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"Analysis of Water in Food by Near Infrared Spectroscopy"

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Introduction and advantages of NIR Spectroscopy

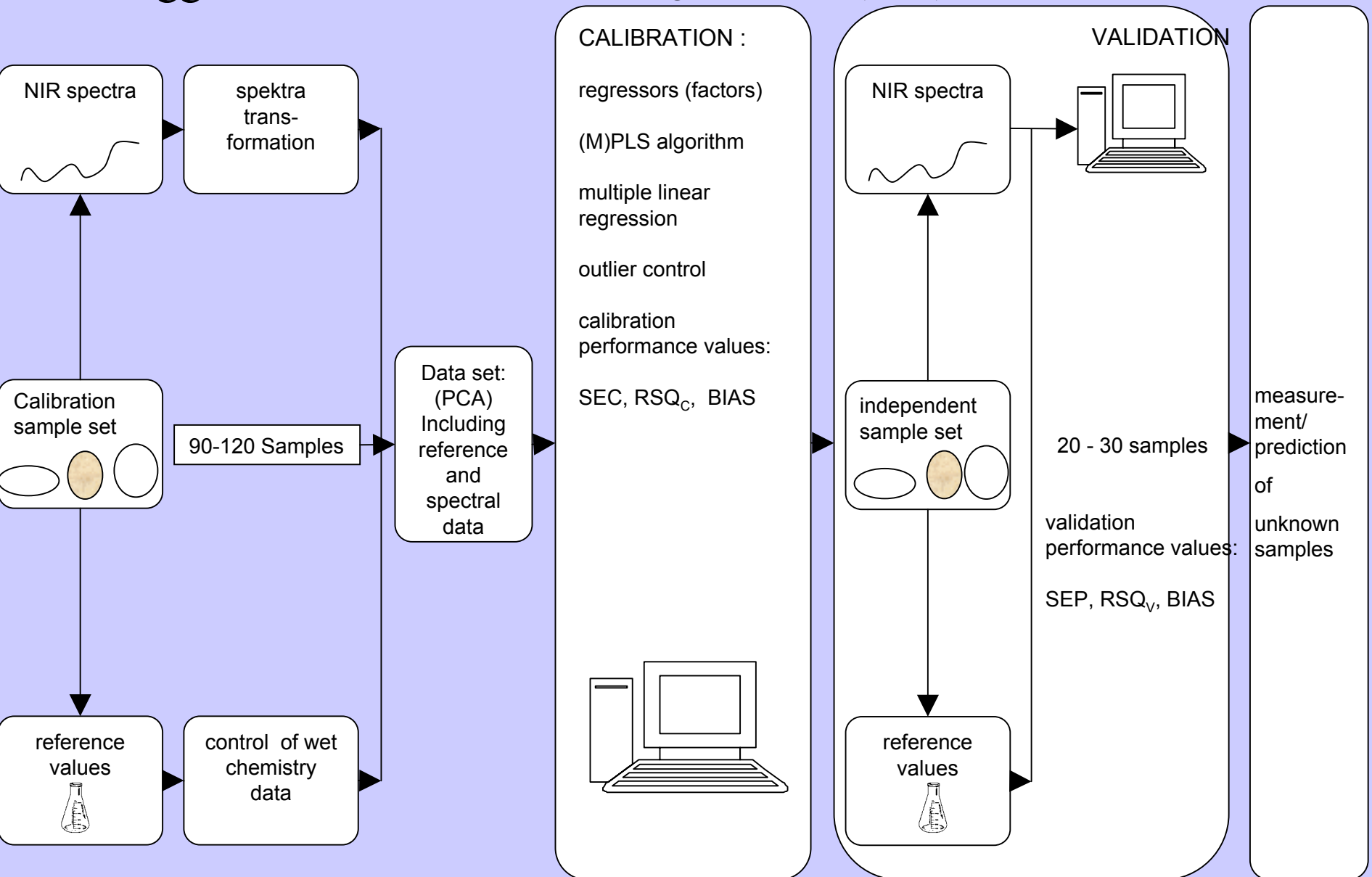
- Spectra chararacterized by overtone and combinations bands of fundamental vibrations occurring in the mid infrared
- Nondestructive method; minimal sample preparation; no reagents, no wastes
- Multi-analytical technique, values of several parameters from only one spectrum
- Analysis of chemical and physical properties / parameters
- Simple to use, reduction of analytical effort
- Assessment on the spot, mobile analysis

