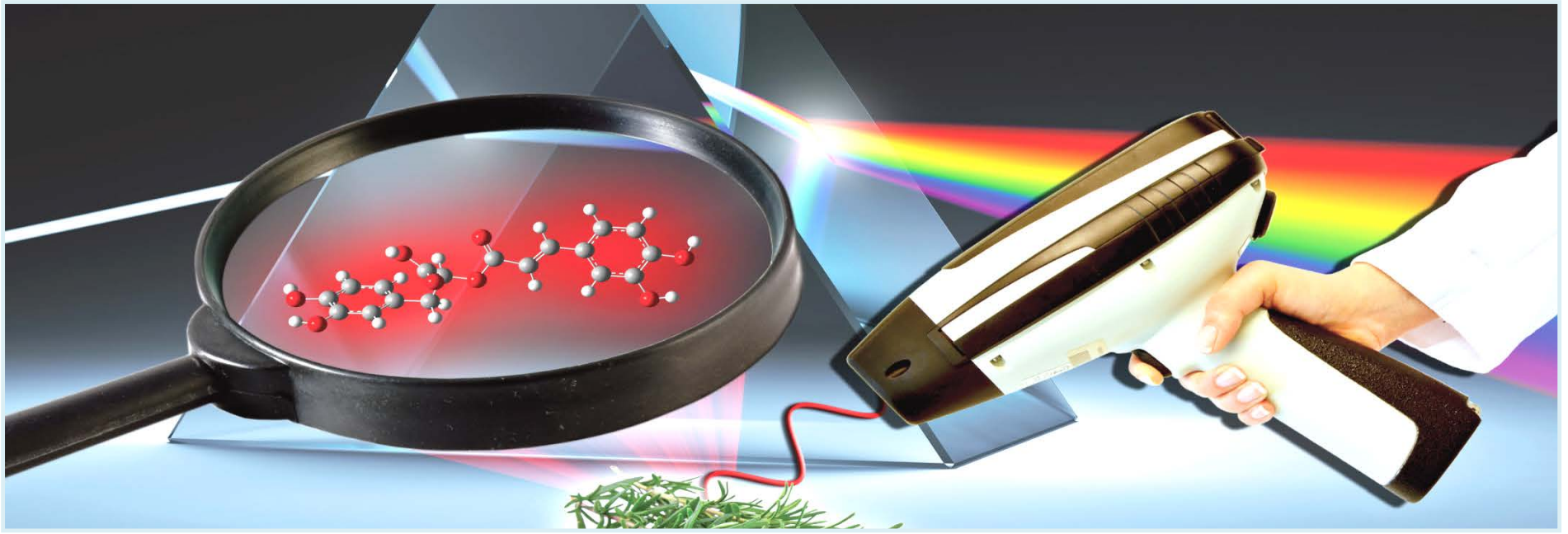
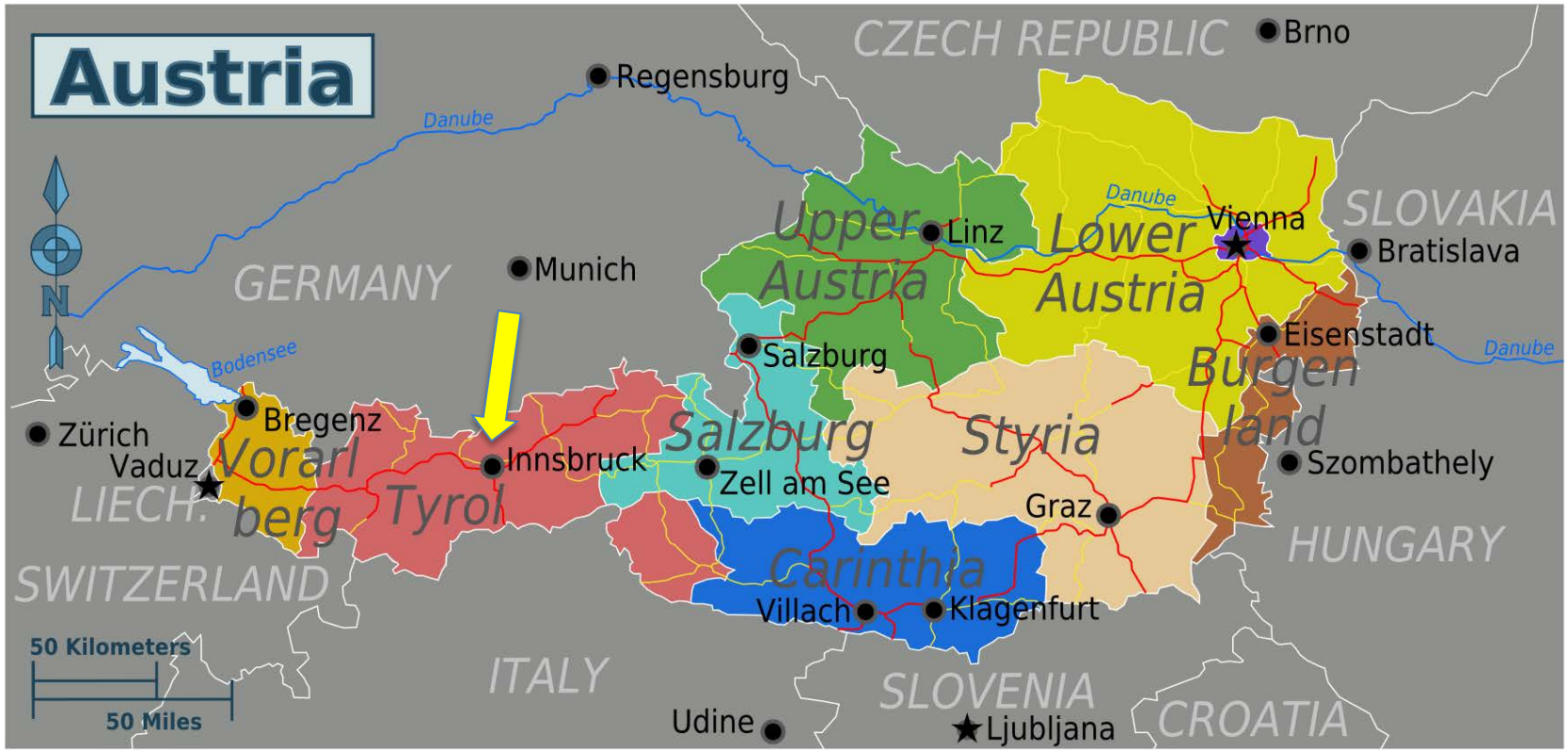
Chambersburg, 30th July 2018

Celebrating 20th Anniversary of NIR Spectroscopy at University of Innsbruck (Austria): Contributions to material-, bio-, medicinal plant- and food analysis

Christian Huck
Institute of Analytical Chemistry and Radiochemistry
Leopold-Franzens University Innsbruck Austria

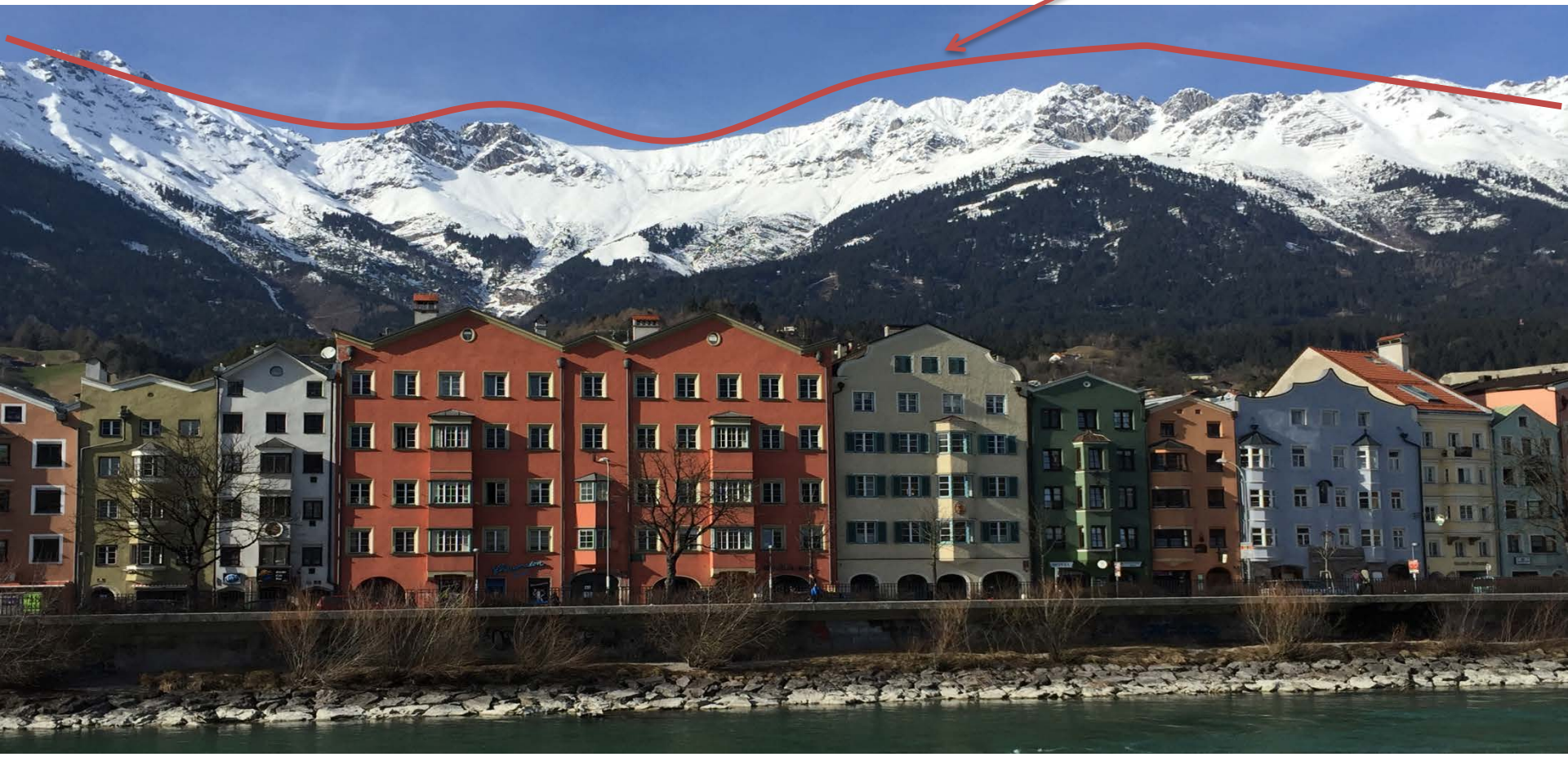


Innsbruck – Heart of the Alps



www.weltkarte.com

Innsbruck – Heart of the Alps



Innsbruck – Capital of the Alps

Innsbruck – Capital of the Alps

Innsbruck – Capital of the Alps

Tirol

Innsbruck – Capital of the Alps

The Alps

The Alps

The Alps

Center for Chemistry and Biomedicine

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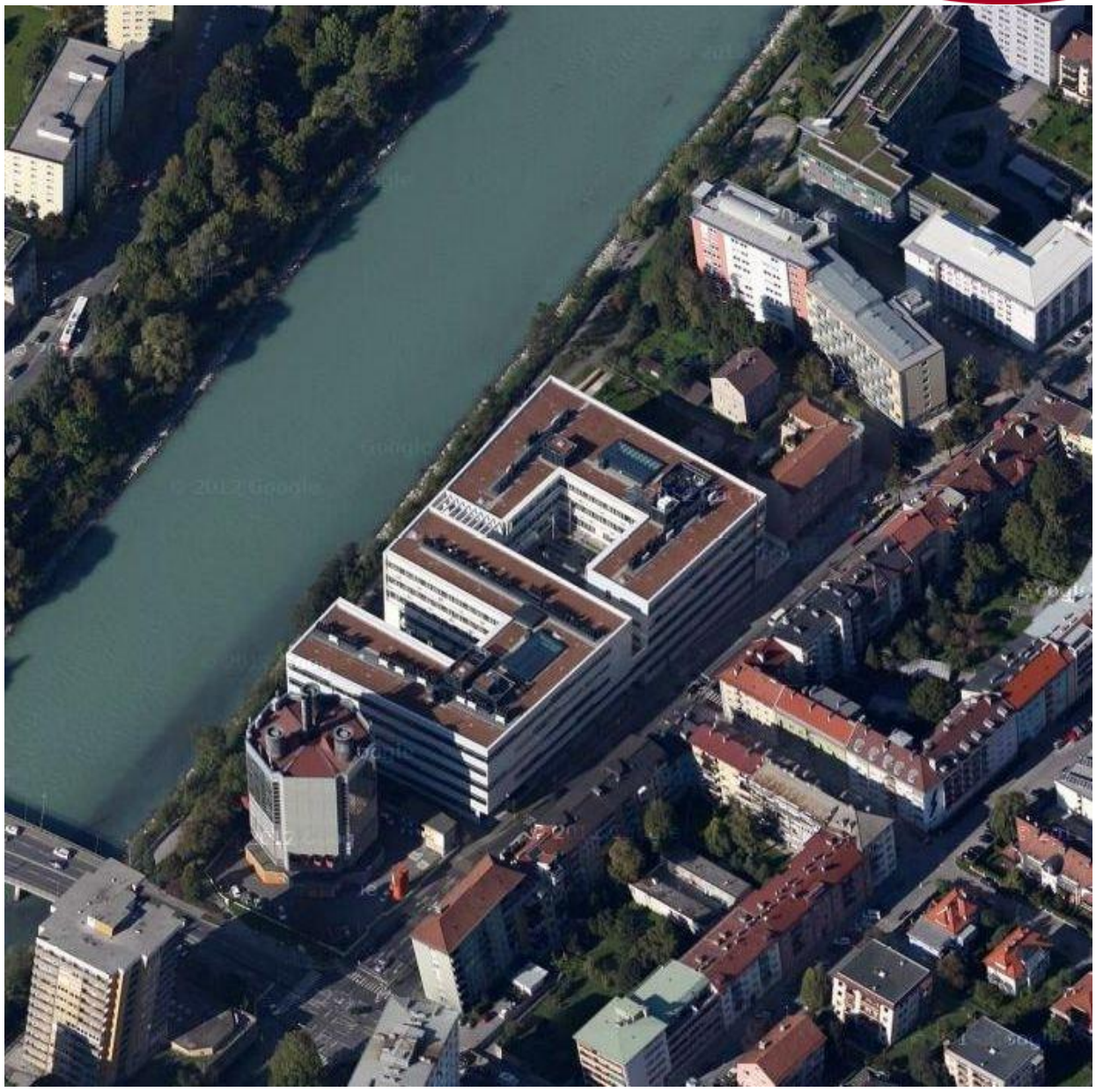
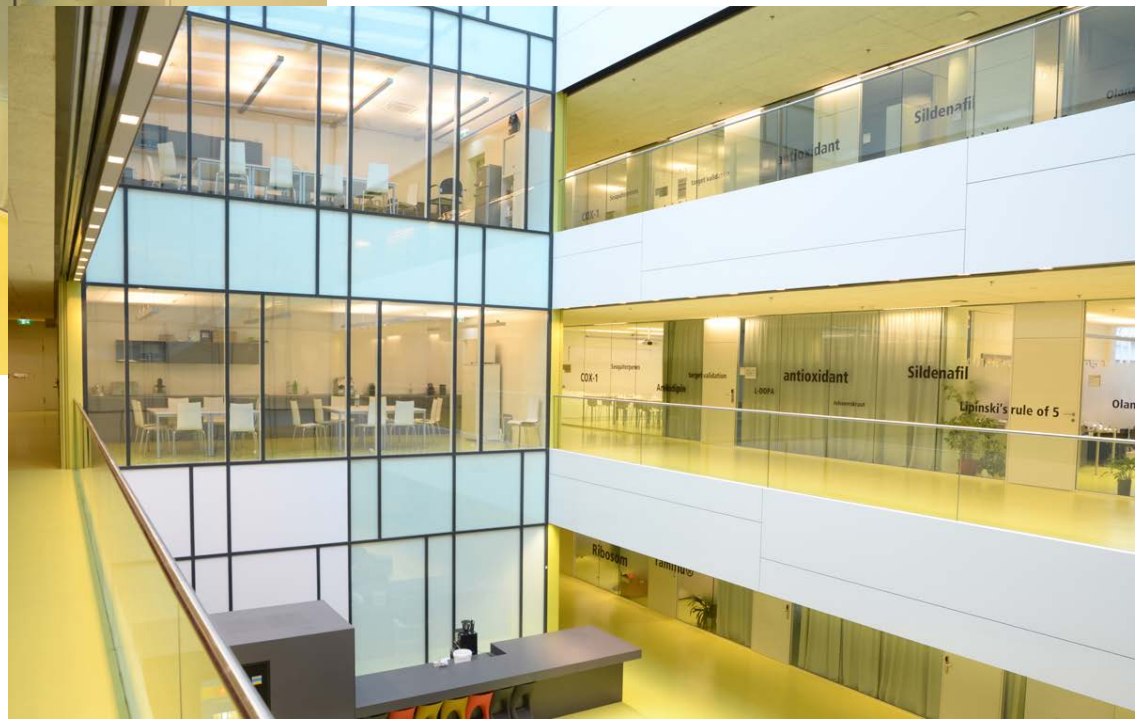


Center for Chemistry and Biomedicine



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At a Glance

Students (total)	**28,225**
International students	11,009 (39.0%)
Degrees awarded	**3,994**
Programs	**124**
Lectures	**Approx. 4,000/semester**
Staff (total)	**4,574** (persons)
Academic	3,164 (persons)
Non-academic	1,432 (persons)
Publications	**3,540**
Publications in Web of Science	**1,067**
Co-authored with international scholars	727 (68,1%)
Budget (total)	**263.6 million Euro**
Third party funding and other revenue	**58.4 million Euro**

As of: April 2015

In Memoriam: Tomas Hirschfeld (1939–1986)

Tomas Hirschfeld, an internationally recognized chemist and inventor well known for his work in both analytical cytology and analytical chemistry, died on April 24, 1986, from complications of heart disease. He was 46 and is survived by his wife, Judith, and three daughters.

Tomas served as a semiofficial oracle at all but the most recent analytical cytology conferences, between which he worked tirelessly and with great success at making his seemingly fantastic predictions of the future come true. He was born in Uruguay of German Jewish parents and received his bachelor's degree from Vasquez Acevedo College and Ph.D. degrees in chemistry and chemical engineering from the National University of Uruguay, becoming a polyglot in modern languages by necessity and a polyglot in science by aptitude and interest.

In 1969, after working briefly for North American Rockwell, Tomas joined the staff of Block Engineering, where, as a diversion from his work in Fourier transform infrared and Raman spectroscopy, he played a major role in the development of multiple illumination beam flow cytometers and in the extension of the sensitivity of cytometry to detection and measurement of single virus particles and even of individual molecules. In 1979, he moved to the Chemistry and Materials Science Department at Lawrence Livermore National Laboratory, where his efforts turned to the development of chemical microsensors utilizing fluorescence and optical tunneling measurements made through fiber optics. He also served as affiliate professor of Chemistry at the University of Washington.

A prolific inventor, Tomas held over 100 patents. He was the only person ever to receive the IR-100 award, given by "Research and Development" magazine to the 100 best inventions of the year, five times; numerous additional commercial products based on his inventions are still in development. He won both the Louis Straight and Meggers awards from the Society for Applied Spectroscopy, and earlier this year received the Pittsburgh Conference Award. He was also an author of almost 200 scientific articles and served on the editorial boards of several journals. His prodigious list of publications is matched by an equally impressive, although less generally appreciated, body of contributions to research in areas related to national security.

Tomas read about an incredible variety of subjects, and it seemed that every time he ran across a property of molecules that had not been exploited for analytical purposes, he would consider that nature had issued him

a direct challenge, in response to which he would attempt not only to tame the physical effect involved, but to make it measurable using a few cents' worth of materials, simple electronics, and a personal computer. He had more ideas in a week than many smart people have in a year, and could bring new viewpoints to a discussion of almost any scientific problem. He was often right; more remarkably, when he was wrong, his analyses could frequently point others toward the right answers.

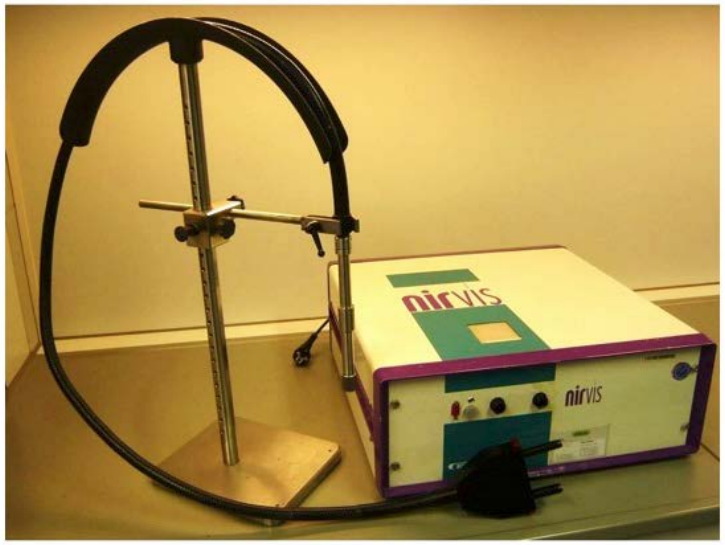
Most recently, Tomas focused his attention on the development of microdevices and microsensors, forecasting that success in this field would reward those who could "plagiarize from nature," allowing the use of miniaturization and machine intelligence to return measurement power to the end user (Hirschfeld T: Instrumentation in the next decade. Science 230:286–91, 1985). His premature death reminds us that there are areas in which nature's engineering could be improved upon; his vision and enthusiasm inspire those of us who knew him to redouble our efforts in that direction.

Howard M. Shapiro, M.D.
West Newton, Massachusetts 02165

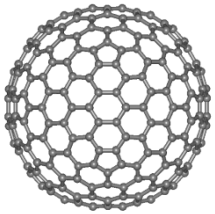
What happened in 20 years between 1998 and 2018 ?

