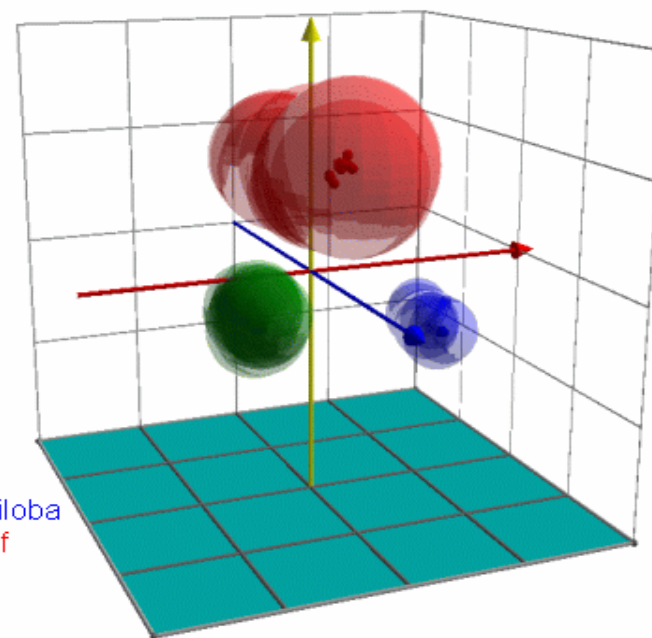
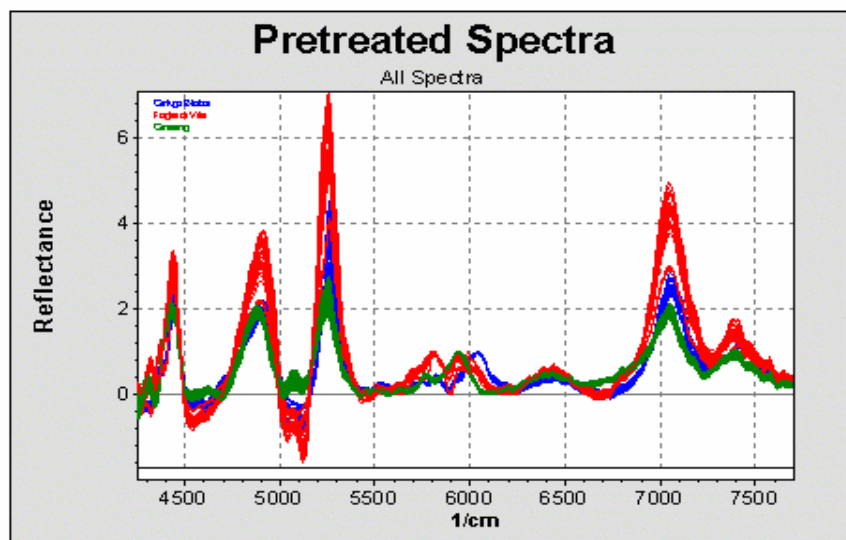
NIR spectrometry – practical examples

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 Ginkgo Biloba, Ginseng and Wine Leaf. One of the expected difficulties is to identify products from different harvests as one property.



Ginkgo Biloba
Wine Leaf
Ginseng

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



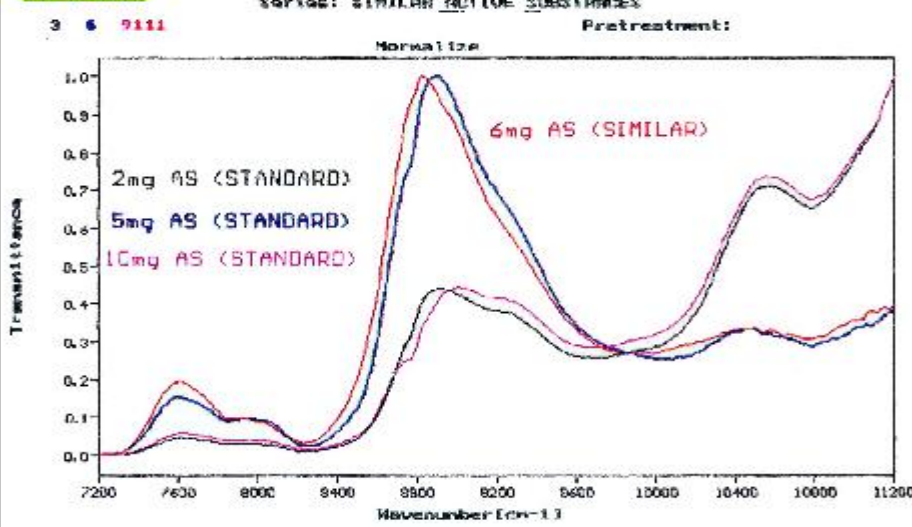
NIR spectrometry – practical examples

Tablets: active substance

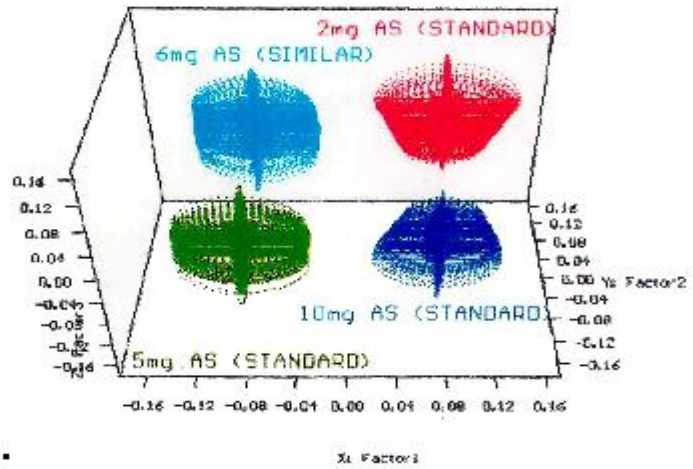
NIRTAB

Task:

Distinction of tablets with different contents of active substance.



3-Factor Plot for Qualitative Model of SIMILAR ACTIVE SUBSTANCES
Displayed are the 129 spectra in the series



Result:

The distinction is possible.

Measuring principle:

Diffuse transmission (20 scans).