Disadvantages of NIR Spectroscopy

- Time consuming and labourious calibration procedures (NIRS-method development)
- Individual method development for each food group
- Weak sensitivity to minor constituents
- Limitation in method transfer due to optic differences between instruments

Developing a method for NIR spectrometric determination:

Egg constituents Lit.: Büning-Pfaue et al (2001)



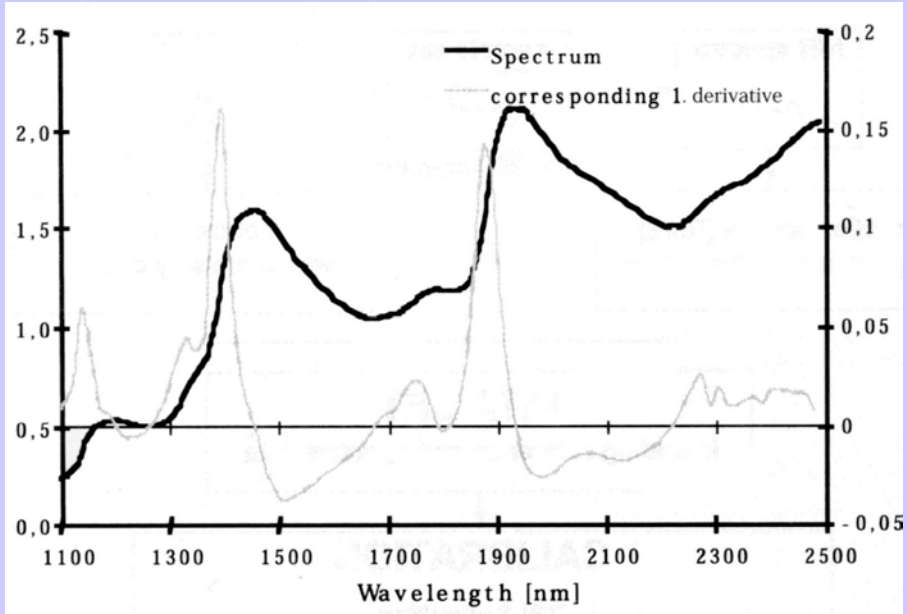
NIRS method development: Raw data pretreatment, method precision

- mathematically preprocessed raw data remove defects in the spectra
  - first and second derivative
  - multiclative scatter correction minimizes particle size effects
- Performance values describe the precision of NIRS-methods, terms to check the multivariate model:
  - SEC, "**S**tandard **E**rror of **C**alibration"
  - SEP, "**S**tandard **E**rror of **P**rediction"
  - Bias, ~ Average difference between measured and predicted values
  - "maximum error range" (± 2 SEP, if Bias negligible)

Status of water in food, influence on NIR spectra

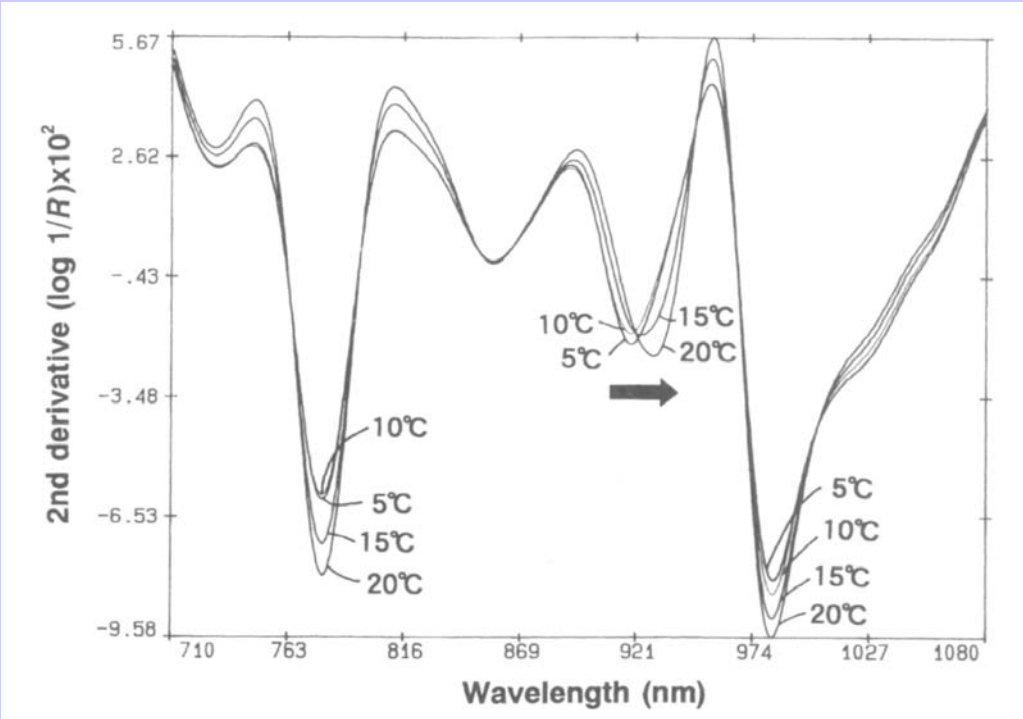
- Strong absorber, regions of
  1400 – 1460 + 1900 – 1950 nm
- Intensities of bands alter with changes in hydrogen bonds and hydration
- 4 maxima: (970 + 1190) 1450 + 1940 nm
  different overtone O-H-
  stretching and O-H-bending
  band and combinations