… this is your new instrument

You should work with **New Infrared Spectroscopy (NIRS) !!**



1998 2001 2006 2003 2008



TREND IN ANALYTICAL CHEMISTRY

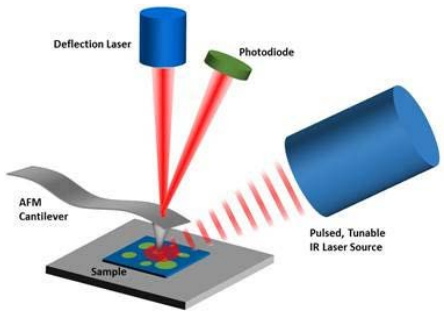
Analytical Chemistry

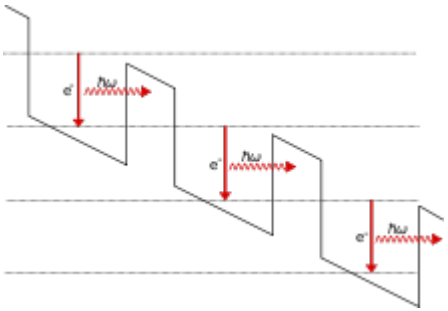
Higher Performance

- Resolution
- Sensitivity
- Selectivity

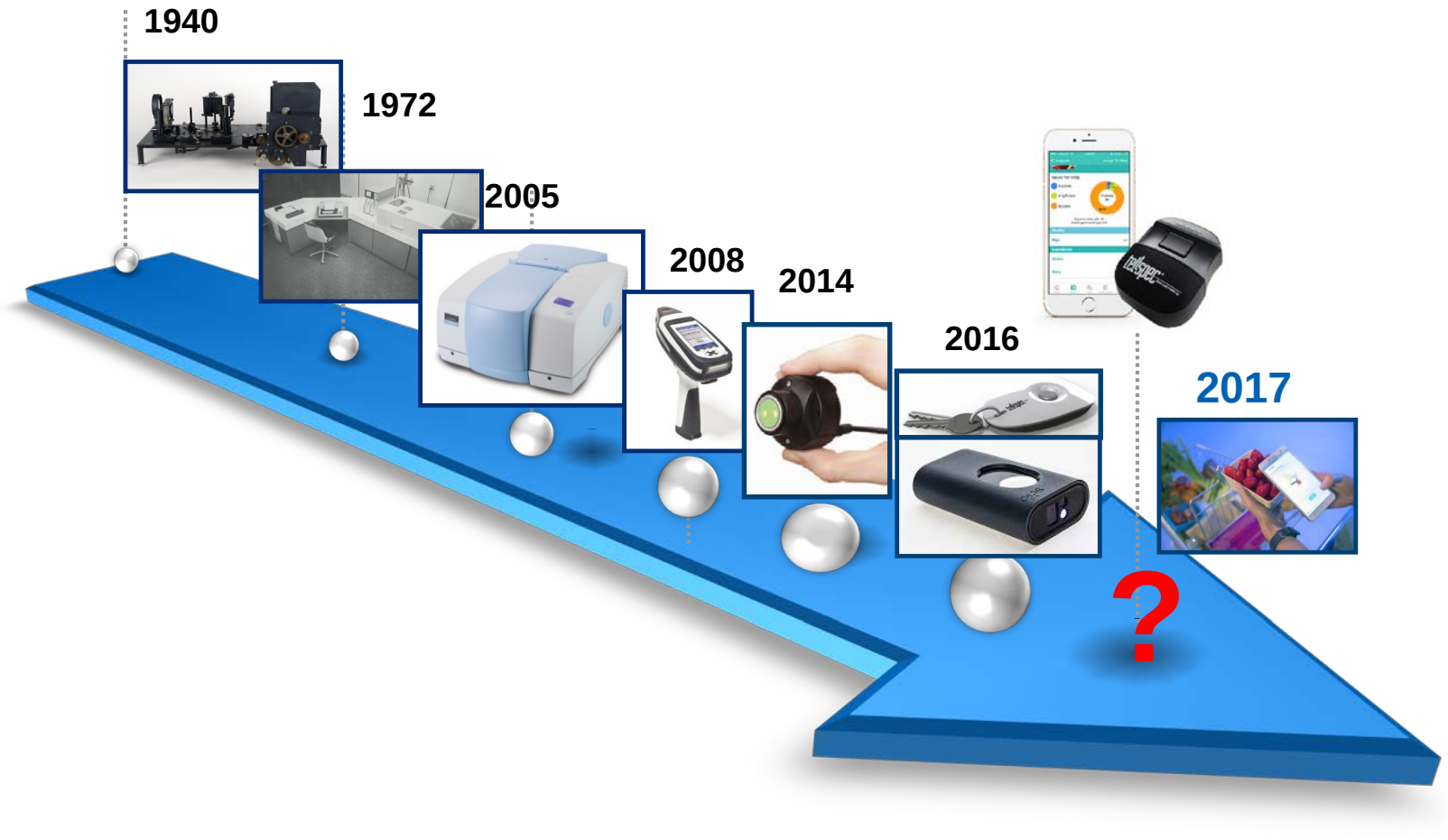
Miniaturisation

- Small, portable
- Cheap
- Easy use





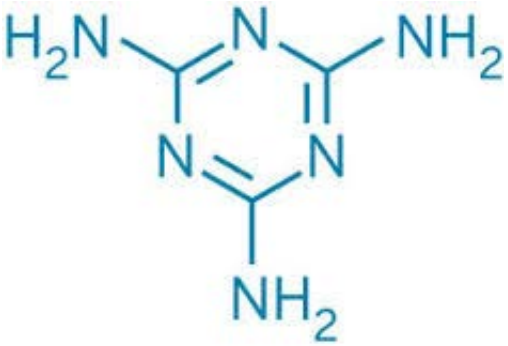
TREND IN ANALYTICAL CHEMISTRY



Huck, C.W. Hocheffiziente neue Schwingungsspektroskopische Methoden. GIT-Laborfachzeitschrift, 5, 2-5 (2016)

MOTIVATION

MILK SCANDAL IN 2008



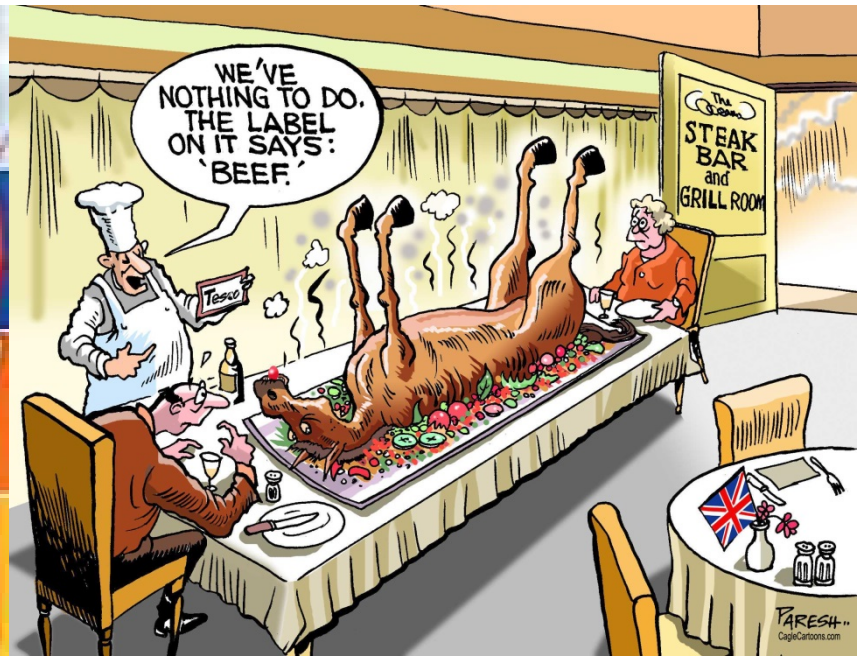
Melamine

China reported an estimated 300,000 victims in total. Six infants died from kidney stones and other kidney damage with an estimated 54,000 babies being hospitalized

Branigan, Tania (2 December 2008). "Chinese figures show fivefold rise in babies sick from contaminated milk". The Guardian. London.

MOTIVATION

HORSE MEAT SCANDAL IN 2013



Of 27 beef burger products tested, 37% were positive for horse DNA, and 85% were positive for pig DNA.

"FSAI Survey Finds Horse DNA in Some Beef Burger Products". Food Safety Authority of Ireland. 15 January 2013. Retrieved 16 January 2013.

Charlebois S., Schwab A., Henn R., Huck C.W. An exploratory study for measuring consumer perception towards mislabeled food products and influence on self-authentication intentions. Trends Food Sci. & Technol., 50, 211-218 (2016)

Examples of recent severe food safety incidents

Year	Incident	Region	Fatal casualties [persons]	Other health injuries [persons]	Estimated economy hit [EUR]
2017	Fipronil eggs contamination	EU	N/A	N/A	not yet estimated
2016	Plastic contamination of Mars chocolate	Worldwide (55 countries)	N/A	N/A	>10 M
2016	Punjab sweet poisoning	Pakistan	33	52	N/A
2015	*Escherichia coli* outbreak	US	N/A	22	>80 M
2013	Horse meat scandal	EU	N/A	N/A	N/A
2008	Milk adulteration with melamine	China	6	300 000	N/A
2007	Salmonella contamination of Cadbury sweet	UK	N/A	42	N/A

APPLICATION FIELDS

NIR, ATR, Raman, Imaging/Mapping

Material analysis

Medicinal Plants

- Harvest time
- Fast Quality Control
- Provenience

Food

- Safety, fraud
- Fast Quality Control
- Provenience

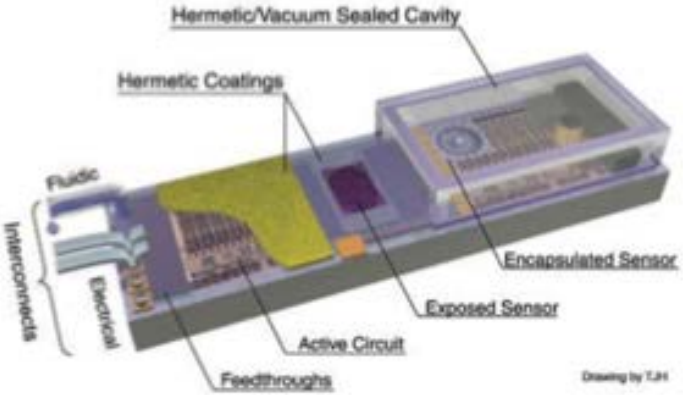
Bioanalysis

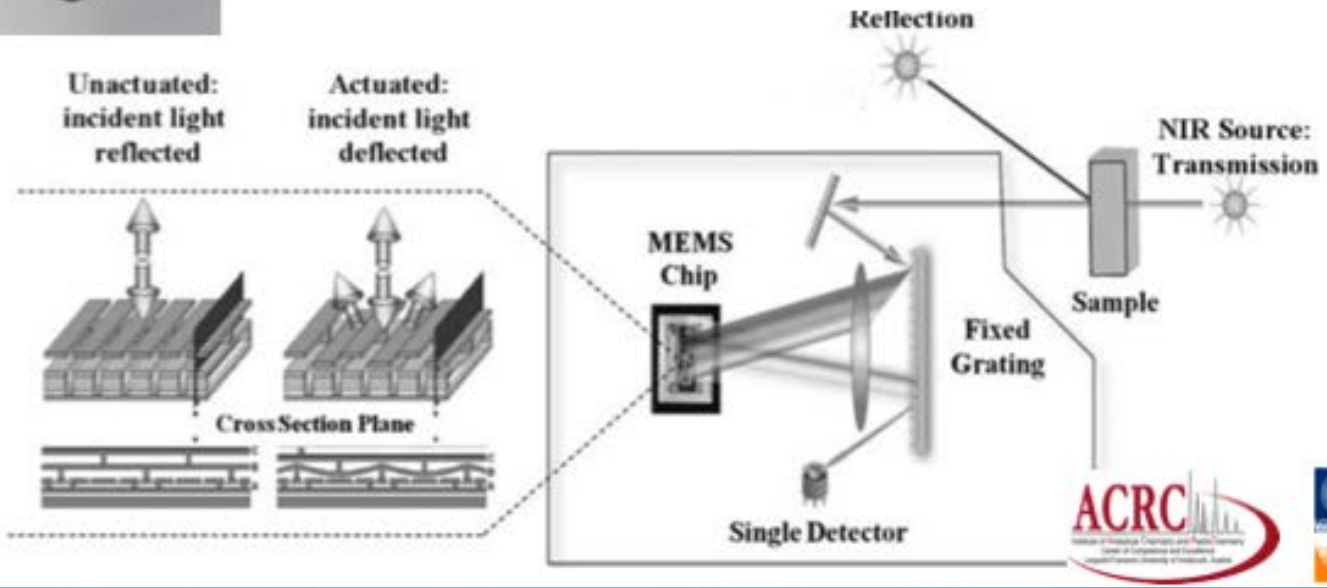
- Cancer Research

Huck C.W. Advances of Vibrational Spectroscopic Technologies in Life Sciences. Molecules, 22, 278 (2017)
Türker-Kaya S., Huck C.W. A review of mid-infrared and near-infrared imaging: principles, concepts and applications in plant tissue analysis. Molecules, 22, 168 (2017)
Huck C.W. Selected latest applications of molecular spectroscopy in natural product analysis. Phytochem. Lett., http://dx.doi.org/10.1016/j.phytol.2016.12.028 (2016)

Miniaturisation

MEMS is an acronym for **micro-electro-mechanical Systems**

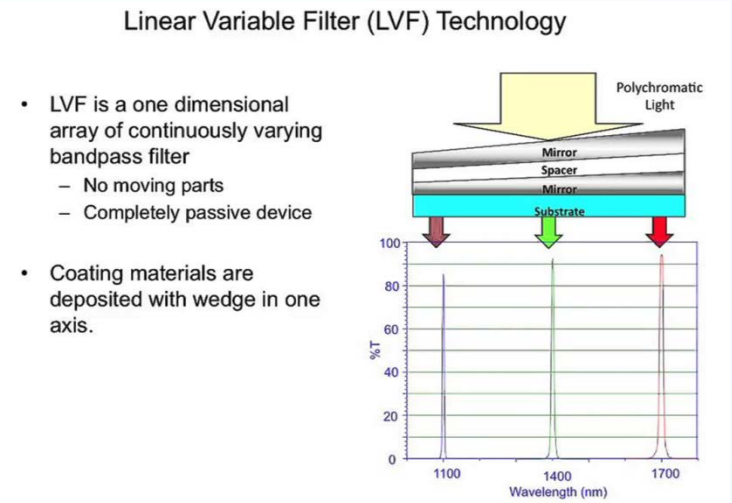




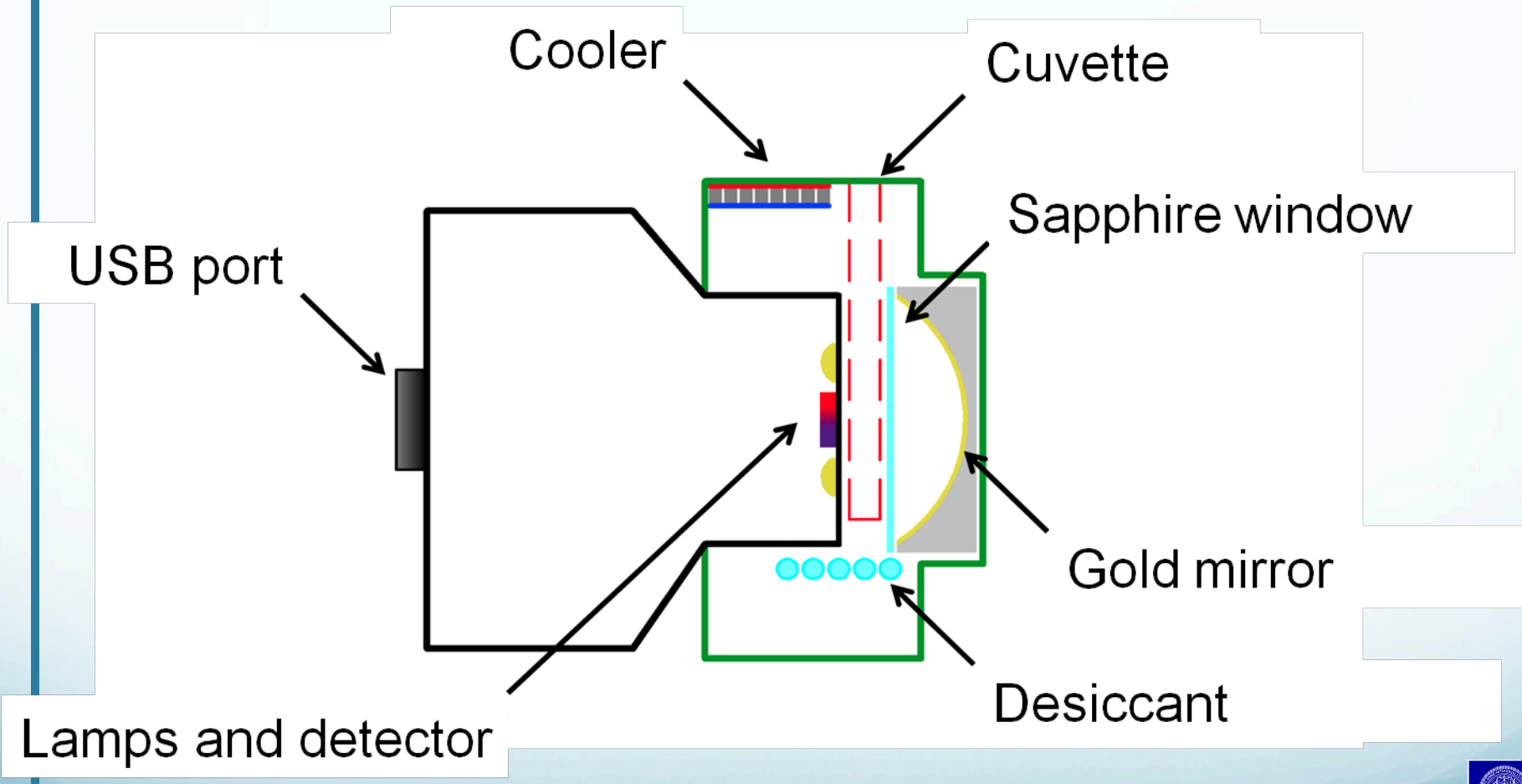
Miniaturisation

…developed by JDS Uniphase Corporation

- worlds smallest NIR spectrometer
- extremely fast analyses
- highly cost-effective
- USB powered



Miniaturisation



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Miniaturisation

EU directive 2009/28/EG:

“Enforced use of ecologically derived fuel in the transport sector“

- gasoline containing ≤ 5% wt. EtOH
- gasoline containing ≤ 10% wt. EtOH

A mobile quantification platform is desirable!

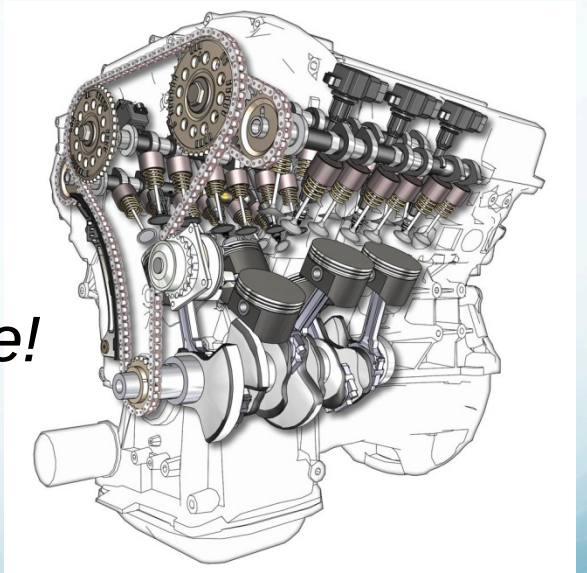

Image: Swaroopvarma *via* Wikipedia, *2006*, Public Domain

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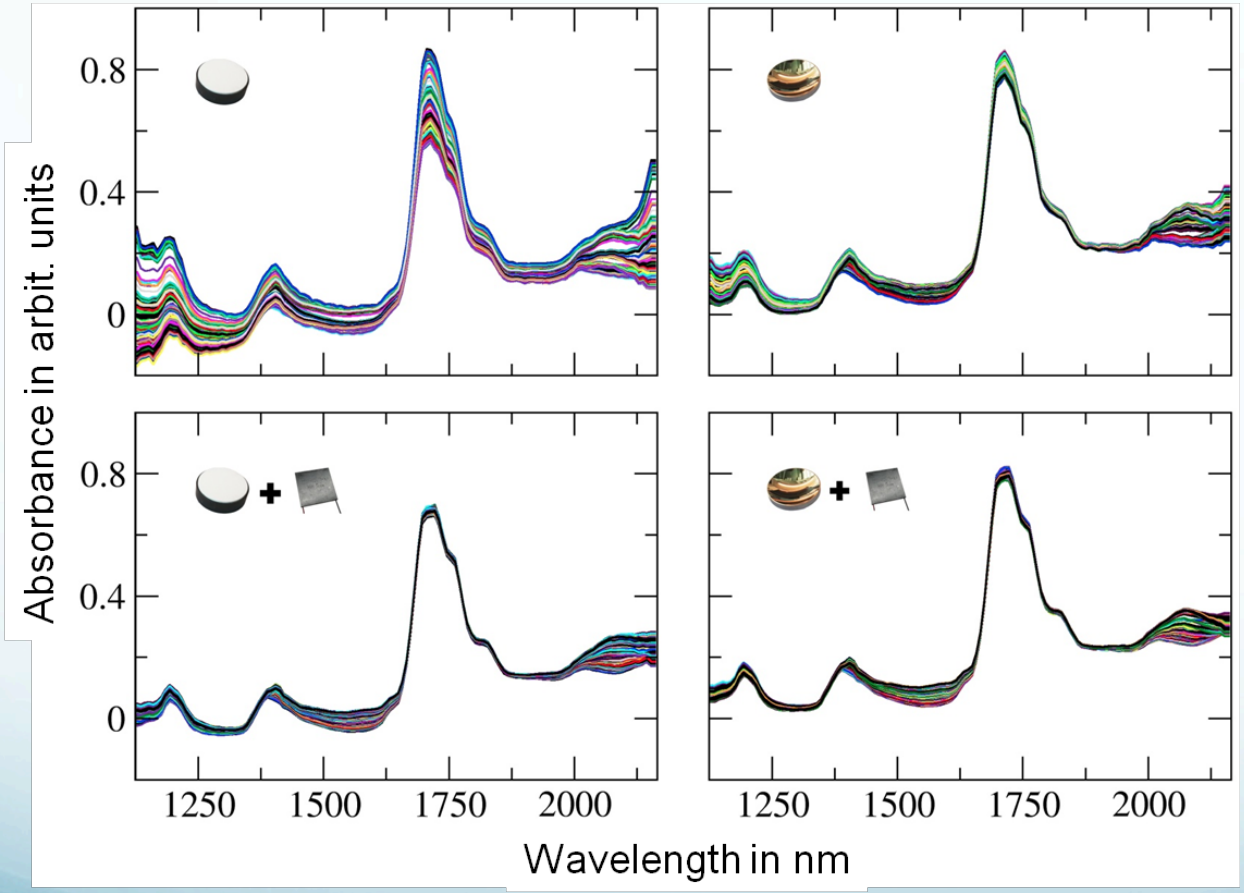
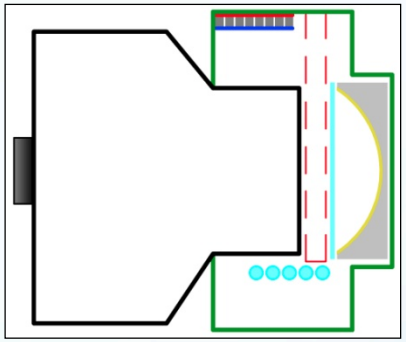
Miniaturisation