Hydrogen bonds influenece
the NIR absorption (1450 nm);
50 nm);
varying



Potato NIR spectrum and corresponding derivative, Lit.: Hartmann & Buening-Pfaue, 1998

Influence of sample temperature on NIR absorption due to water Lit. (review): Iwanomoto et al (1995)



- large spectral variations: changes of the hydrogen-bonded water structure
- different spectral differences example: water in meat
- absorption band (ca. 1400 nm) decreases in intensity together with dehydration process: sliced pear flesh („free“ water)

Repeatability file: Minimizing unwanted spectral effects due to changes of the hydrogen-bonded water structure

Lit: Westerhaus (1990)

- a "repeatability file" contains spectra of the same sample measured repeatedly under different conditions
- during calibration development such wavelength regions are neglected which are affected by the change in sample conditions
- the goal of this file is to make the calibration equation insensitive to changes in temperature (changes of hydrogen-bonded structure), (and instruments – i.e. method transfer)

but not to reduce the method`s accuracy

Test of a “repeatability“ file - comparing the alternative by exclusion of the sensitive water bands from calibration; samples: rapeseed; Lit: Tillmann & Paul (1998)

Tab. 1 A: NIRS-Determination of **dry** samples (rapeseed); equilibrated validation statistics using the exclusing of (water) wavevelength segments (1 & 2) alternative the "Repeatability Files" (R 1 + R 2)

Parameter:	Version:	SEP:	BIAS:	RSQ:
Oil	Control	0.76	0.18	0.5
	Wavelength-Elimination 1	0.83	0.18	0.94
	Wavelength-Elimination 2	0.85	0.14	0.93
	"Repeatability-File" R 1	0.72	0.1	0.95
	"Repeatability-File" R 2	0.77	0.21	0.95
1 B:	NIRS-Determination of **moisty** samples (rapeseed)			
Oil	Control	3.01	0.47	0.11
	Wavelength-Elimination 1	1.72	1.04	0.36
	Wavelength-Elimination 2	1.74	1.17	0.38
	Repeatability-File R 1	1.21	0.31	0.42
	Repeatability-File R 2	0.98	0.27	0.59