NIR spectra of gasoline with up to 10% w/w ethanol





Lutz O.M.D., Bonn G.K., Rode B.M. & Huck C.W.
Analytica Chimica Acta *2014 826 61*

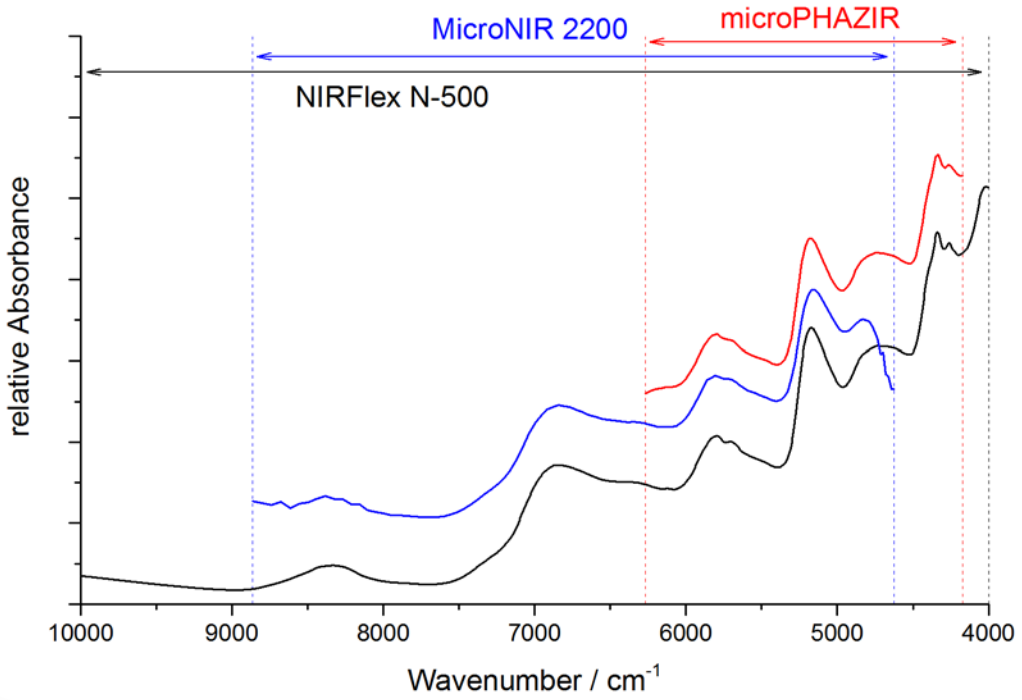
Miniaturisation

The PLS regression models of ethanol admixed gasoline

	R^2_{val}	SEP (%)	LOD (%)	LOQ (%)
	0.483	2.45	8.68	26.04
	0.993	0.35	0.93	2.79
 + 	0.991	0.33	1.37	4.11
 + 	0.997	0.21	0.68	2.04

benchtop vs. miniaturization

device	wavenumber range / cm^{-1}	resolution / cm^{-1}
NIRFlex N-500	10000 - 4000	8
microPHAZIR	6266 - 4173	Ø 21
MicroNIR 2200	8865 - 4626	Ø 33



NIRFlex N-500

microPHAZIR

MicroNIR 2200

Therefore,
new approaches for
more critical evaluation is needed!

WORKFLOW

benchtop

miniaturization

NIR-spectroscopy

reference measurements

HΨ = EΨ
quantum chemical calculation

multivariate data analysis

$\mathbf{X} = \mathbf{T}\,\mathbf{P}^{T} + \mathbf{E}$

2D-COS

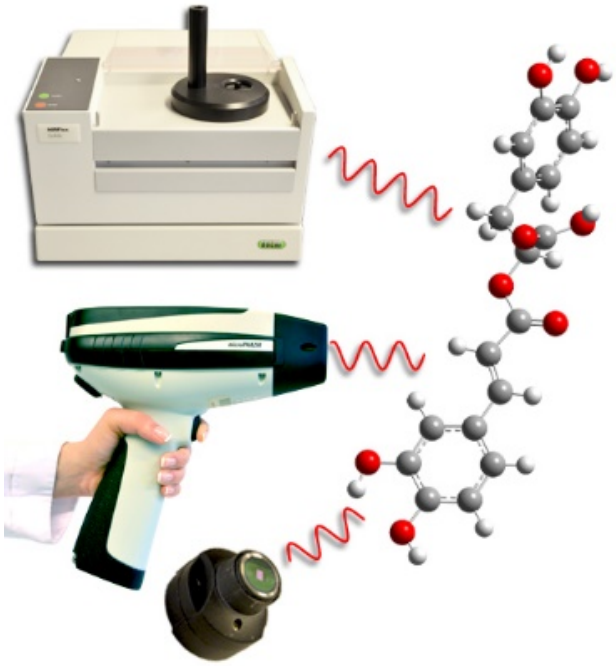
mLOD

critical evaluation

2D CORRELATION SPECTROSCOPY
„the eye of the spectrometer“

2D-COS used as “the eye of the spectrometer“

Visual perception



Example: rosmarinic acid content in powdered rosemary leaves (60 samples).

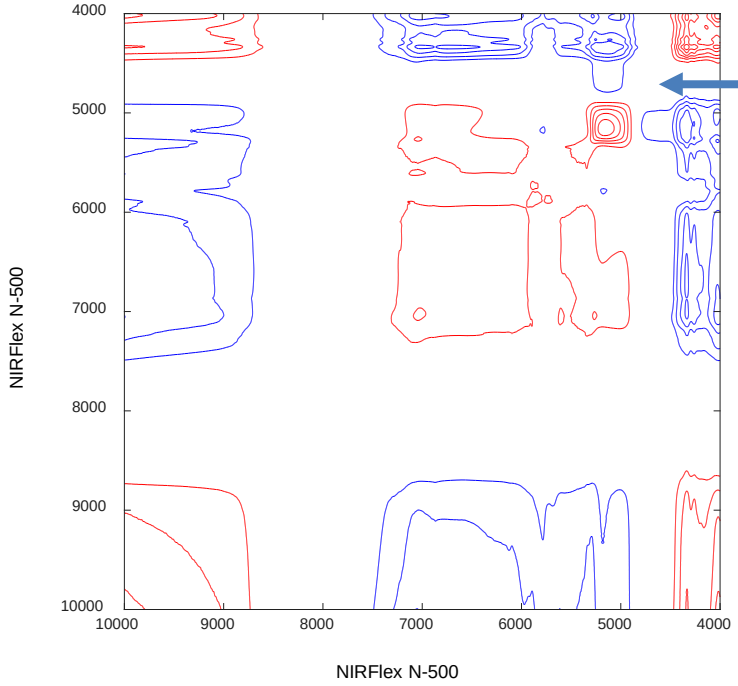
2D CORRELATION SPECTROSCOPY

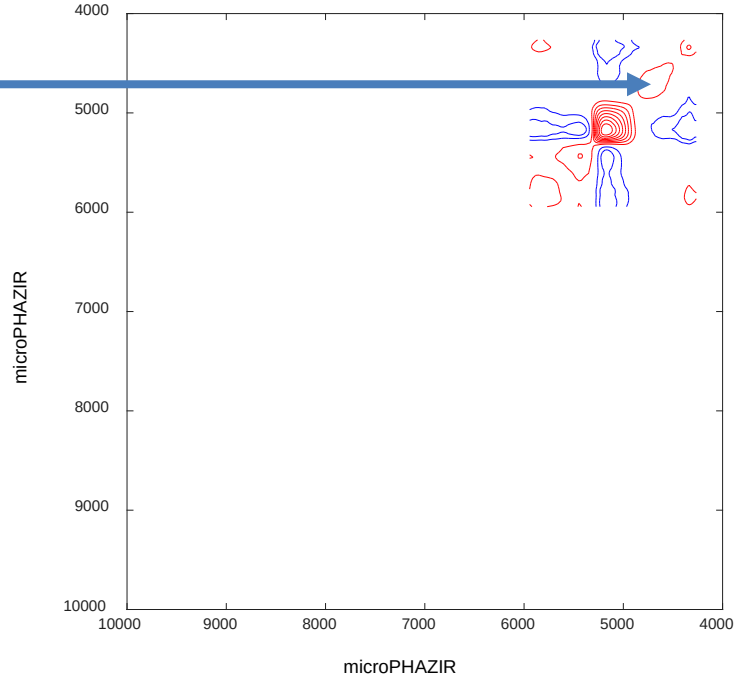
„the eye of the spectrometer“

60 rosemary samples

Benchtop „ NIRFlex N-500“

Miniaturized „microPhazir“





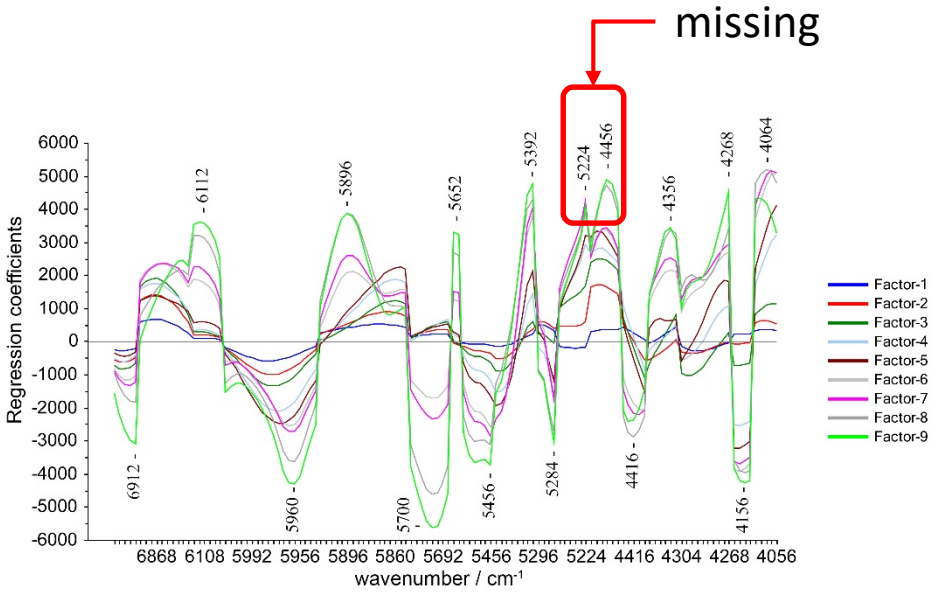
autopeak appearance in the visual perception of the microPHAZIR!

2D CORRELATION SPECTROSCOPY

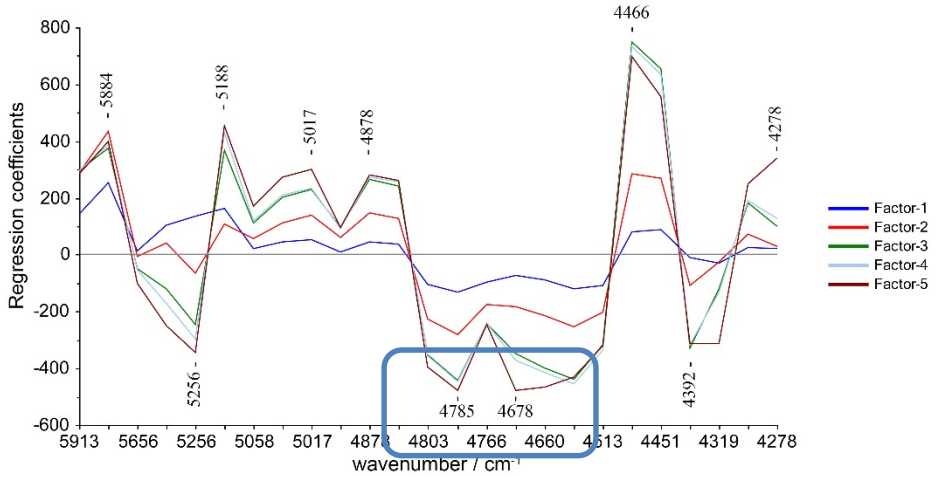
„the eye of the spectrometer“

60 rosemary samples

Benchtop „ NIRFlex N-500“



Miniaturized „microPhazir“



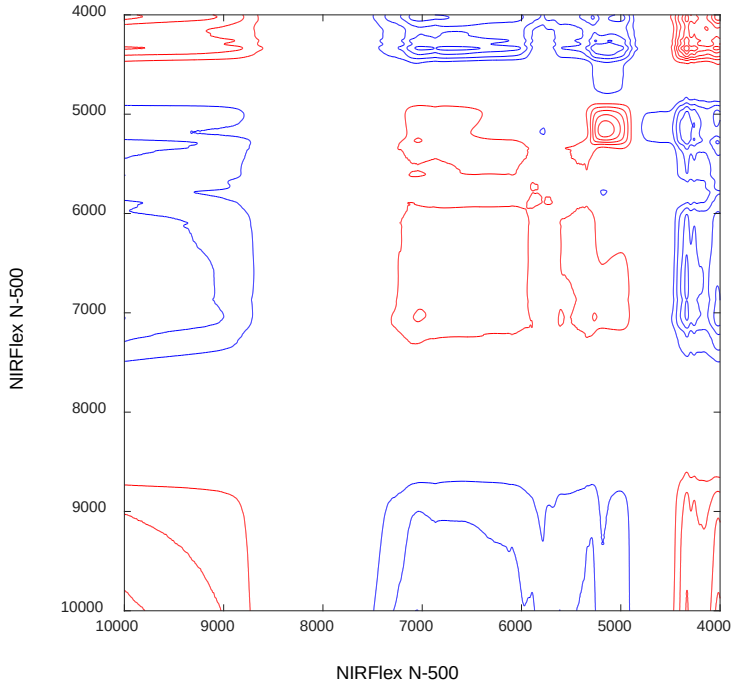
This region is crucial for the PLS-regression of microPhazir and unnecessary for NIRFlex N-500!

2D CORRELATION SPECTROSCOPY

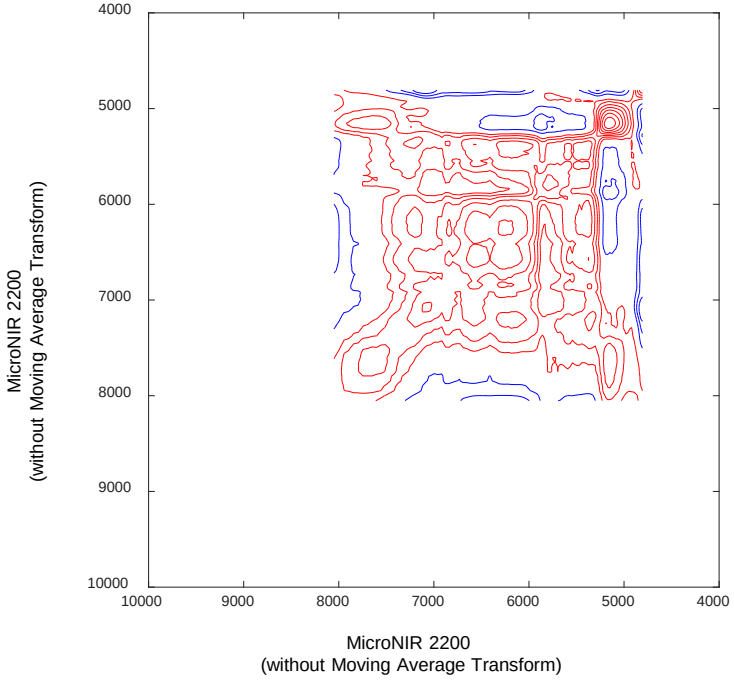
„the eye of the spectrometer“

60 rosemary samples

Benchtop „ NIRFlex N-500“



Miniaturized „MicroNIR 2200“



MicroNIR 2200: no working PLS-regression model!

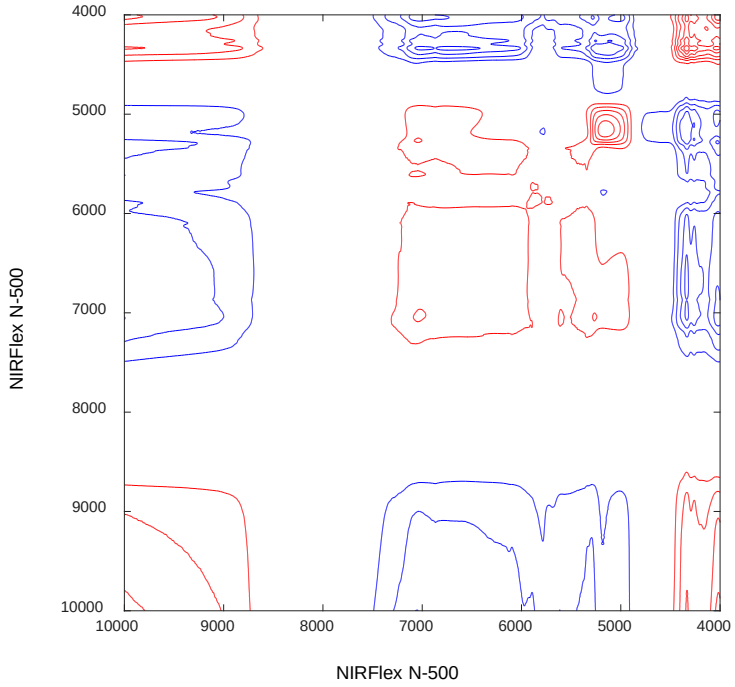
Is there something wrong?

2D CORRELATION SPECTROSCOPY

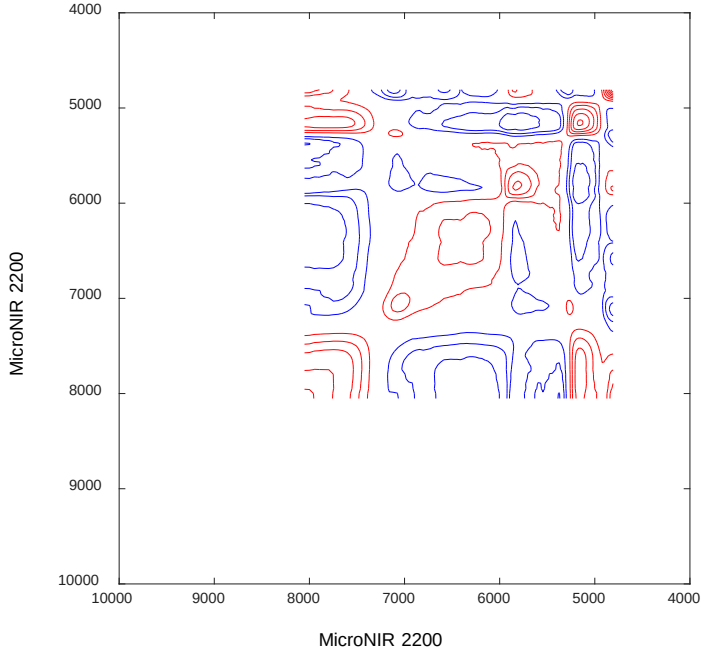
„the eye of the spectrometer“

60 rosemary samples

Benchtop „ NIRFlex N-500“



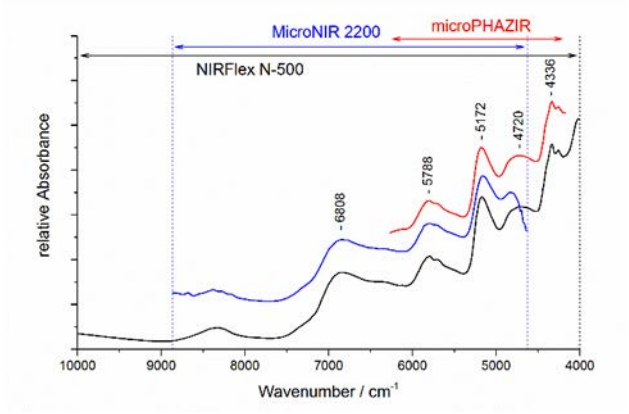
Miniaturized „MicroNIR 2200“ smoothed



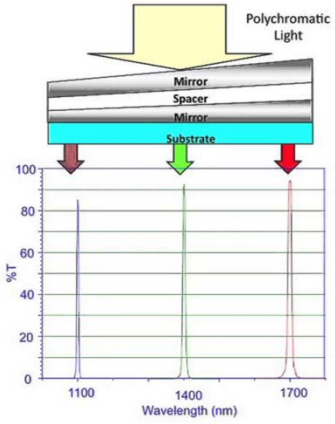
MicroNIR 2200: spectra have to be smoothed for a working PLS-regression model!