NIRS methods, analysing water in food

- First applications: In the grain industry

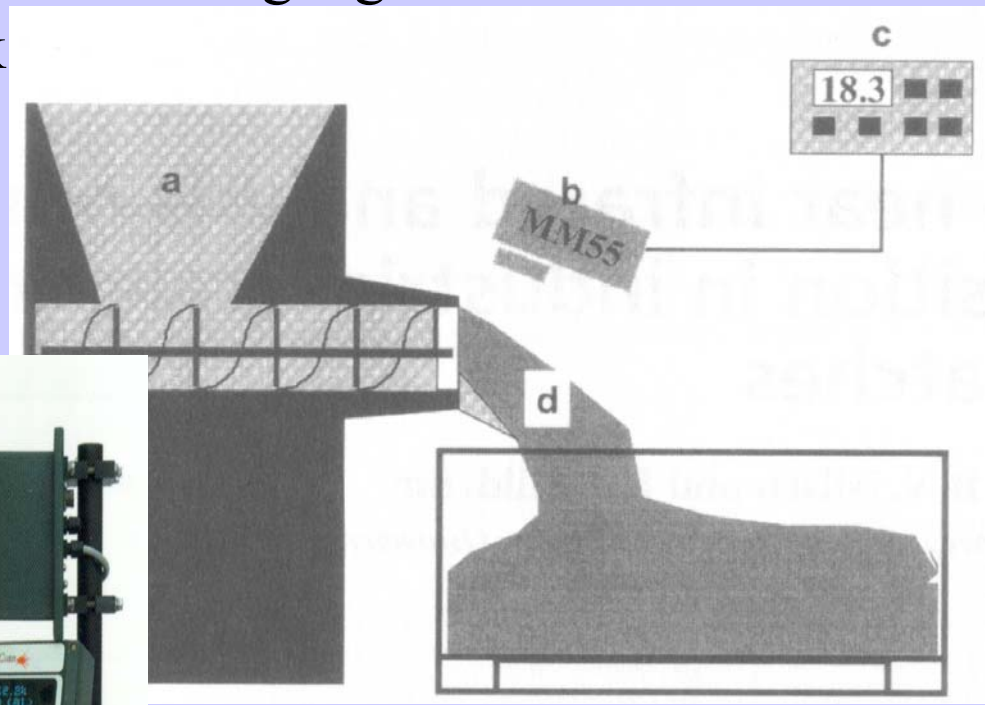
- Nowadays: a wide rage of foods : Snack foods, coffee, cookies & crackers, starches, soy bean & corn meals, lecithine, cereals, milk, milk powder, milk, butter, cheese, sweets ....
- even in high moisture .., in liquid .., in solid or semi-solid food (in cuvettes or by optiv probes)

- Analysis of intact samples e. g. fruits, vegetable, meat and fish (by using moving sample cells, fibre optics)

- Miniaturizing of spectrometers: New powerful analytical tools

NIRS-applications in industrial processes

- NIR-process sensor in response to industry`s need,
- Operating as a single discrete gauge or as a sensor in a multi-point network



Success in NIRS-Application (i.g. analysis of water in raw material ...goods entry control ...)

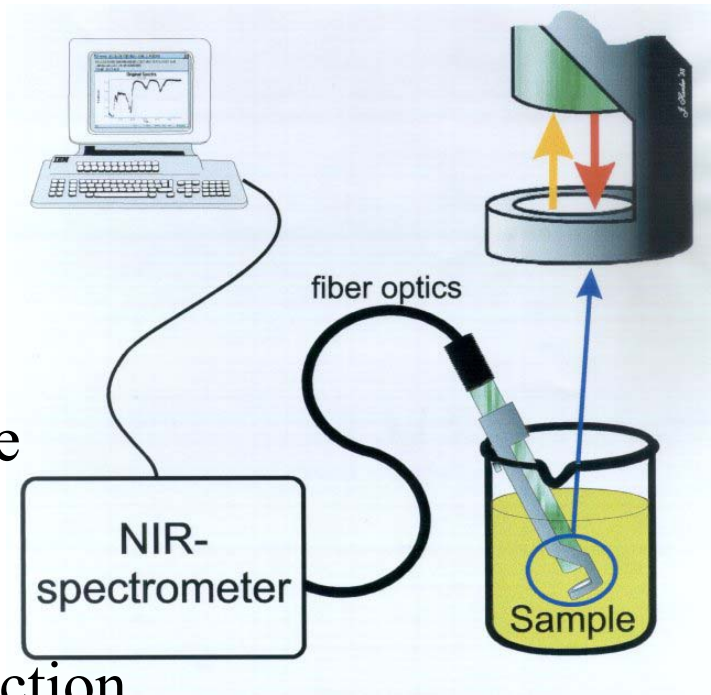
NIRS analysis keeps the operator interaction to a minimum, enabling untrained personel to do routine analysis, gives users a