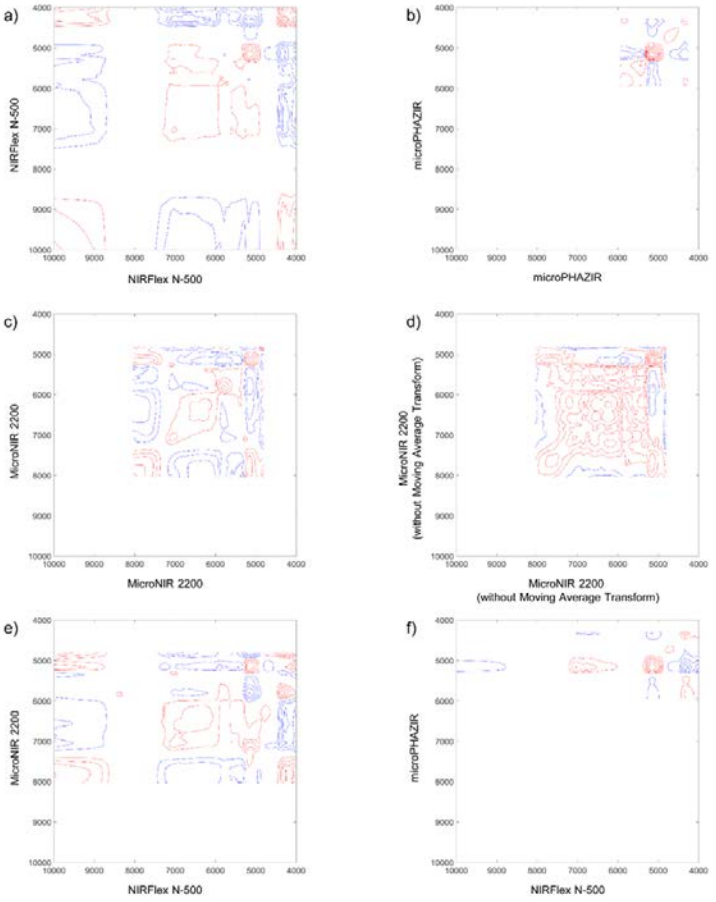
MEDICINAL PLANTS

Rosmarini folium



NIR spectra of 60 Rosmarini folium samples



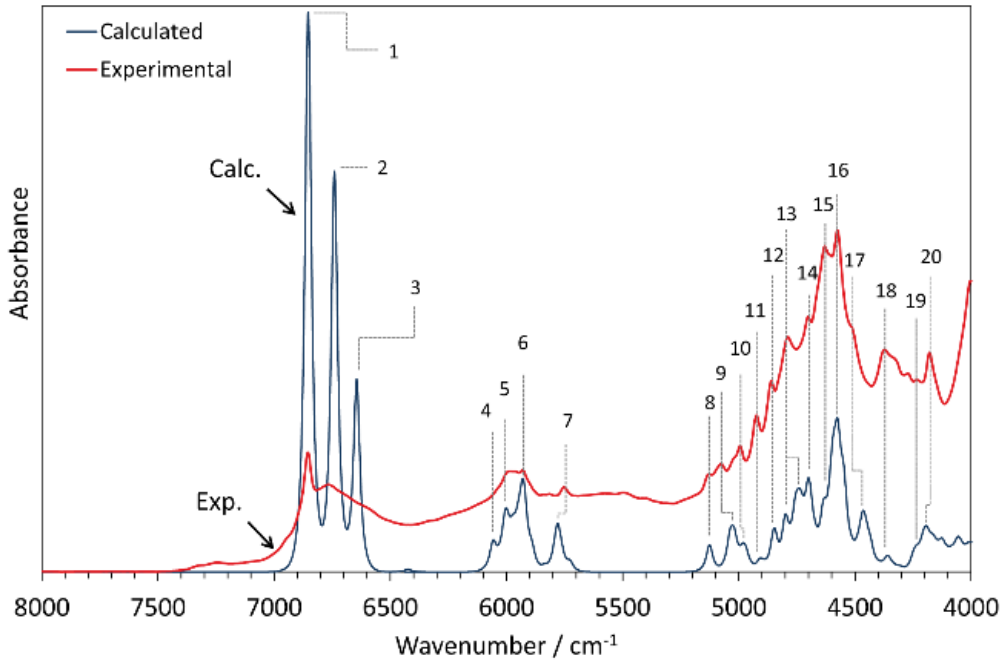


spectrometer	NIRFlex N-500		microPHAZIR		MicroNIR 2200	
samples	60		60		60	
outliers	6		8		4	
range / %	1.138 – 2.425		1.138 – 2.425		1.138 – 2.425	
validation method	CV	TSV	CV	TSV	CV	TSV
R^2	0.91	0.91	0.73	0.73	0.84	0.85
SECV / % SEP / %	0.072	0.069	0.12	0.11	0.091	0.11
SECV/SEC SEP/SEC	1.46	1.43	1.28	1.24	1.55	2.09
factors	8	8	5	5	11	12
RPD	3.27	3.41	1.88	2.06	2.46	2.14

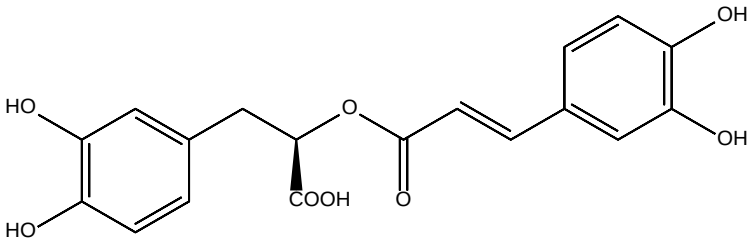
Kirchler C.G., Pezzei C.K., Bec, K.B., Mayr S., Ishigaki M., Ozaki Y., Huck C.W. Critical evaluation of spectral information of benchtop vs. portable near-infrared spectrometers: Quantum chemistry and two-dimensional correlation spectroscopy for a better understanding of PLS regression models of the rosmarinic acid content in Rosmarini folium. Analyst 142 (2017) 455

THEORETICAL NIR SPECTROSCOPY
Quantum chemical calculations

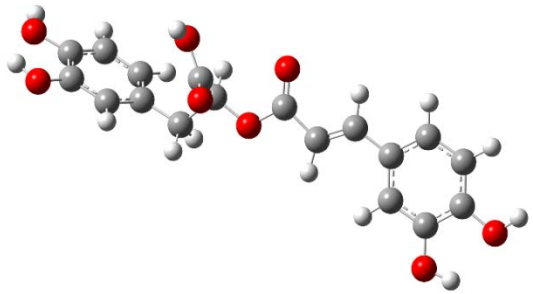
Collaboration with Dr. Krzysztof Beć



The experimental and theoretical NIR spectrum of rosmarinic acid obtained through fully anharmonic (GVPT2) DFT-B3LYP/N07D calculation.



rosmarinic acid



Optimized structure (DFT-B3LYP/N07D) of the molecule of rosmarinic acid.

Kirchler C.G., Pezzei C.K., Bec, K.B., Mayr S., Ishigaki M., Ozaki Y., Huck C.W. Critical evaluation of spectral information of benchtop vs. portable near-infrared spectrometers: Quantum chemistry and two-dimensional correlation spectroscopy for a better understanding of PLS regression models of the rosmarinic acid content in Rosmarini folium. Analyst 142 (2017) 455

THEORETICAL NIR SPECTROSCOPY
Quantum chemical calculations

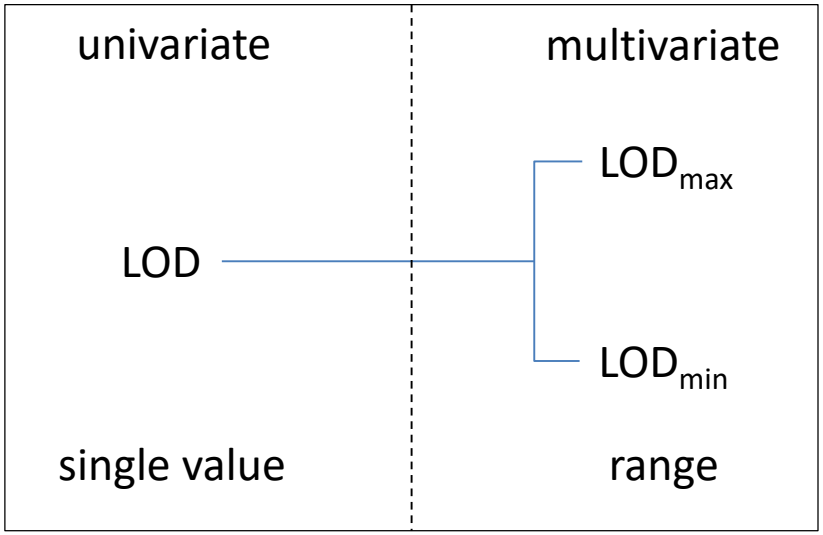
Band assignments in NIR spectrum of rosmarinic acid, based on DFT-B3LYP/N07D calculation

Wavenumber / cm^{-1}		Major contributions
Exp.	Calc.	
6854.9	6853	2νOH (ar)
5128.0	5126	[ν C=O, δ_{ip}OH (carboxyl)] + [νOH (carboxyl)]
4994.9	4980	[δ_{ring}, δ_{ip}OH (ar)] + [νOH (ar, meta-)]; [δ_{ring}, δ_{ip}OH (ar)] + [νOH (ar, meta-)]
4788.3	4798	[νCC] + [νOH (ar, para-)]; [νCC] + [νOH (ar, para-)]; [νCC] + [νOH (ar, meta-)]; [δCCH (carboxyl)] + [νOH (carboxyl)]; [δCH (ar), δ_{ip}OH (ar)] + [νOH (ar, para-)]; [δCH (ar), δ_{ip}OH (ar)] + [νOH (ar, para-)]
4701.0	4701	[δCH (aliph)] + [νOH (ar, meta-)]; [δCH (ar), δ_{ip}OH (ar)] + [νOH (ar, meta-)]
~4508	4465	[δ_{ring}, δ_{ip}OH (ar)] + [νCH (ar)]; [δ_{ring}] + [νCH (ar)]; [δ_{ring}, δ_{ip}OH (ar)] + [νCH (ar)]; [νC-O (carboxyl), δ_{ip}OH (carboxyl)] + [νOH (carboxyl)]; [δ_{ring}] + [νCH (ar)]; [δ_{ring}, δ_{ip}OH (ar)] + [νCH (ar)]
4179.4	4194	[δCH (aliph)] + [νCH (ar, aliph, opp.-phase)]; [δ_{sciss} CH_2] + [$\nu_s CH_2$]; [δCH (aliph)] + [νCH (ar, aliph, in-phase)]

multivariate approach for calculating the LOD.

Problem: instrumental signals are not specific for a particular analyte.

Instead of a single LOD value, an LOD interval is calculated which depends on the variability of the background composition of the calibration samples.

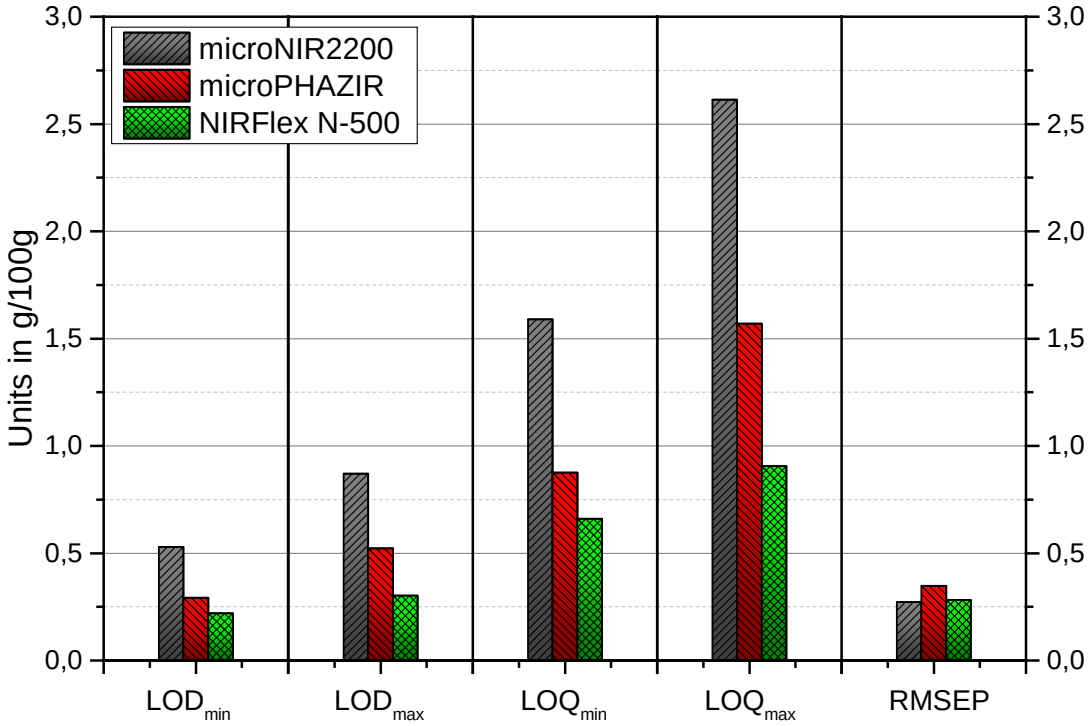


F. Allegrini, A.C. Olivieri, IUPAC-Consistent approach to the limit of detection in partial least-squares calibration. Anal. Chem. 86 (15) (2014) 7858–7866

Determining melamine in milk powder

device	LOD_{min}	LOD_{max}	RMSEP
MicroNIR 2200	0.53	0.87	0.27
microPHAZIR	0.29	0.52	0.35
NIRFlex N-500	0.22	0.30	0.28

LOD, LOQ and RMSEP values in %.

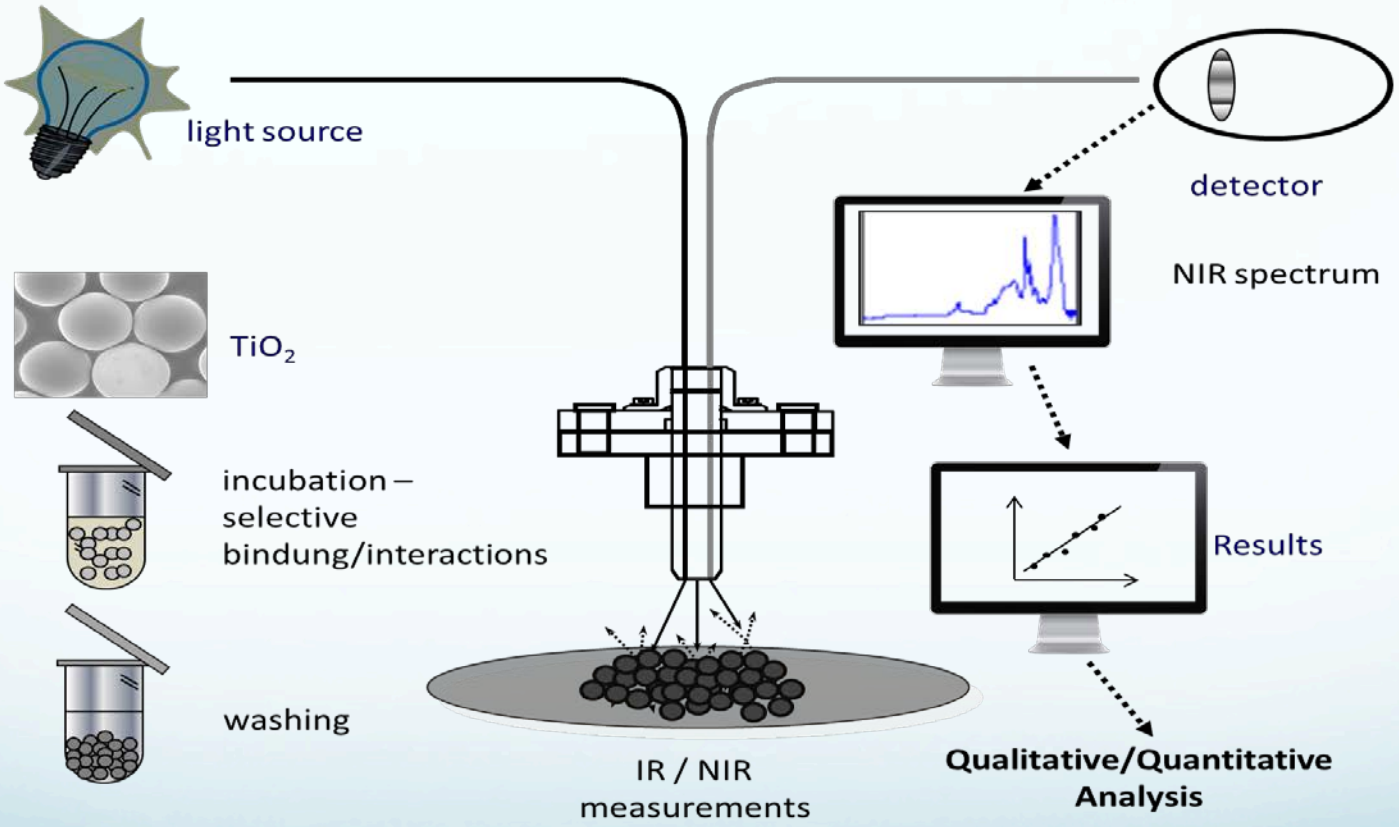


LOD, LOQ and RMSEP values of the used spectrometers in comparison.

Henn R., Kirchler C.G., Grossgut M.E., Huck C.W. Comparison of sensitivity to artificial spectral errors and multivariate LOD in NIR spectroscopy – Determining the performance of miniaturizations on melamine in milk powder. Talanta 166 (2017) 109-118

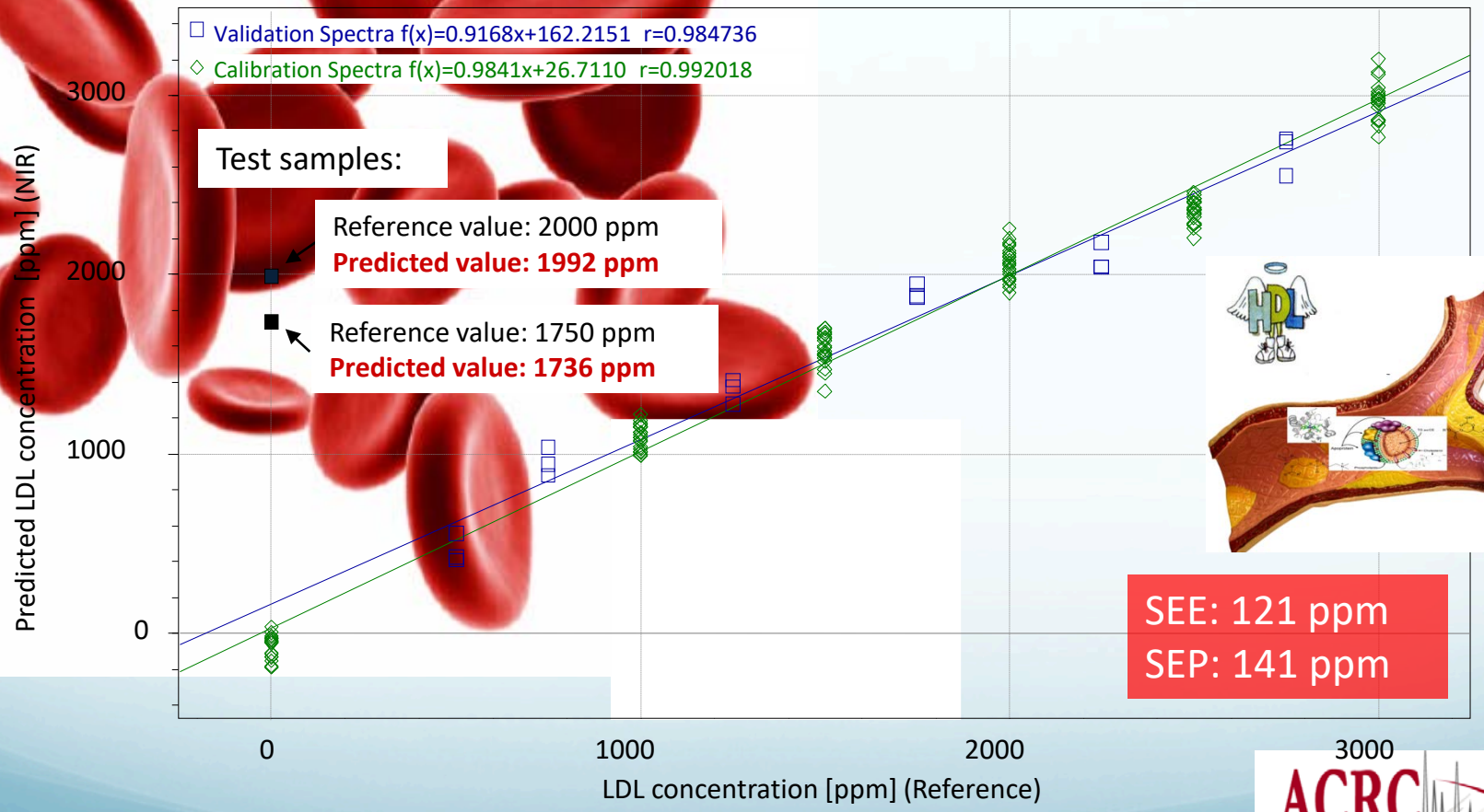
SEIRS

Surface enhanced infrared spectroscopy



LDL-cholesterol

TiO_2 beads were used as an adsoption material for selectively removing LDL-cholesterol from aqueous liquids, in particular plasma or serum



PCR model for predicting the LDL concentration bound onto TiO_2 beads

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Leopold-Franzens University of Innsbruck, Austria

universität innsbruck

Received: 4 December 2017 | Accepted: 22 February 2018

DOI: 10.1002/jbio.201700365

Journal of BIOPHOTONICS

FULL ARTICLE

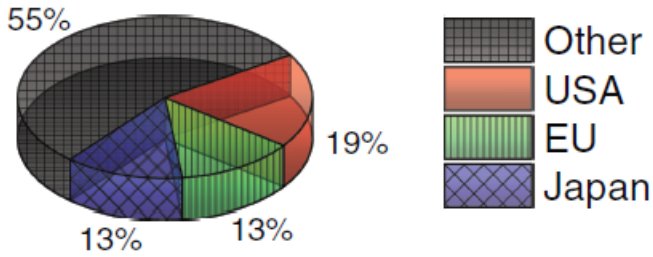
Hemodialysis monitoring using mid- and near-infrared spectroscopy with partial least squares regression