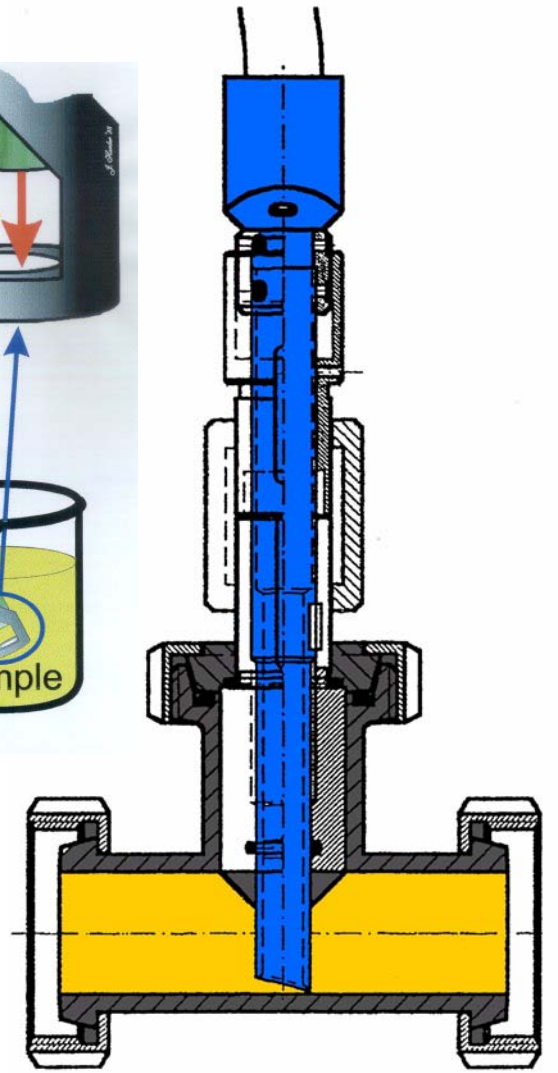
optimum flexibility while minimizing analysing costs

NIR (water) measurements for liquid samples ...

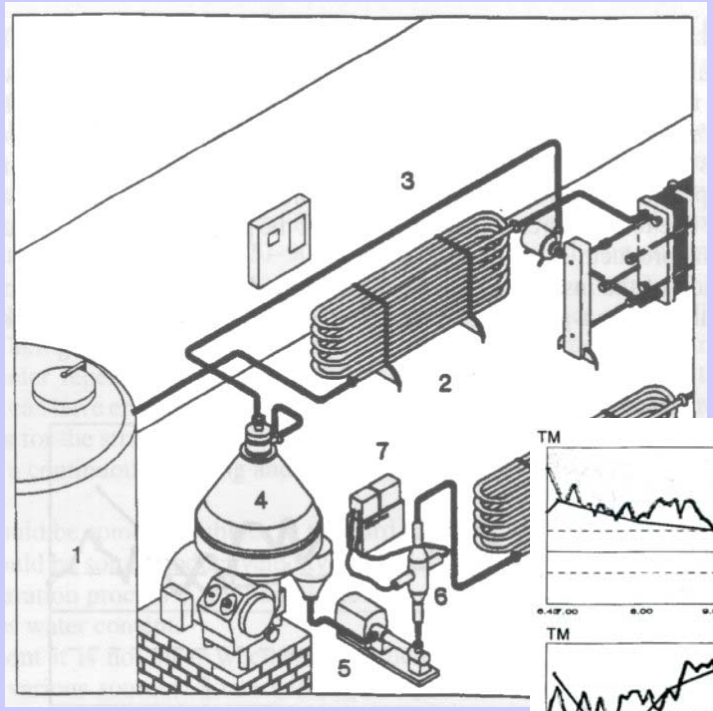
- off-line technique: transmission in cuvettes/sample cups (laboratory)
- at-line and on / in line technique (pictures):

  direct reflectance & transflectance (production line / performed with fiber optics on/in production line)

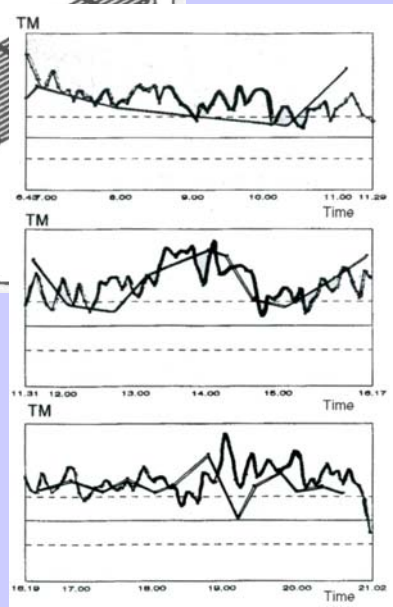




Determination of water in cottage cheese as an in-line NIRS-measurement Lit.: Wüst et al. (1996)