Raphael Henn[1†] | Christian G. Kirchler[1†] | Zora L. Schirmeister[1,2] | Andreas Roth[2] | Werner Mäntele[2] | Christian W. Huck[1*]

TABLE 3 PLSR results for the 5-component mixture in dialysate derived from MIR and NIR spectra

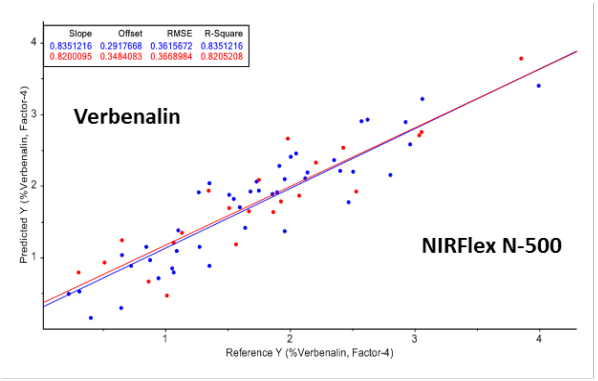
Model			PT	Spectral regions in cm^{-1}	Factor	R^2	RMSECV in mg/dL	RMSEP in mg/dL	LOD_{min} in mg/dL	LOD_{max} in mg/dL	LOQ_{min} in mg/dL	LOQ_{max} in mg/dL
Urea	CV	NIR	SNV	8648-7348	4	0.97	12	—	10	24	29	72
				6332-5496								
				4584-4508								
		MIR	mc	1794-1324	4	0.99	7.9	—	7.3	16	22	47
			SG 1/17	1201-1075								
	TV	NIR	SNV	8648-7348	4	0.98	—	19	—	—	—	—
				6332-5496								
				4584-4508								
		MIR	mc	1794-1324	5	0.99	—	6.6	—	—	—	—
			SG 1/17	1201-1075								
Glucose	CV	NIR	SNV	9004-8664	4	0.89	37	—	36	73	108	218
				6320-5756								
		MIR	mc	1451-1324	3	0.96	22	—	11	34	33	103
			SG 2/17	1201-950								
	TV	NIR	SNV	9004-8664	4	0.86	—	54	—	—	—	—
				6320-5756								
		MIR	mc	1451-1324	2	0.99	—	11	—	—	—	—
			SG 2/17	1201-950								
Lactate	CV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1777-1700	5	0.95	8.3	—	6.5	14	20	43
			SG 1/17	1576-1324								
				1201-1075								
	TV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1777-1700	8	0.99	3.0	—	—	—	—	—
			SG 1/17	1576-1324								
				1201-1075								
Phosphate	CV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1201-950	8	0.99	1.1	—	0.5	1.9	1.6	5.6
	TV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1201-950	8	0.95	—	2.0	—	—	—	—
Creatinine	CV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1777-1700	5	0.98	1.5	—	1.9	3.5	5.8	11
			SG 1/17	1576-1075								
	TV	NIR	—		—	—	—	—	—	—	—	—
		MIR	mc	1777-1700	4	0.96	—	2.1	—	—	—	—
			SG 1/17	1576-1075								

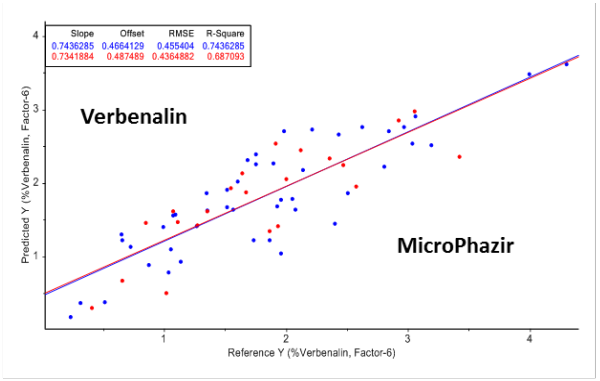
Abbreviations: -, value not available; PT, data pretreatments; mc, mean centering; SG x/y, Savitzky-Golay derivative (x, derivative order; y, number of smoothing points); SNV, standard normal variate; CV, cross-validation; TV, test-set validation.

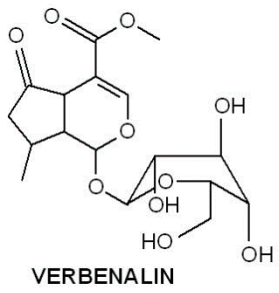


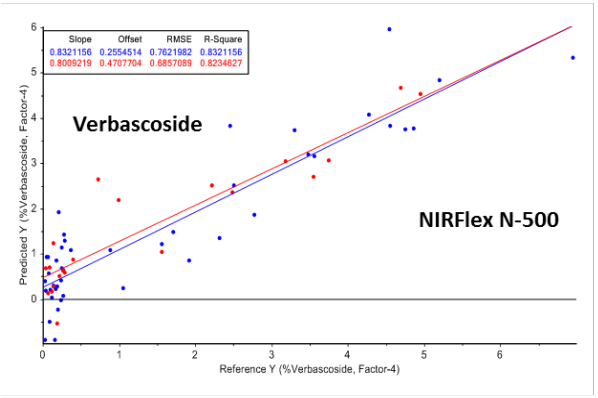
global dialysis patients 2013 (total = 2.552.000)

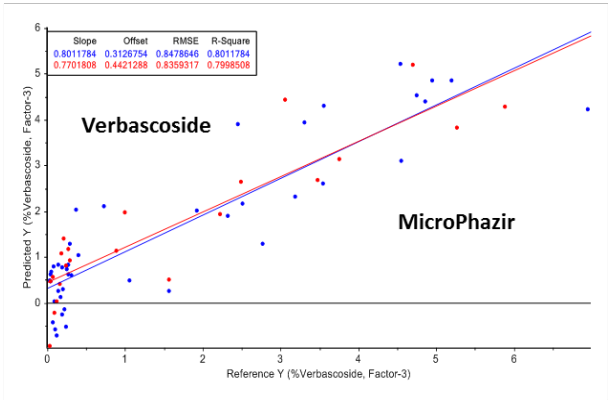
Verbena officinalis

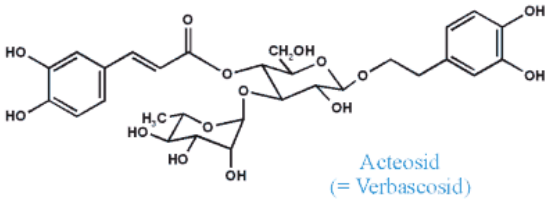






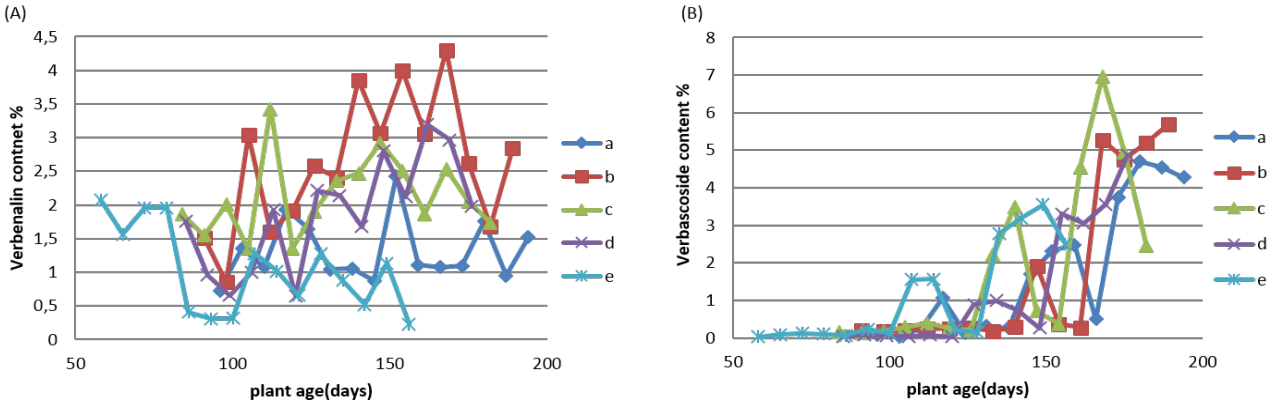


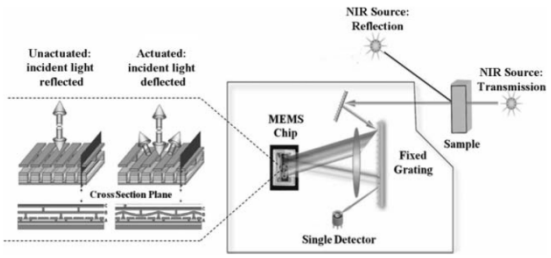




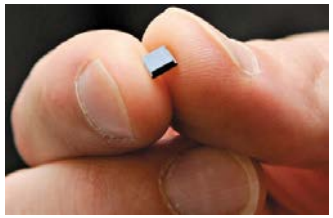
Schönbichler S.A., Bittner L.K.H., Pallua J.D., Popp M., Abel G., Bonn G.K., Huck C.W.
Simultaneous Quantification of Verbenalin and Verbascoside in Verbena officinalis by ATR-IR and NIR Spectroscopy
J. Pharm. Biomed. Anal. 84, 97 - 102 (2013)

Verbena officinalis





Graphical representation of the verbenalin (a) and verbascoside (b) content related to the dried plant material during flowering. Letter a-e stand for the five different seeding dates in March and April.

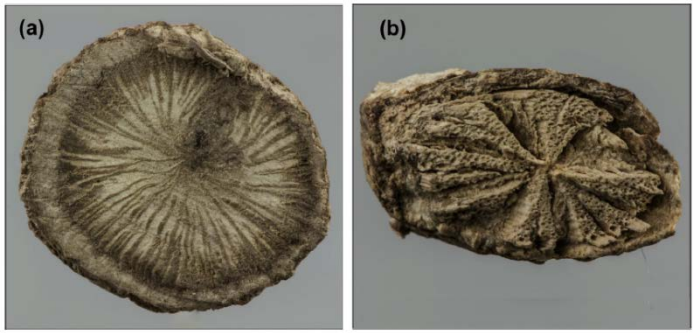


Pezzei C.K.; Schönbichler S.A.; Kirchler C.G.; Schmelzer J.; Hussain S.; Huck-Pezzei V.A.; Popp M.; Krolitzek J.; Bonn G.K.; Huck C.W. Application if benchtop and portable near-infrared spectrometers for predicting the optimum harvest time of Verbena officinalis
Talanta, 2017, http://dx.doi.org/10.1016/j.talanta.2017.03.067

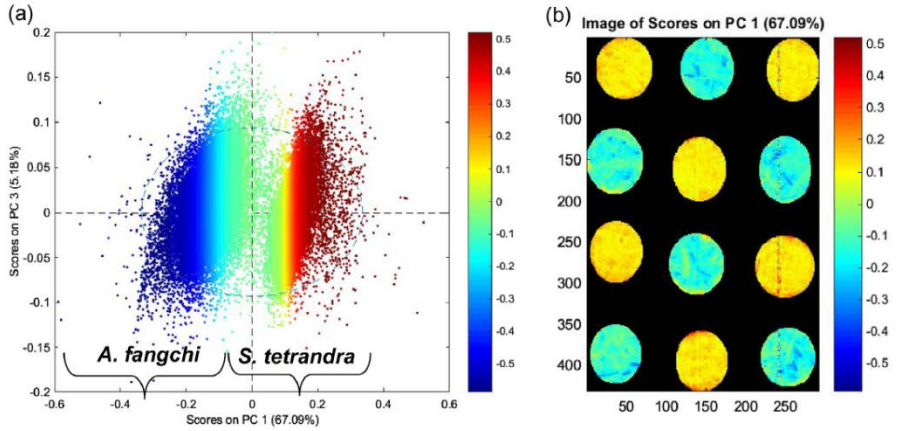
Applications NIR Imaging

Discrimination of different plant samples

Stephania tetrandra (‘‘hang fang ji”) and Aristolochia fangchi (‘‘guang fang ji”) are two different plant species used in Traditional Chinese Medicine (TCM). Both are commonly referred to as ‘‘fang ji” and S. tetrandra is mistakenly substituted and adulterated with the nephrotoxic A. fangchi as they have several morphological similarities. A. fangchi contains aristolochic acid, a carcinogen that causes urothelial carcinoma as well as aristolochic acid nephropathy (AAN).



Root material of the two traditional Chinese medicines called ‘‘fang ji”: (a) Aristolochia fangchi and (b) Stephania tetrandra



Principal component analysis of the (a) score scatter plot and (b) score image indicating the distribution of particles between the two species

Vermaak, I.; Viljoen, A.; Lindström, S.W. **Hyperspectral imaging in the quality control of herbal medicines – The case of neurotoxic Japanese star anise**. J. Pharm. Biomed. Anal. 2013, 5, 207-213.

I) Online ProcessControl in a Drier Environment

Fermentation

Reprocessing of Fermentation Broth

Scission to 7-ACA

Cefalosporin Products

Filtration

Different purification and reprocessingsteps (chromatography, osmosis, ultrafiltration)

Drying→Filling

Preliminary Compound CephC

Online Monitoring

PAT

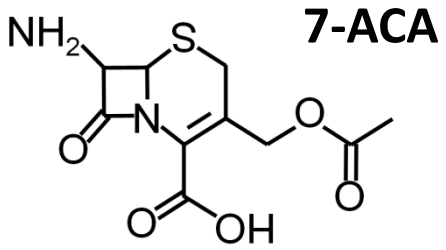
Chemical Step 1 &2 (sylilation, chloration, methanolysis, hydrolysis)

Phase Separation

Filtration →Precipitation

Centrifugation

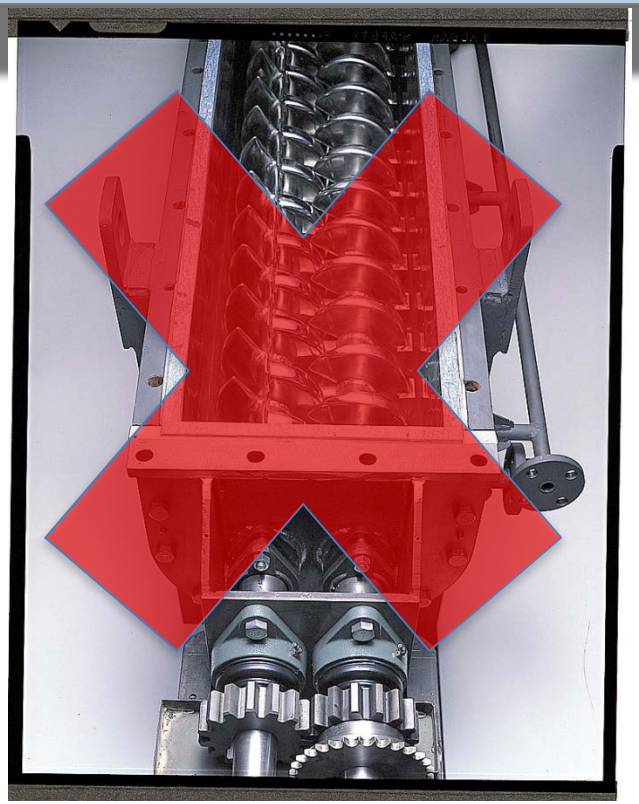
Drying →Filling

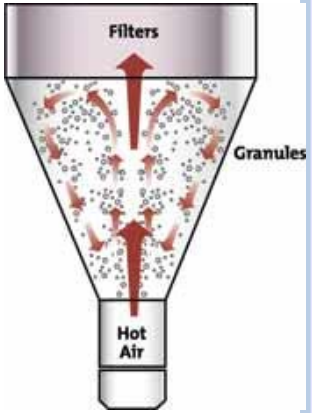


7-ACA

Quality Conformity Test

Replacement of Paddle by Fluidized Bed Dryer





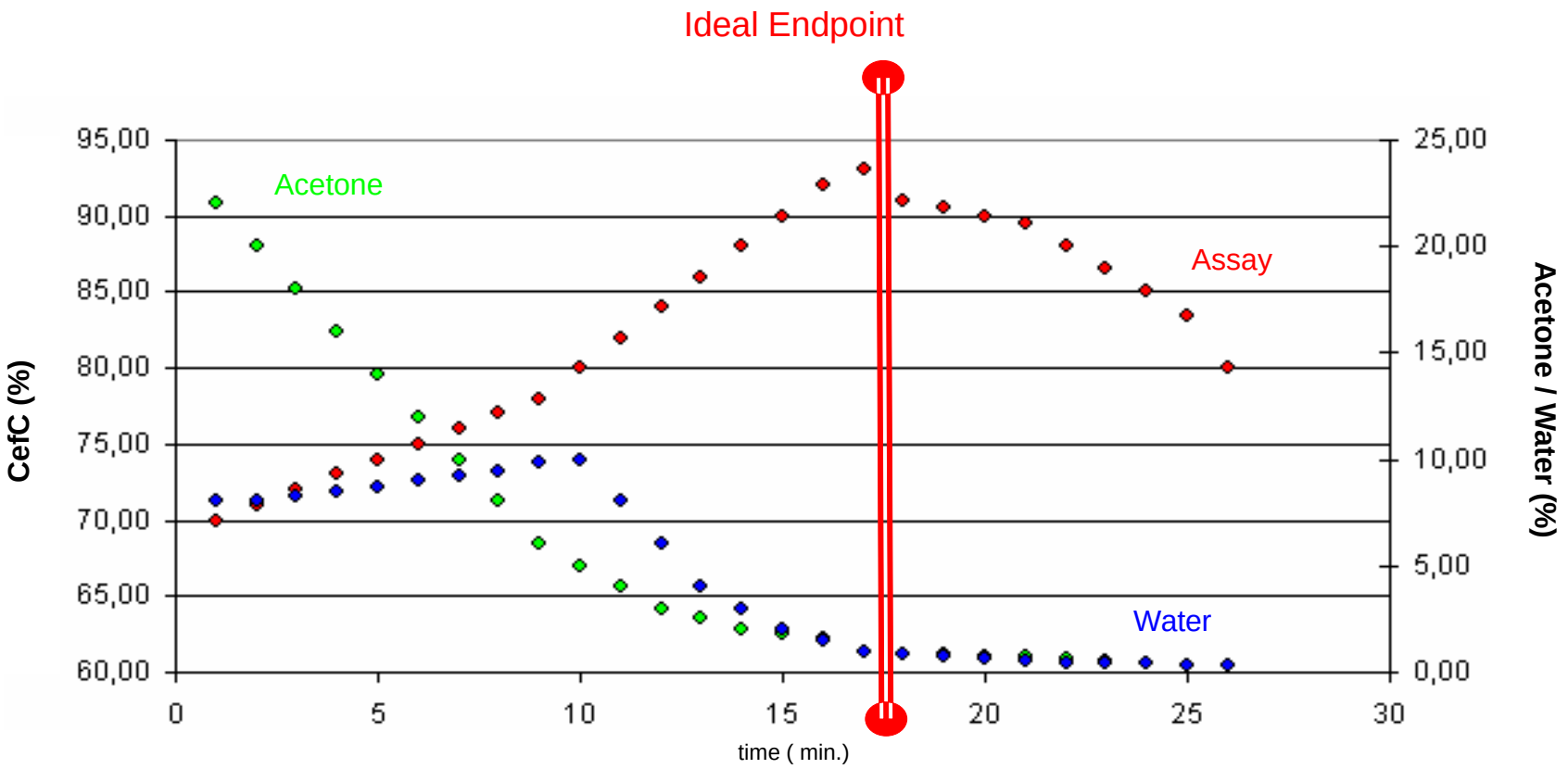
-Limitedproductquality
-Slowdryingprocess
-Mechanical stress of product
-Long-termdirectheatimpact

+ Capacityimprovement
+ Short exposure to gas

temperatures of
130° C

Monitoring of the Drying Progression

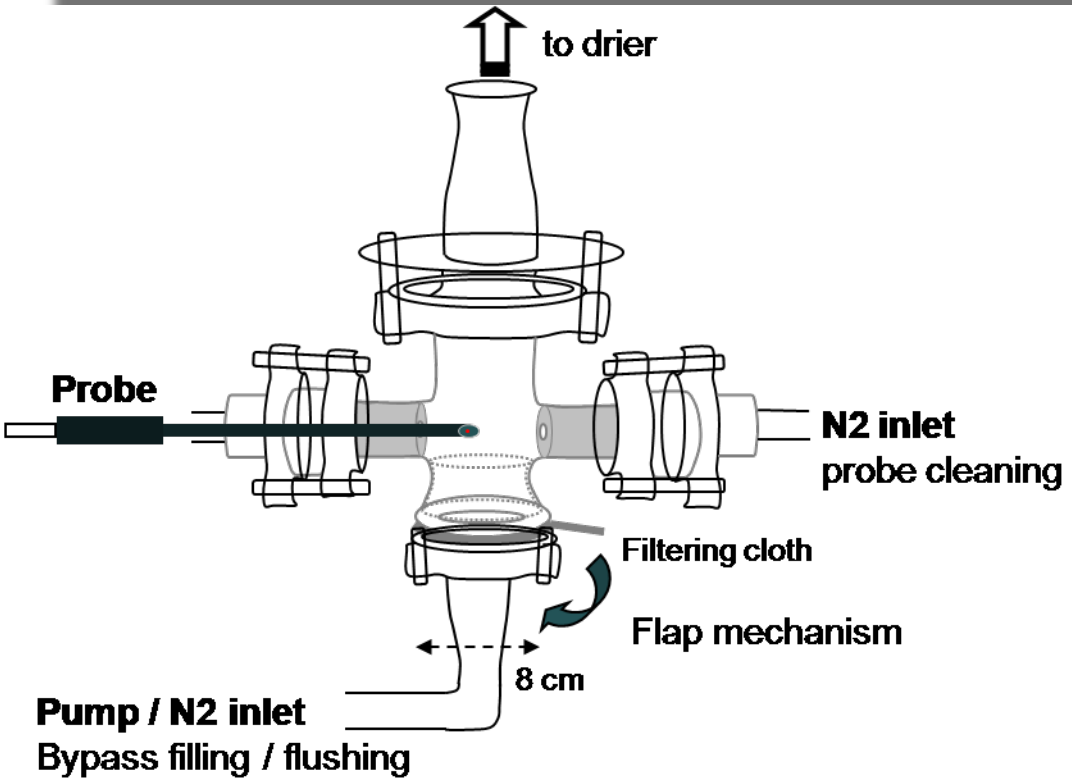
Schematic view of the drying progression

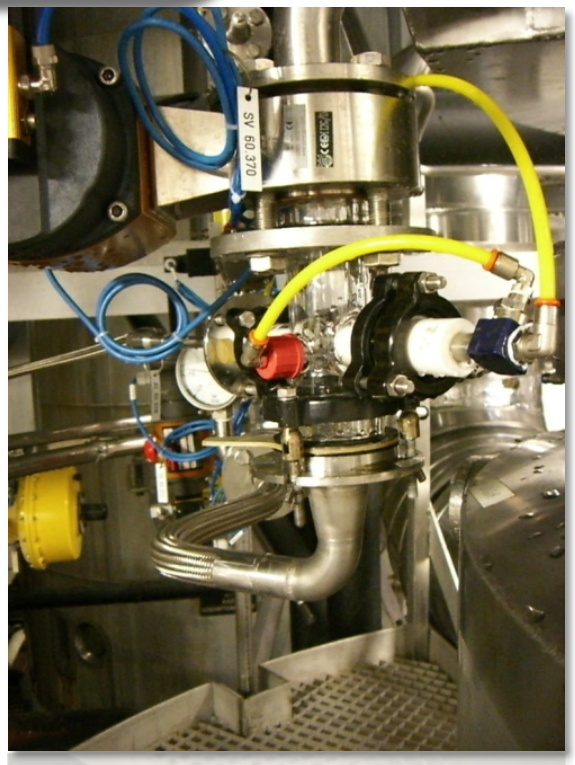


Key Parameters of the Fluidized-Bed Drying Process Related to the Mass of the Moist and Dried Products

	MOIST PRODUCT		DRIED PRODUCT
Assay	70 – 80 %	N_2-Circulation	≥ 88 %
Water content	8 – 10 %		≤ 2 %
Acetone	25 – 30 %		≤ 1 %

Installation of a Bypass System





→ quick and reliable filling/purging procedure

→ reproducible sample density

→ probe tip cleaning mechanism

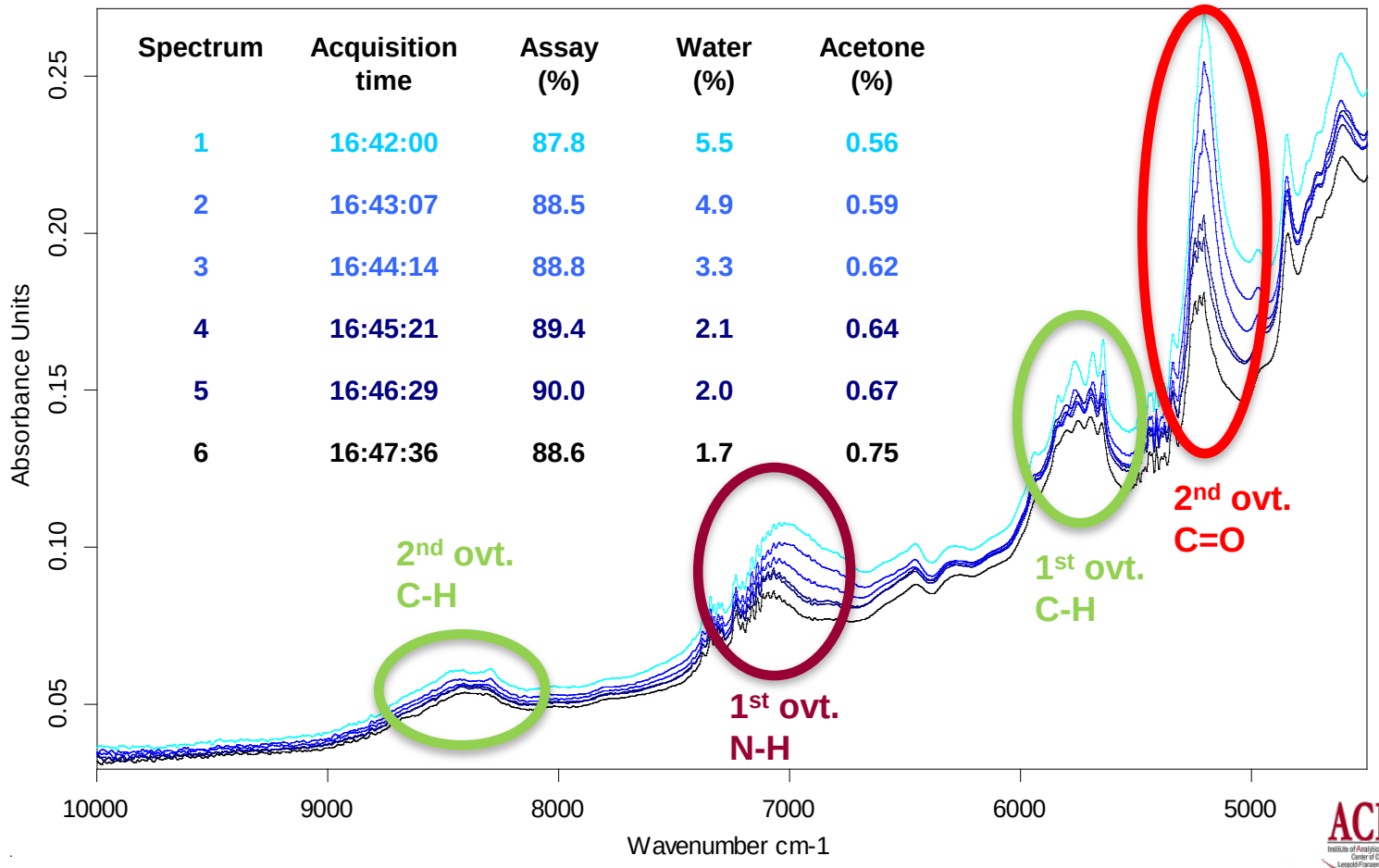
→ optical and easy mechanical access

Calibration

Instrumentation:BRUKER Matrix-F ProcessSpectrometer; Opus Process Quant Software Package

Spectra acquisition: process probe (PP) / laboratory probe (LP), resolution: 8 cm^{-1} / 24 scans (~ 15 s)

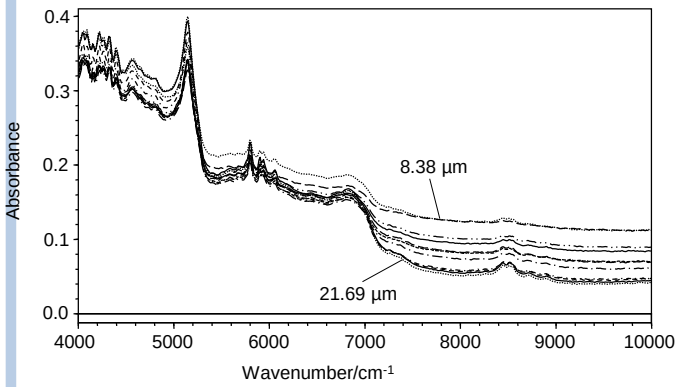
Spectrum	Acquisition time	Assay (%)	Water (%)	Acetone (%)
1	16:42:00	87.8	5.5	0.56
2	16:43:07	88.5	4.9	0.59
3	16:44:14	88.8	3.3	0.62
4	16:45:21	89.4	2.1	0.64
5	16:46:29	90.0	2.0	0.67
6	16:47:36	88.6	1.7	0.75

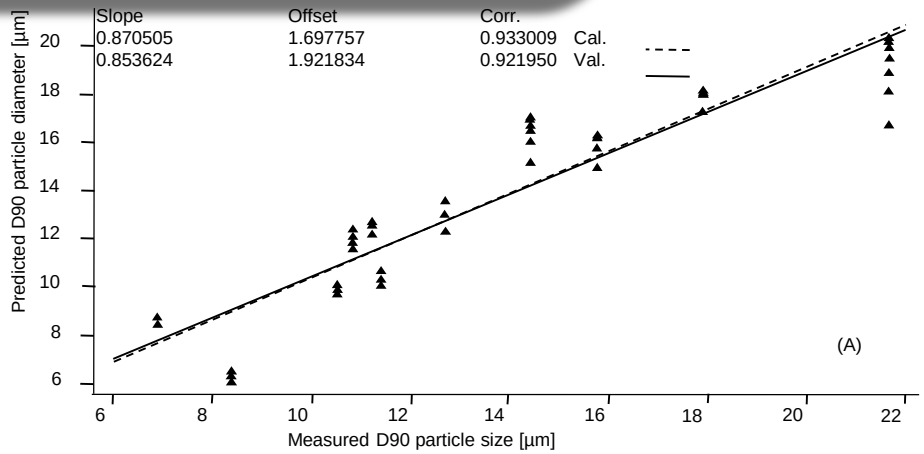


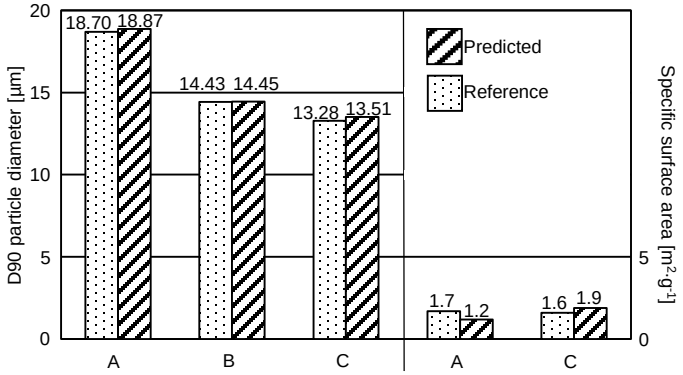
Results

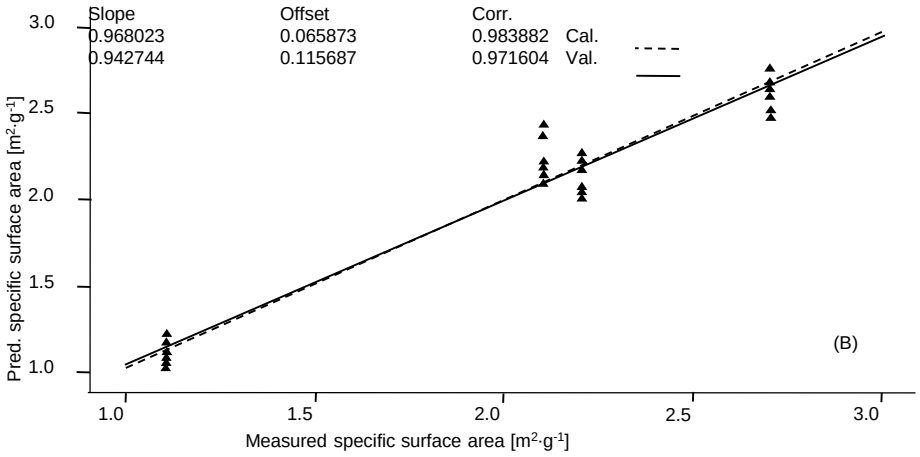
PLS calibrations

Particle Size and Surface Area





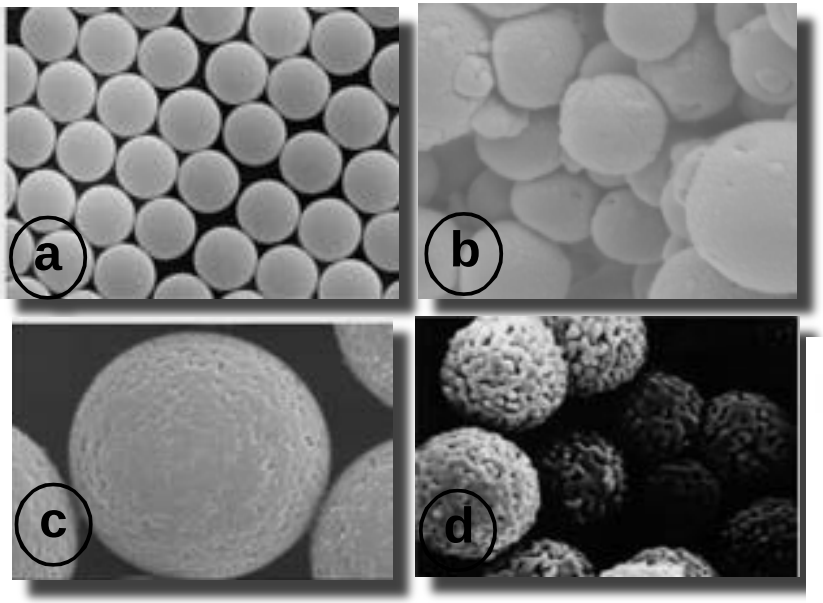




Physicochemical Properties of Silica Materials

Physical Properties

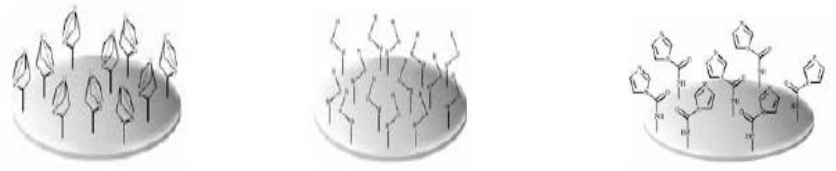
- Particle size distribution
- Porosity, Pore volume
- Specific surface area



ELMI-pictures of silica particles with different porosity:
a, non-porous (1000 x); **b**, 60 Å (5000 x); **c**, 300 Å (6000 x); **d**, 1000 Å (10000 x)

Chemical Properties

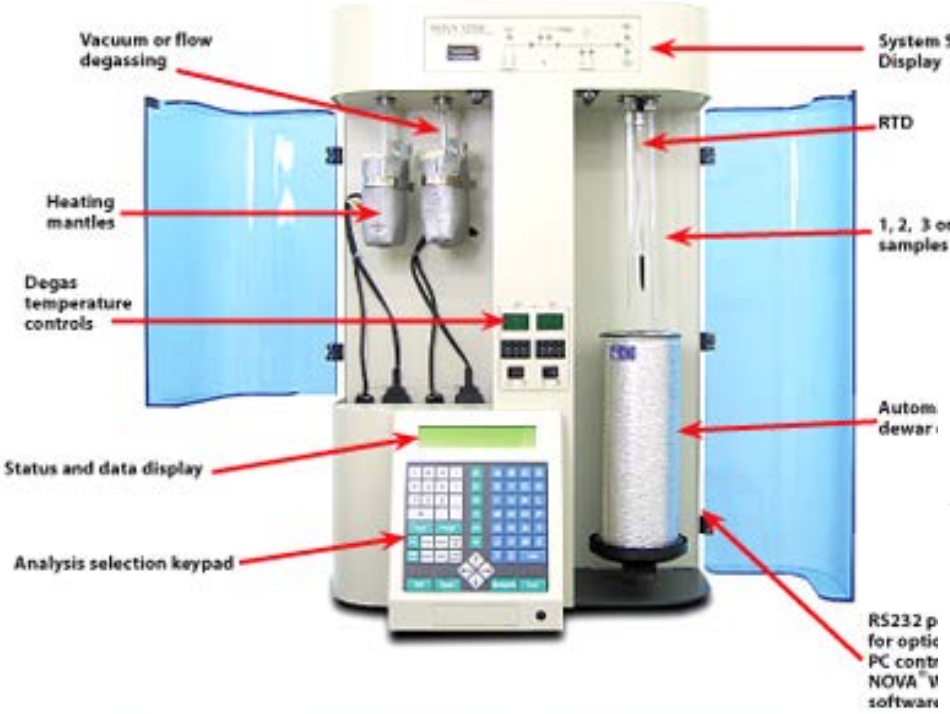
Hydrophobic | Anionic | Cationic



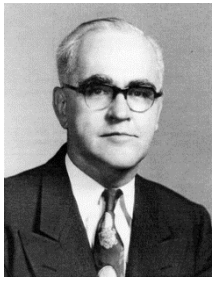
Metal Ion | Hydrophilic | Activated Surface

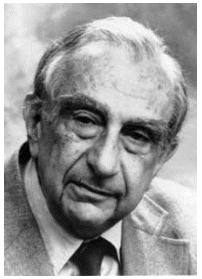
Antibody – Antigen | Receptor – Ligand | DNA – Protein

Specific Surface Area – BET (Brunauer Emmett Teller)

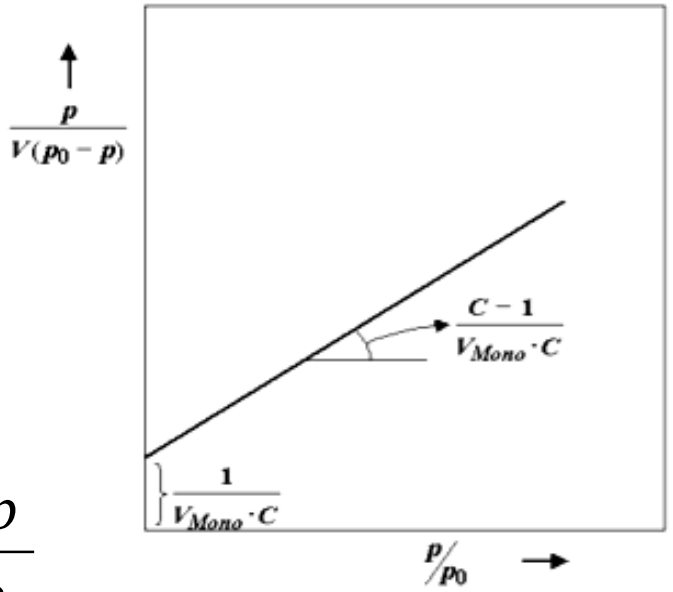


Rear of Instrument: RS 232 Port for PC Control via NOVAWin 2.0 Printer Port



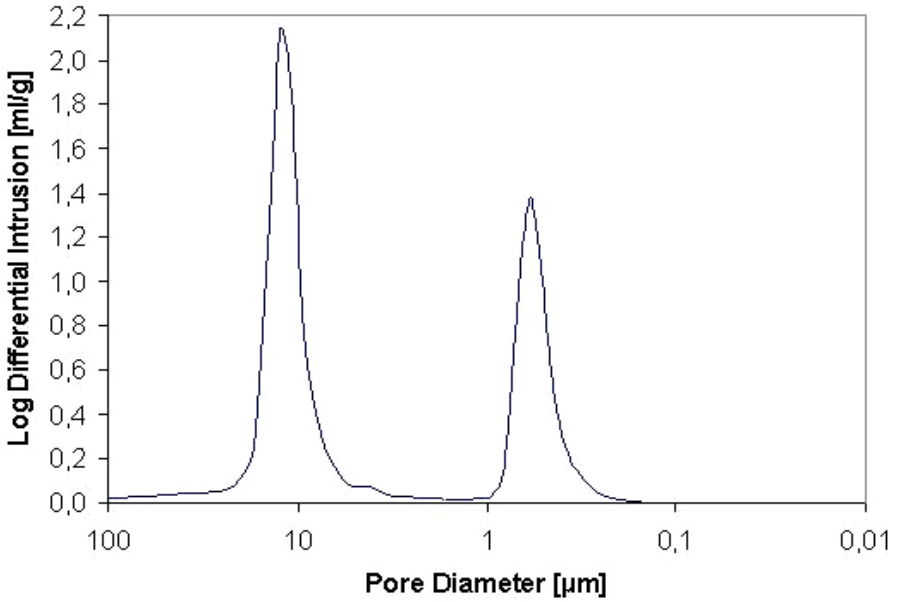


Emmett Teller



$$\frac{p}{V(p_0 - p)} = \frac{1}{V_{Mono} \cdot C} + \frac{C-1}{V_{Mono} \cdot C} \cdot \frac{p}{p_0}$$