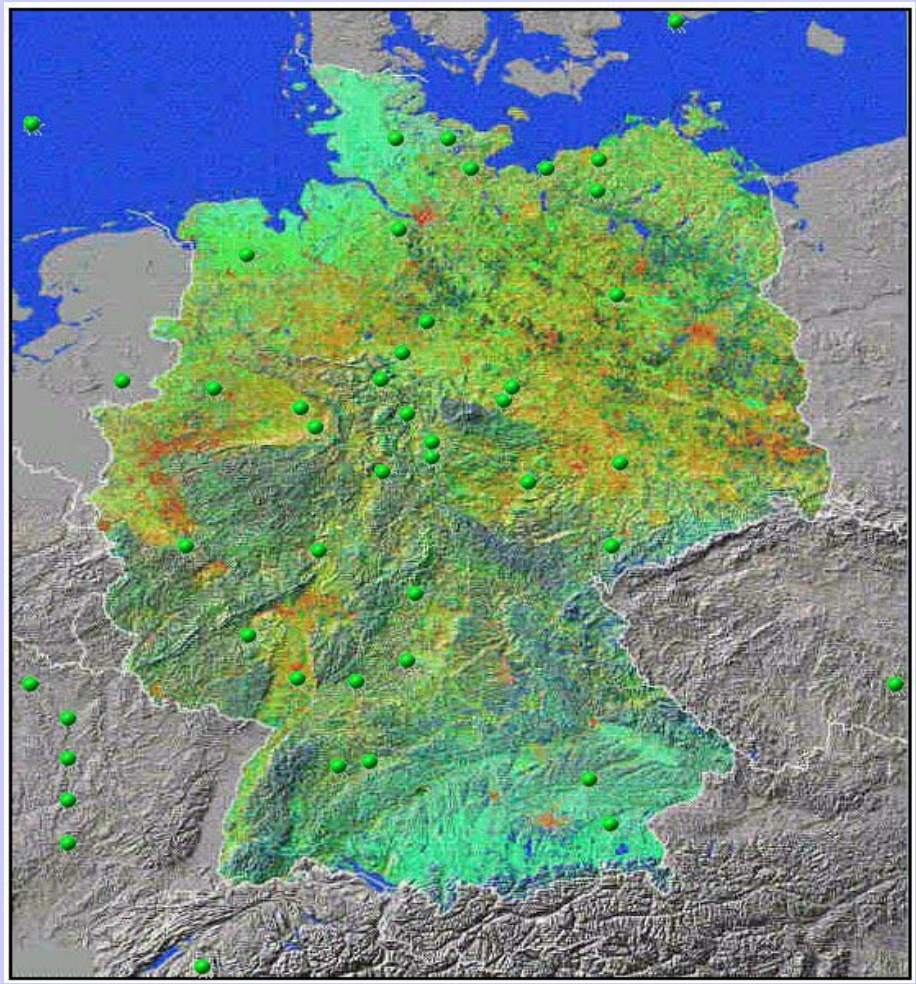


2: heater
4: separator
6: in-line-device



- Schematic diagram of the production line for cottage cheese
- In-line device, trans-mission measurement, 700 – 1100 nm, (No. 6); results of the solid con-tent (d. m.) measurements as a function of time; maximal differences („errors“): 0.25 %

Networking of NIRS Instruments



Networked NIRS-Instruments: “Association of German Agricultural Experimental and Research Stations“ (www.VDLUFA.de/nirs)

water- / “dry matter“-determination

for rape seed, grain,

forage maize ....

Moisture (water) control during fermentation

Lit.: Suehara et al (2000)

- Moisture has a large effect on reaction rate of fermentation
- Measurement in PE-bags
- Raw (a) and second-derivative (b) NIR spectra of fermented samples for runs of 70.7 %
- water (2.1 days), 51.3 % w (3.0 d) and 24.1 % w (5.0 d)
- Moisture content affects not only the absorption at the wavelength assigned to water but also the absorption at all wavelength measured