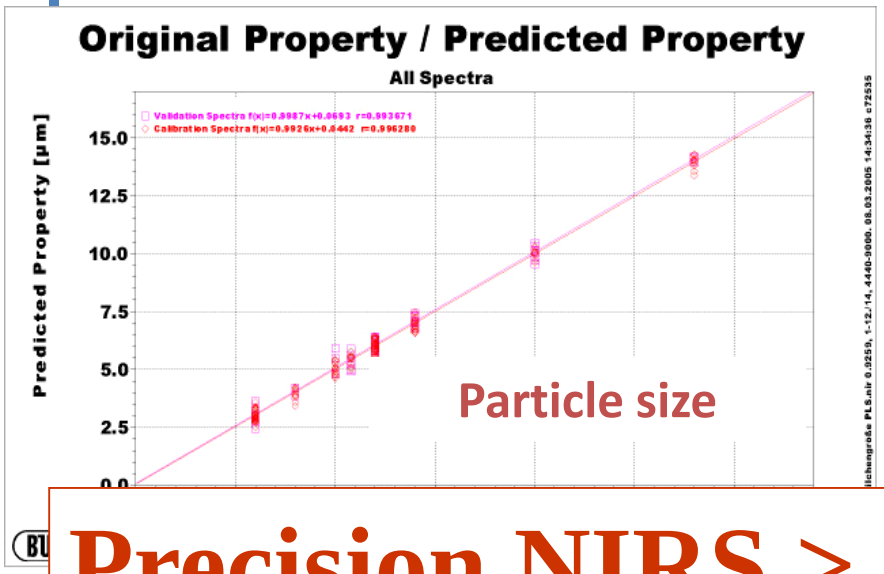
MIP – Mercury Intrusion Porosimetry

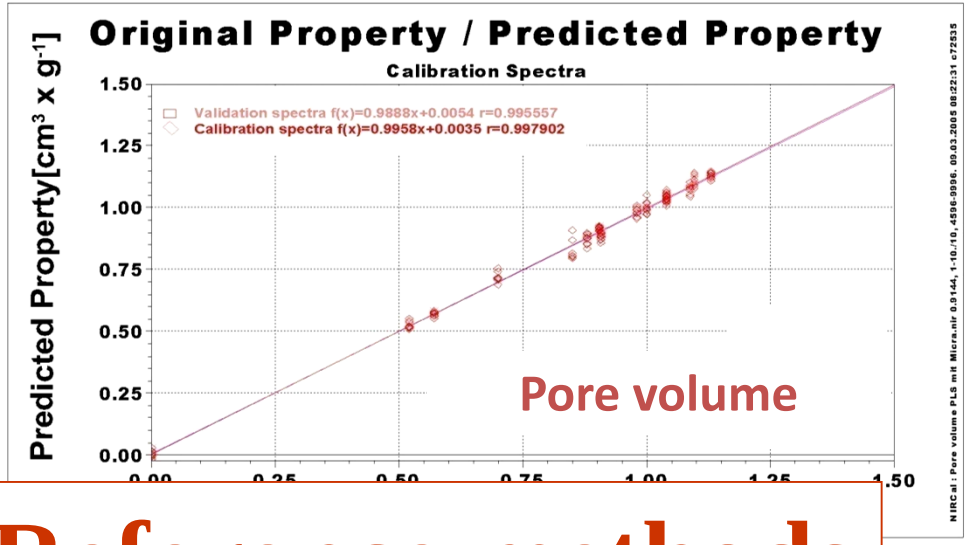


$$p = \frac{-2\gamma \cos\Theta}{r}$$

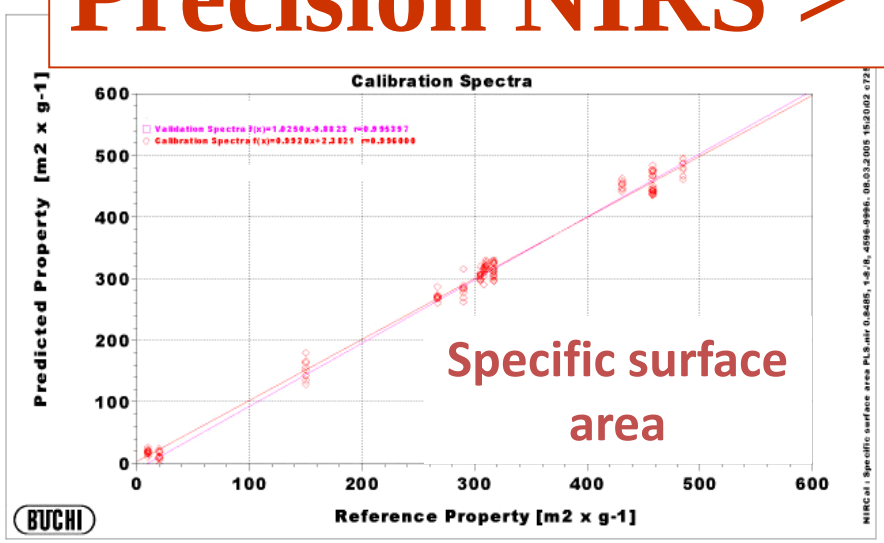
r…..pore radius
γ….surface tension of mercury
Θ…wetting angle
p….pressure

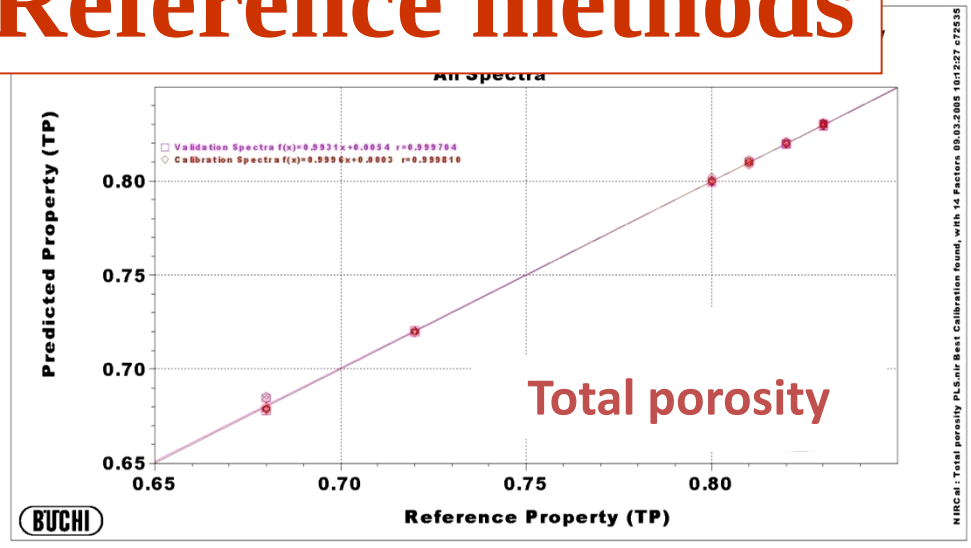
Silica – Physical Properties



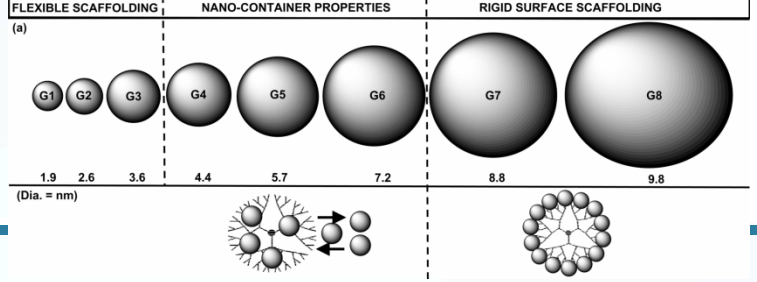


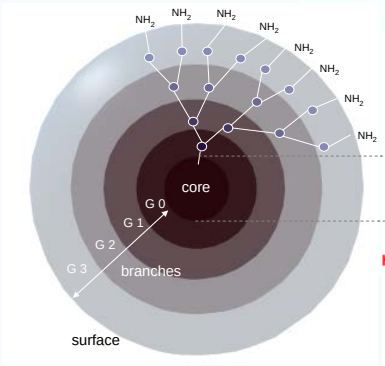
Precision NIRS > Reference methods

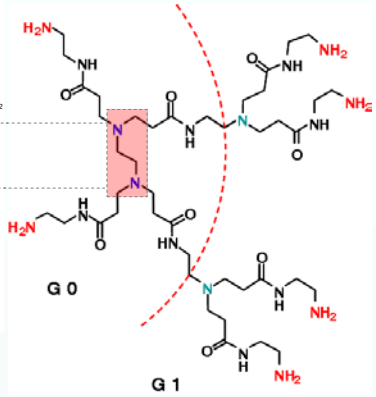


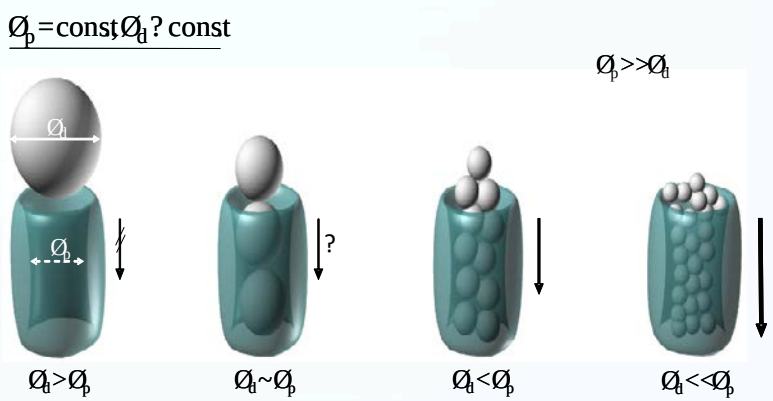


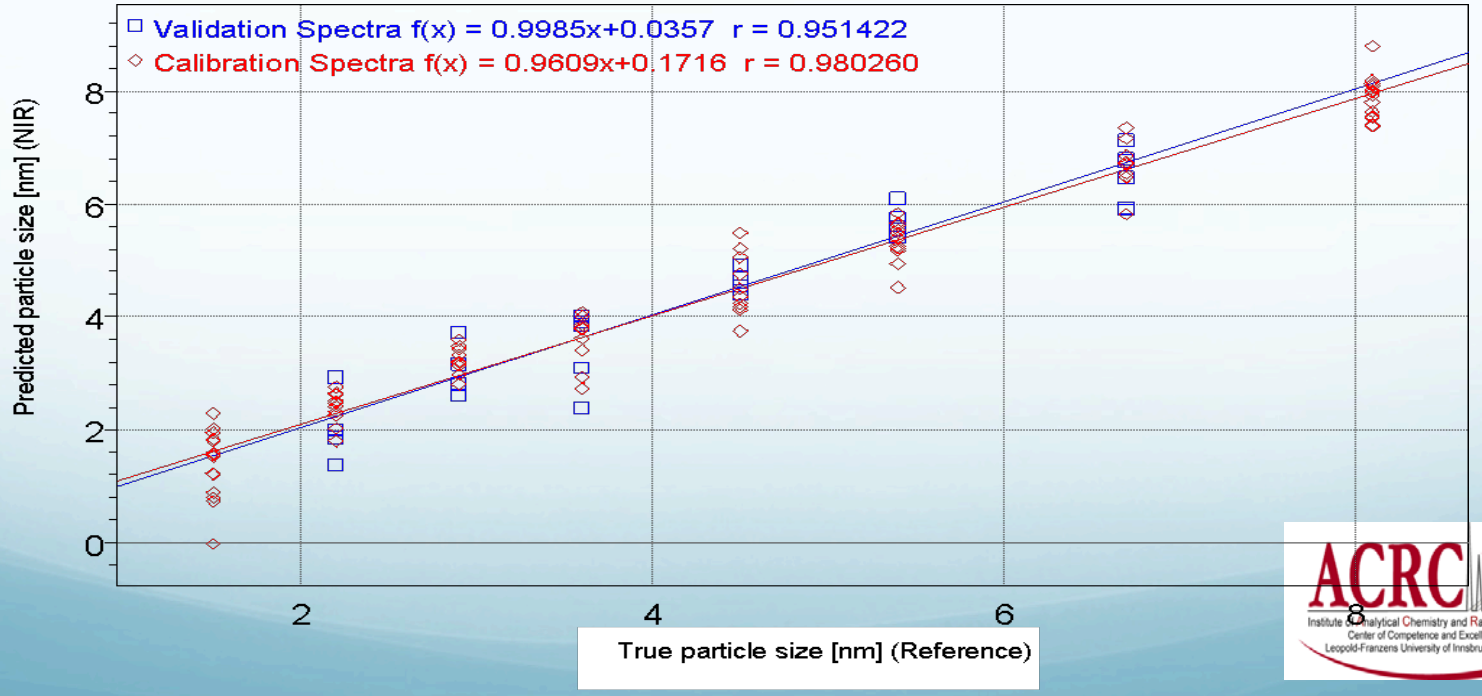
Dendrimere

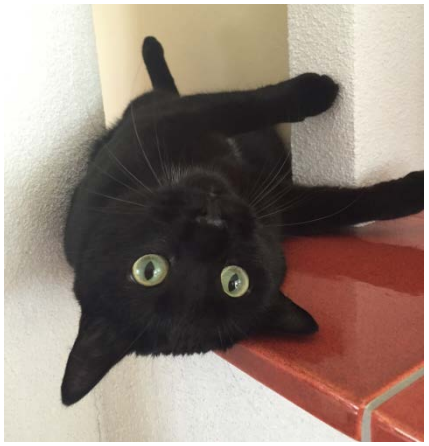

FLEXIBLE SCAFFOLDING
NANO-CONTAINER PROPERTIES
RIGID SURFACE SCAFFOLDING
(a)
G1
G2
G3
G4
G5
G6
G7
G8
1.9
2.6
3.6
4.4
5.7
7.2
8.8
9.8
(Dia. = nm)


core
G 0
G 1
G 2
G 3
branches
surface


G 0
G 1


Ø_p = const, Ø_d ? const
Ø_p >> Ø_d
Ø_d
Ø_p
Ø_d > Ø_p
Ø_d ~ Ø_p
Ø_d < Ø_p
Ø_d << Ø_p

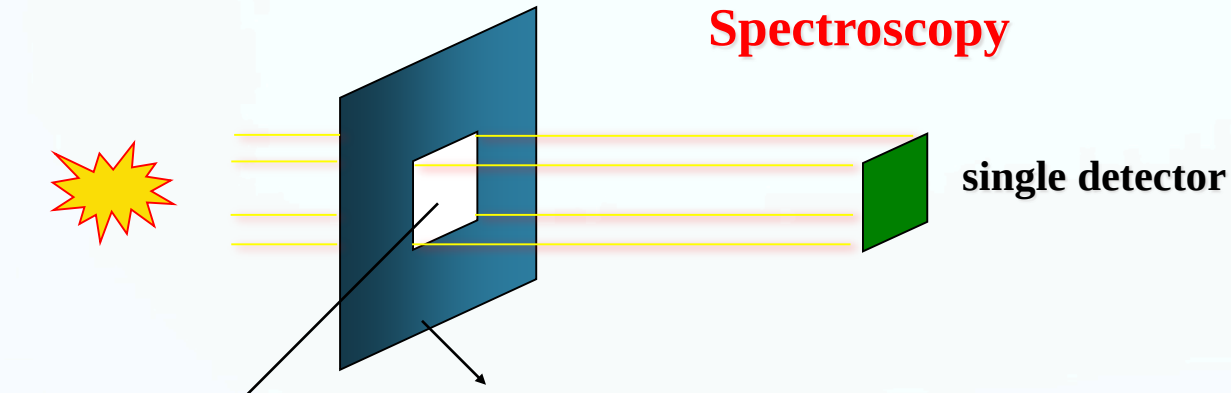

Validation Spectra f(x) = 0.9985x+0.0357 r = 0.951422
Calibration Spectra f(x) = 0.9609x+0.1716 r = 0.980260
Predicted particle size [nm] (NIR)
True particle size [nm] (Reference)
0
2
4
6
8



- Sometimes it is very useful watching the world from another point of view
- You need good experiments
- and good colaborations ....

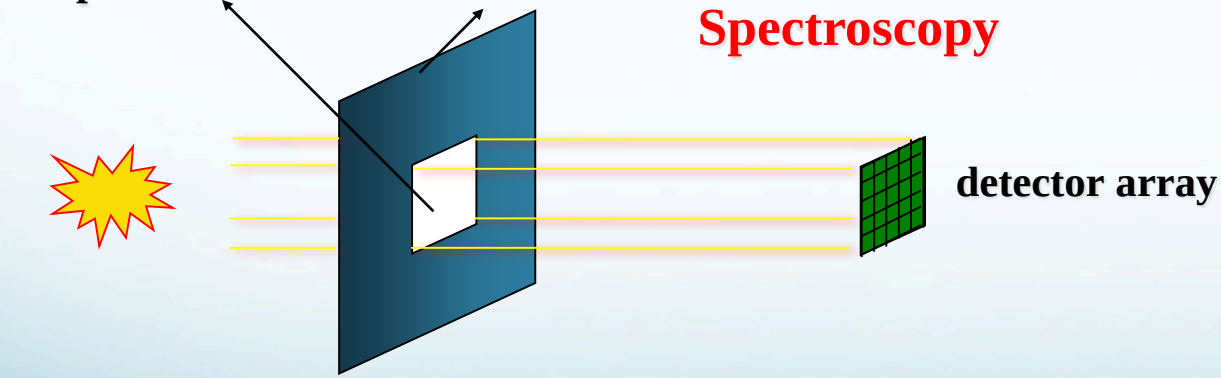
Instrumentation

Conservative Spectroscopy



The spectrum is representative for total irradiated sample area.

Imaging Spectroscopy

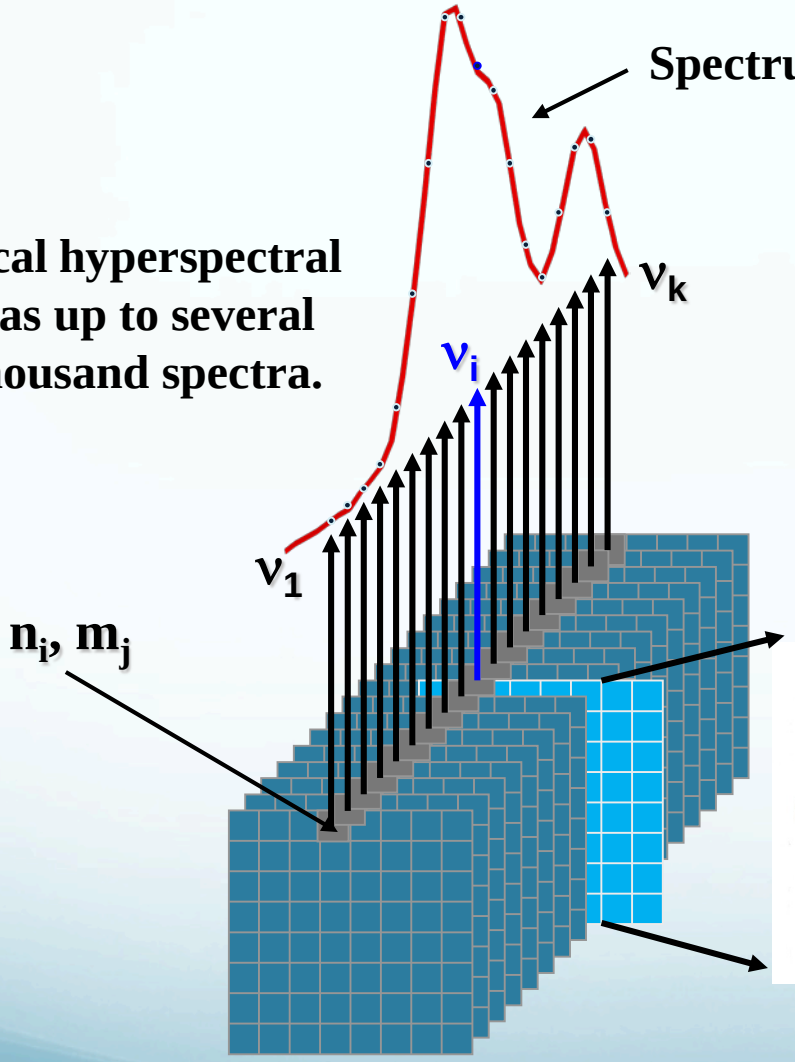


The spectra recorded by the individual detectors represent an image of the irradiated sample area.

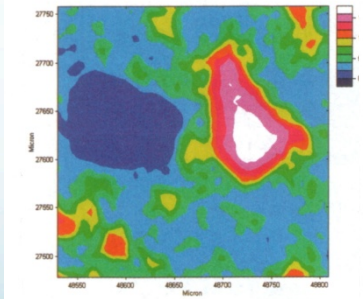
Measurement

Spectrum: from ν_1 to ν_k at pixel (n_i, m_j)

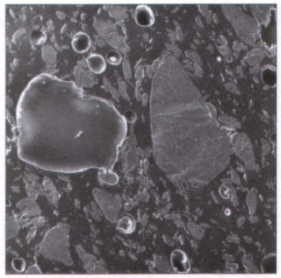
A typical hyperspectral cube has up to several (ten)thousand spectra.



IR image plane:
n × m pixels at ν_i

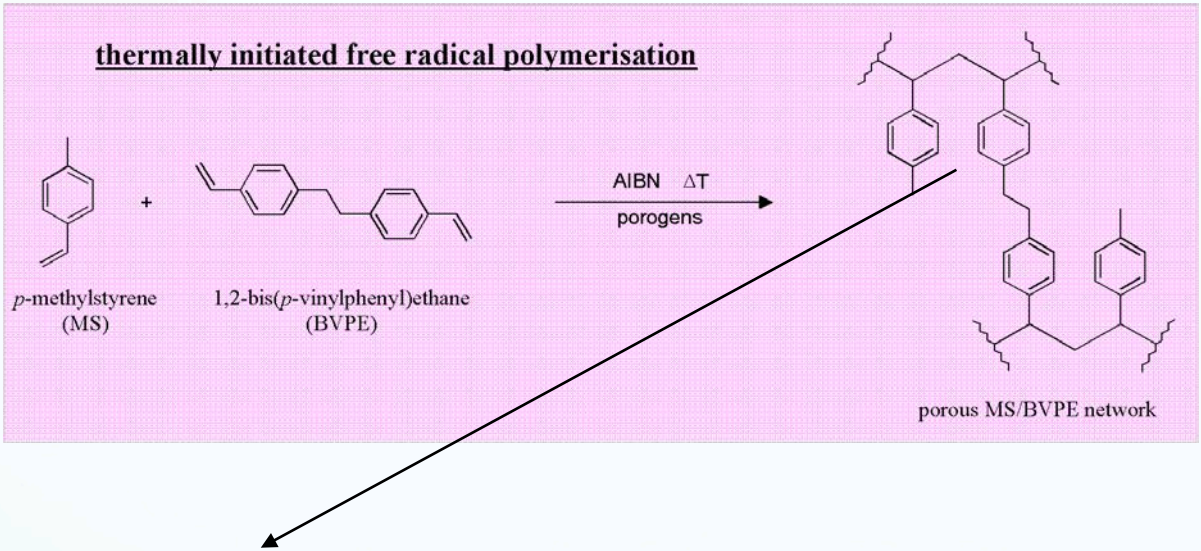


SEM micrograph



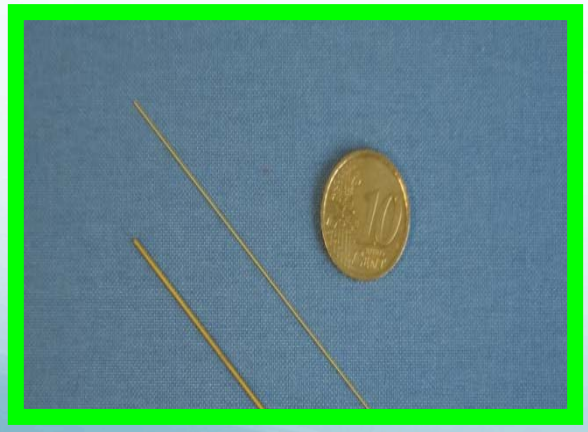
P. Wilhelm et al.,
Spectroscopy Europe, pp14-19 (May 2004)

MONOLITHIC MS/BVPE CAPILLARIES



- highly crosslinked
- high crosslinking homogeneity due to non-conjugated crosslinker
- minimised swelling
- high pressure stability

→ **Applicable to HPLC**



capillary columns
different dimension

80 x 0.2 mm
80 x 0.533 mm

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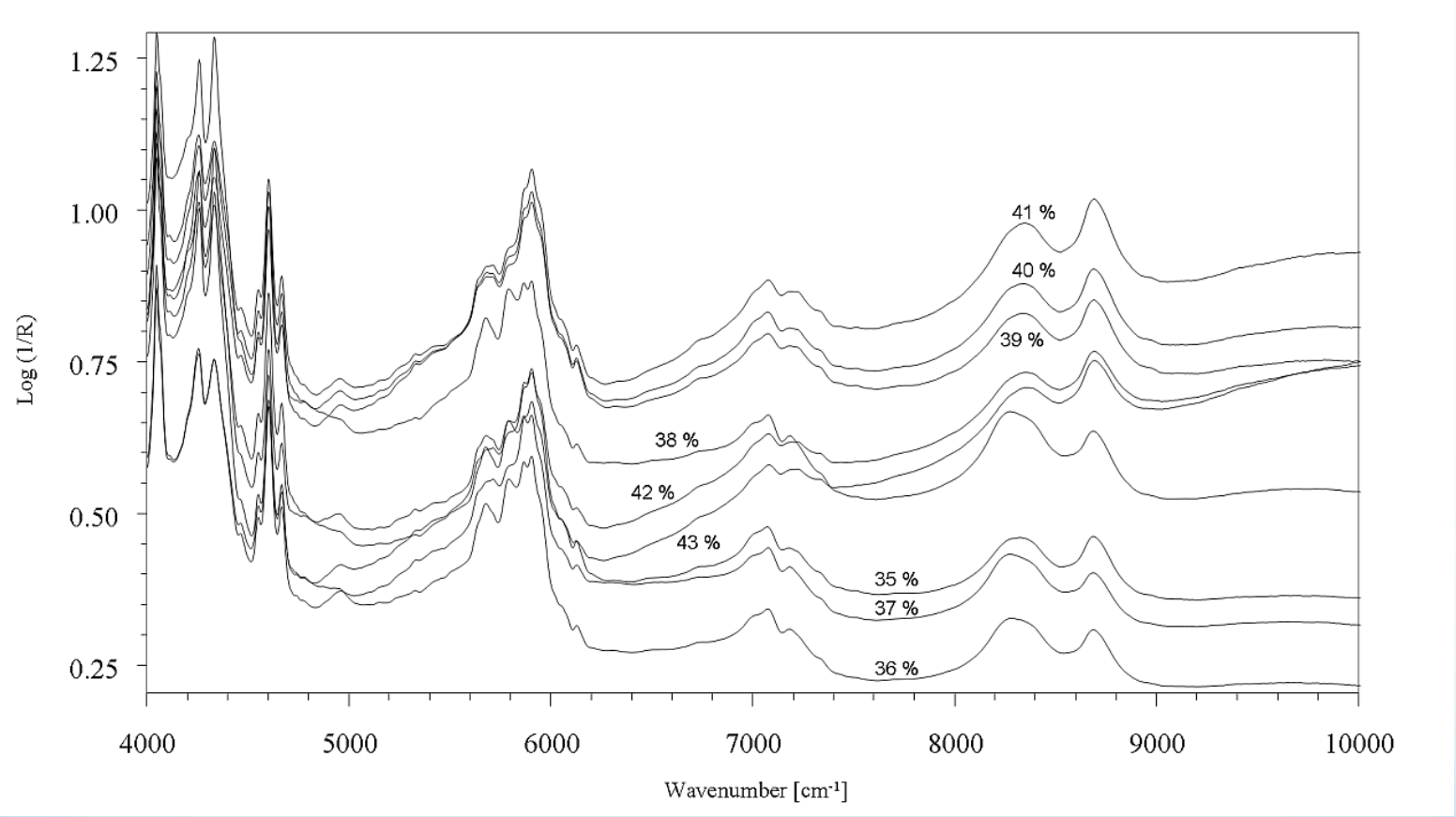
MONOLITHIC MS/BVPE CAPILLARIES



FT-NIR absorbance spectra of MS/BVPE polymers marked with varying amounts of MS/MVPE

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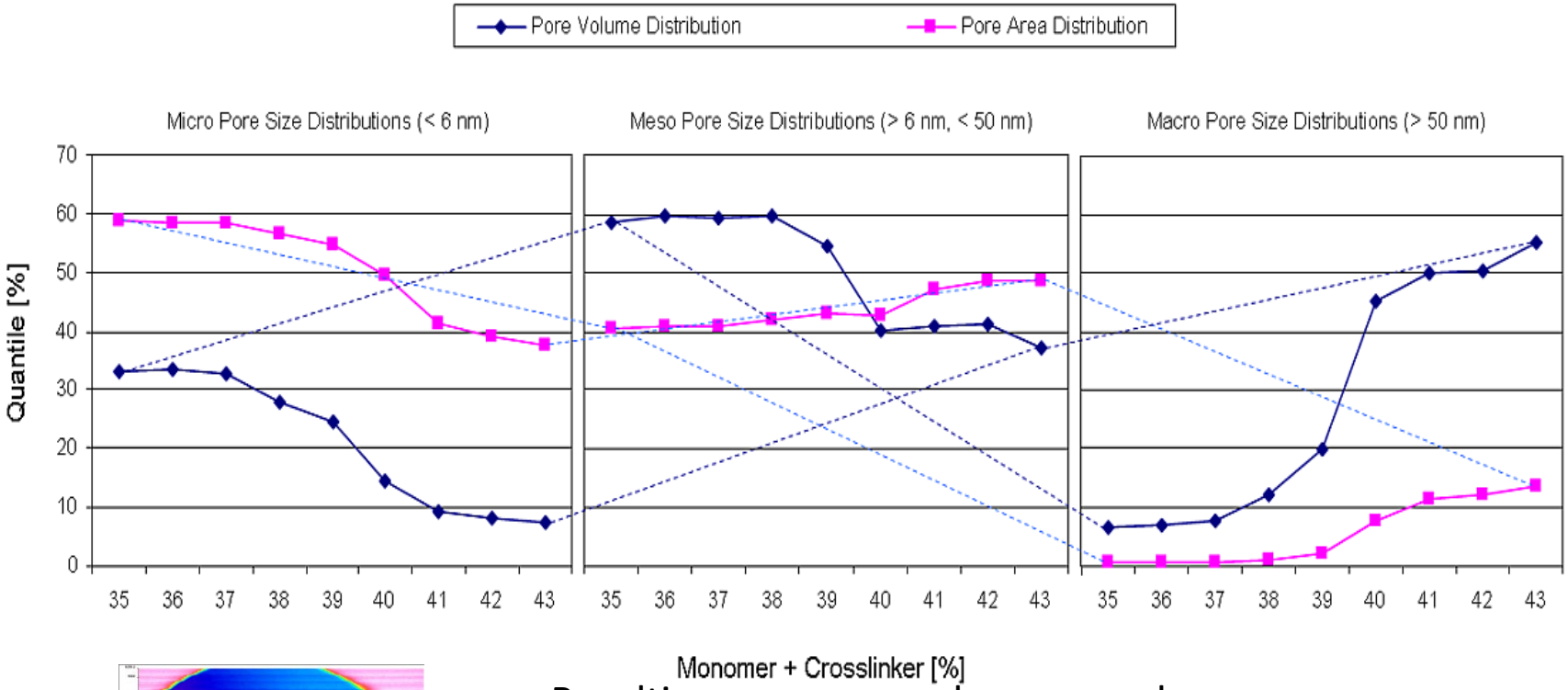
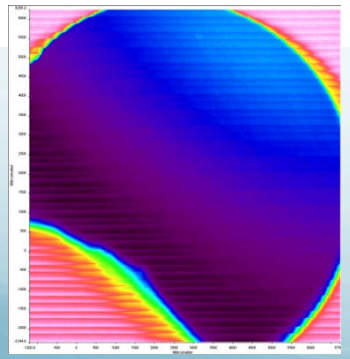
MONOLITHIC MS/BVPE CAPILLARIES





Resulting pore volume and pore area distributions by gradually increasing the MS/BVPE content. Note that not the entire macropore range can be assessed with nitrogen adsorption (only up to d ~ 200 nm).

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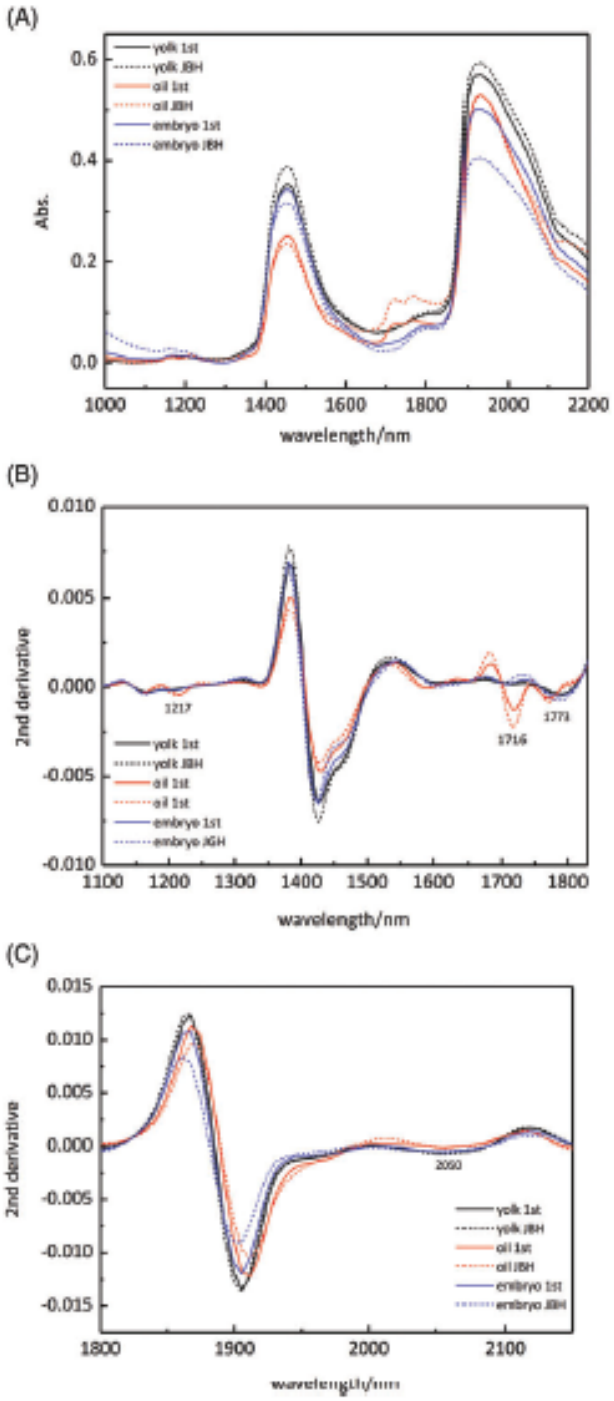
DOI: 10.1002/jbio.201700115

Journal of BIOPHOTONICS

FULL ARTICLE

Noninvasive, high-speed, near-infrared imaging of the biomolecular distribution and molecular mechanism of embryonic development in fertilized fish eggs

Mika Ishigaki[1]* | Takashi Nishii[1] | Paralee Puangchit[1] | Yui Yasui[1] | Christian W. Huck[2] | Yukihiro Ozaki[1]*



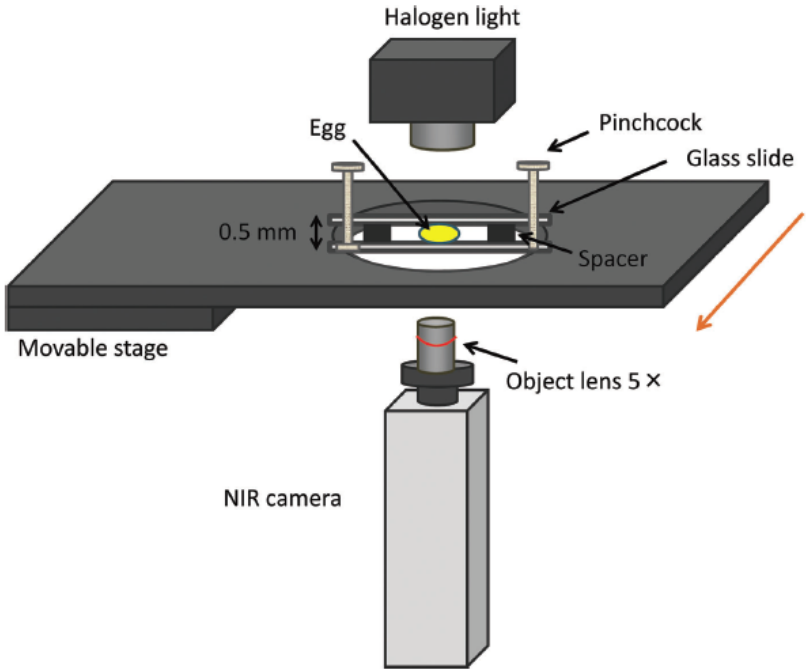
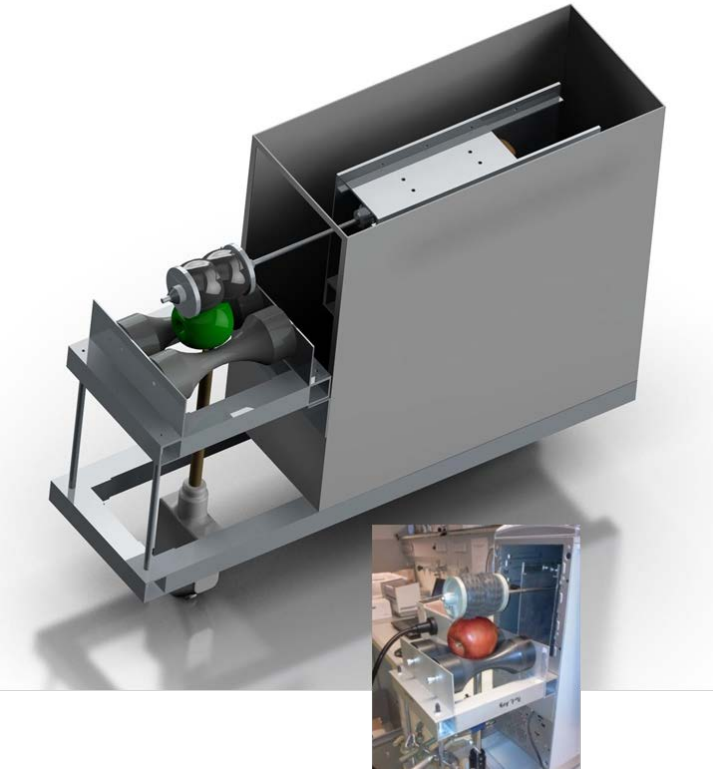
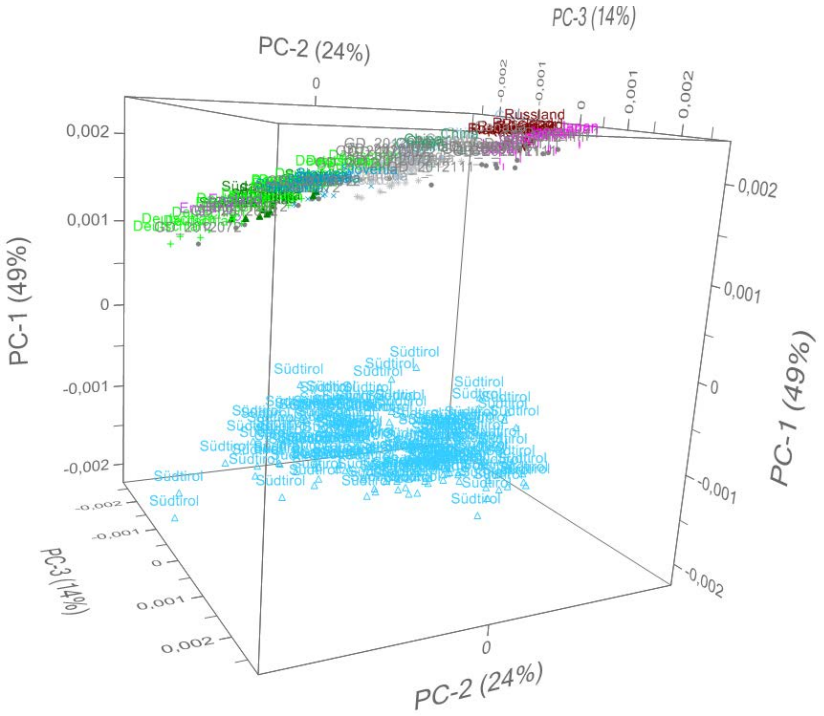


FIGURE 3 (A) NIR spectra in the 1000 to 2200 nm region of the yolk, oil droplets and embryo of medaka eggs on the first day after fertilization (solid line) and the day just before hatching (dashed line) with baseline corrections. (B) Second-derivative spectra in the 1100 to 1820 nm and (C) 1800 to 2200 nm

Automatic Sample Rotation for Simultaneous Determination of Geographical Origin and Quality Characteristics of Apples based on Near Infrared Spectroscopy (NIRS)





Schmutzler M., Huck C.W. Simultaneous detection of total antioxidant capacity and total soluble solids content by Fourier transform near-infrared (FT-NIR) spectroscopy: A quick and sensitive method for on-site analyses of apples. Food Contr., 66 (2016), 27-37

Schmutzler M., Huck C.W. Automatic Sample Rotation for Simultaneous Determination of Geographical Origin and Quality Characteristics of Apples based on Near Infrared Spectroscopy (NIRS). Vibr. Spectrosc., 72, 97-104 (2014)

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re-cereal

Insights into the total antioxidant capacities of different cultivars of gluten-free grains using benchtop and handheld NIR spectroscopy

Verena Wiedemair[1], Reinhold Ramoner[2], Christian W. Huck[1]

[1]Institute for Analytical Chemistry and Radiochemistry, Innrain 80–82, 6020 Innsbruck, Austria
[2]Health University of Applied Sciences Tyrol, Innrain 98, 6020 Innsbruck, Austria

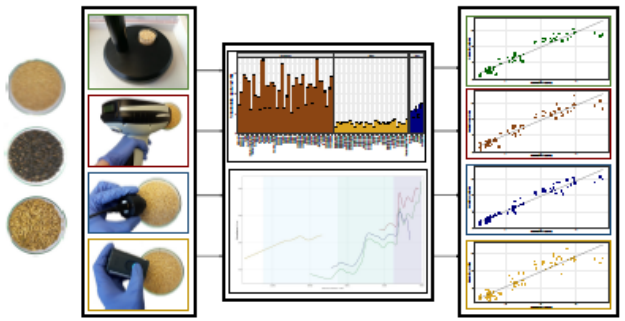
Introduction

Millet, buckwheat and oat are considered to be minor crops, hence chemical profiles for different cultivars are rare. The examination of a sum parameter, like the total antioxidant capacity (TAC) can thus be a first step to systematically assess the quality of different cultivars of mentioned gluten-free grains and thereby serve as an indicator for the selection of cultivars for food processing. Furthermore, miniaturized near-infrared spectroscopy becomes more attractive for agriculture, as the costs for these instruments are quite low and their performance becomes better year after year. Miniaturized NIR spectrometer enable an analysis without expensive laboratory equipment and the new trend of consumer-oriented spectrometer makes sophisticated analysis possible even for laypeople. However, the performance of these instruments first needs to evaluated.

Methods & Materials

77 Gluten-free samples (40 buckwheat, 31 millet, 6 oat) were investigated toward total antioxidant capacity using Folin-Ciocalteu assay and NIRS. All samples were measured milled and intact with one benchtop-sized and three handheld devices.

Spectrometer	Spectral range / cm^{-1}	Resolution / cm^{-1}
NIRFlex N-500	10.000–4.000	8
microPhazir RX	6.270–4.180	21
MicroNIR 2200	8.870–4.630	33
SCiO	13.514–9.346	13



Results

Partial least squares regression models were established using the data for milled and intact samples from all four devices. Spectral pre-treatments include Savitzky Golay 2nd derivative, standard normal variate and orthogonal signal correction. For the MicroNIR 2200 additional smoothing was applied.

Spectrometer	State of the grains	Factors	R^2 (CV)	RMSECV / mgGAE/g	R^2 (TV)	RMSEP / mgGAE/g	LOD_{min} mgGAE/g	LOD_{max} / mgGAE/g	LOQ_{min} / mgGAE/g	LOQ_{max} / mgGAE/g
NIRFlex N-500	Intact	2	0.925	1.34	0.912	1.58	0.87	1.72	2.60	5.15
	Milled	4	0.892	1.60	0.883	1.66	1.24	2.80	3.71	8.39
microPhazir RX	Intact	3	0.921	1.46	0.893	1.37	1.40	2.39	4.19	7.16
	Milled	3	0.913	1.35	0.891	1.78	1.48	2.55	4.43	7.65
MicroNIR 2200	Intact	3	0.951	1.11	0.952	1.02	1.24	1.83	3.70	5.50
	Milled	4	0.910	1.46	0.919	1.44	1.66	3.23	4.96	9.69
SCiO	Intact	2	0.823	1.98	0.895	1.24	1.78	3.03	5.35	9.09
	Milled	2	0.824	2.08	0.849	1.86	1.70	2.62	5.11	7.85

Conclusion and Outlook

NIR can be used for TAC estimation with limitation

- Samples range: 1.40–18.8 mgGAE/g
- RMSEP range: 1.02–1.86 mgGAE/g
- LOD_{max} range: 1.72–3.23 mgGAE/g
- LOQ_{max} range: 3.15–9.69 mgGAE/g

Resolution is not all: the MicroNIR 2200 has the worst resolution, but yields good results.

Handheld spectrometer perform similarly to benchtop device, but

- LOD and LOQ of benchtop are the lowest
- The category milled/intact is more stable for benchtop data

Acknowledgement

Special thanks goes to the European Union, the European Regional Development Fund and the cross-border programme Interreg V-A Italy-Austria 2014–2020 (project "RE-Cereal", ITAT 1005, P-7250-013-042) for financial support.

References

Verena, Wiedemair; Huck, Christian W. (2018): Evaluation of the performance of three hand-held near-infrared spectrometer through investigation of total antioxidant capacity in gluten-free grains. In: *Talanta*. DOI: 10.1016/j.talanta.2018.06.056.

Vol. 29 No. 5 August 2018 ISSN 0960-3360

NIR news

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