RAPID AND NON-INVASIVE FOOD AND FEED QUALITY MONITORING: THE CHEMOMETRIC POINT OF VIEW

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Centre wallon de Recherches agronomiques

Raman Spectroscopy (FT-Raman)

Mid Infrared Spectroscopy (FT-IR)

Near Infrared Spectroscopy (NIR)

FOOD AND FEED QUALITY MONITORING

Instrumentation

Chemometrics

Applications

NIRS IN FOOD/FEED AND AGRICULTURE

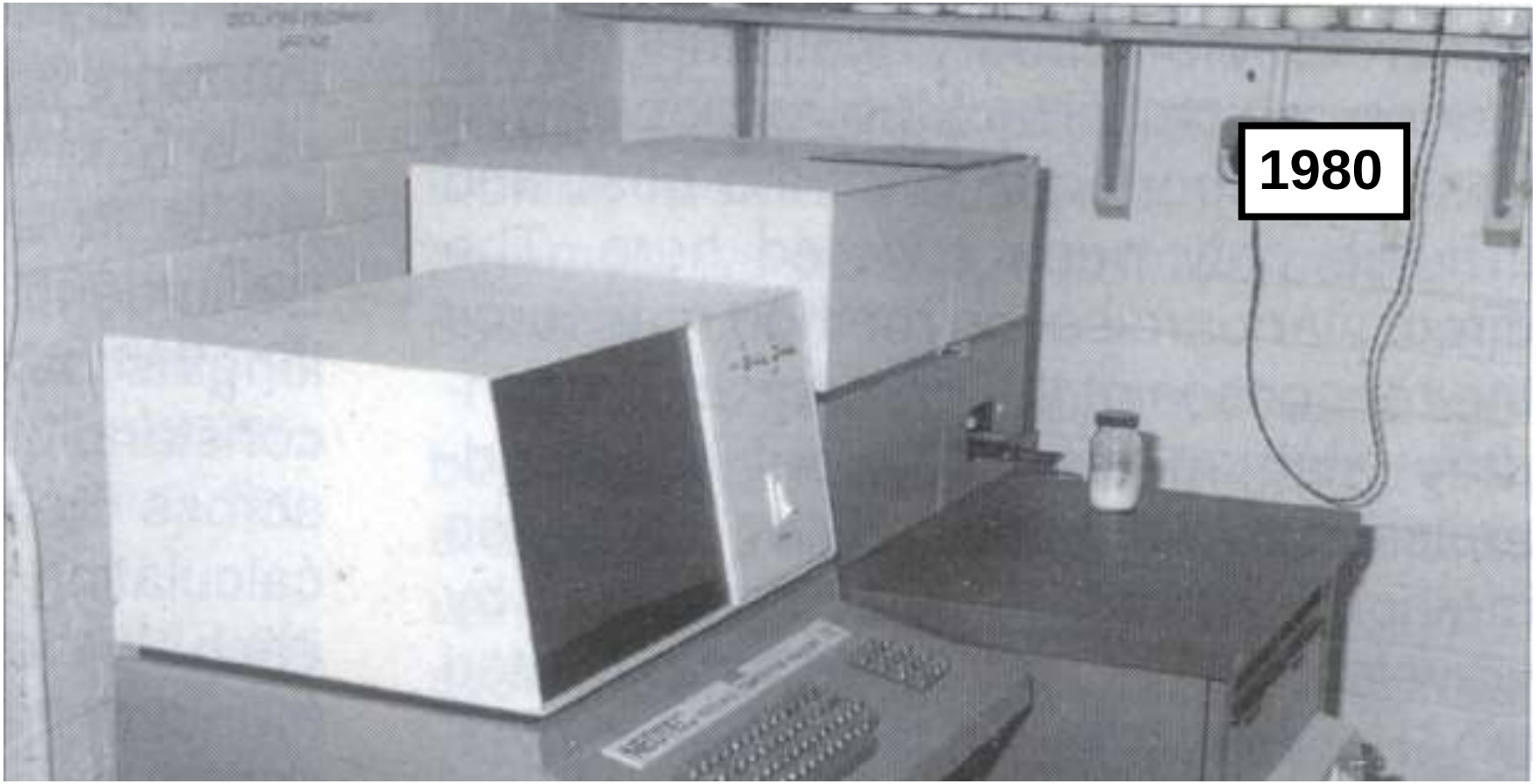
- **use of 'universal' and recognized data bases (models)**
  (+ wireless & internet)

- **chemometrics (new algorithms & computing power)**

- **increase of on-line installations/measurements**

- **new low cost portable spectrometers**

- **new applications for imaging spectroscopy**



Underneath, the big box is full of electronics boards and a panel of switches. It is the computer. A data general minicomputer with 32 kb of ram and 2 floppy disk drivers of 8 inches.
The floppy capacity was 128 kb. One floppy was for the program the second for the data with a maximum of 200 spectra in each.
We calibrated only with a manual step-up regression wavelength by wavelength. If you were lucky, within a day, you had a final model.

P. Dardenne

2007

CRA-W Gembloux

es agronomiques

INSTRUMENT IMPROVEMENTS

-Sources
-Optical components
-Detectors
-Electronics (communication)

Sample presentation:
- large cups
- slurries
- liquids
- on-line (belts, pipes, …)
  - fiber optics
  - remote scanning

INSTRUMENTATION TRENDS

- miniaturization
→ portable

- imaging

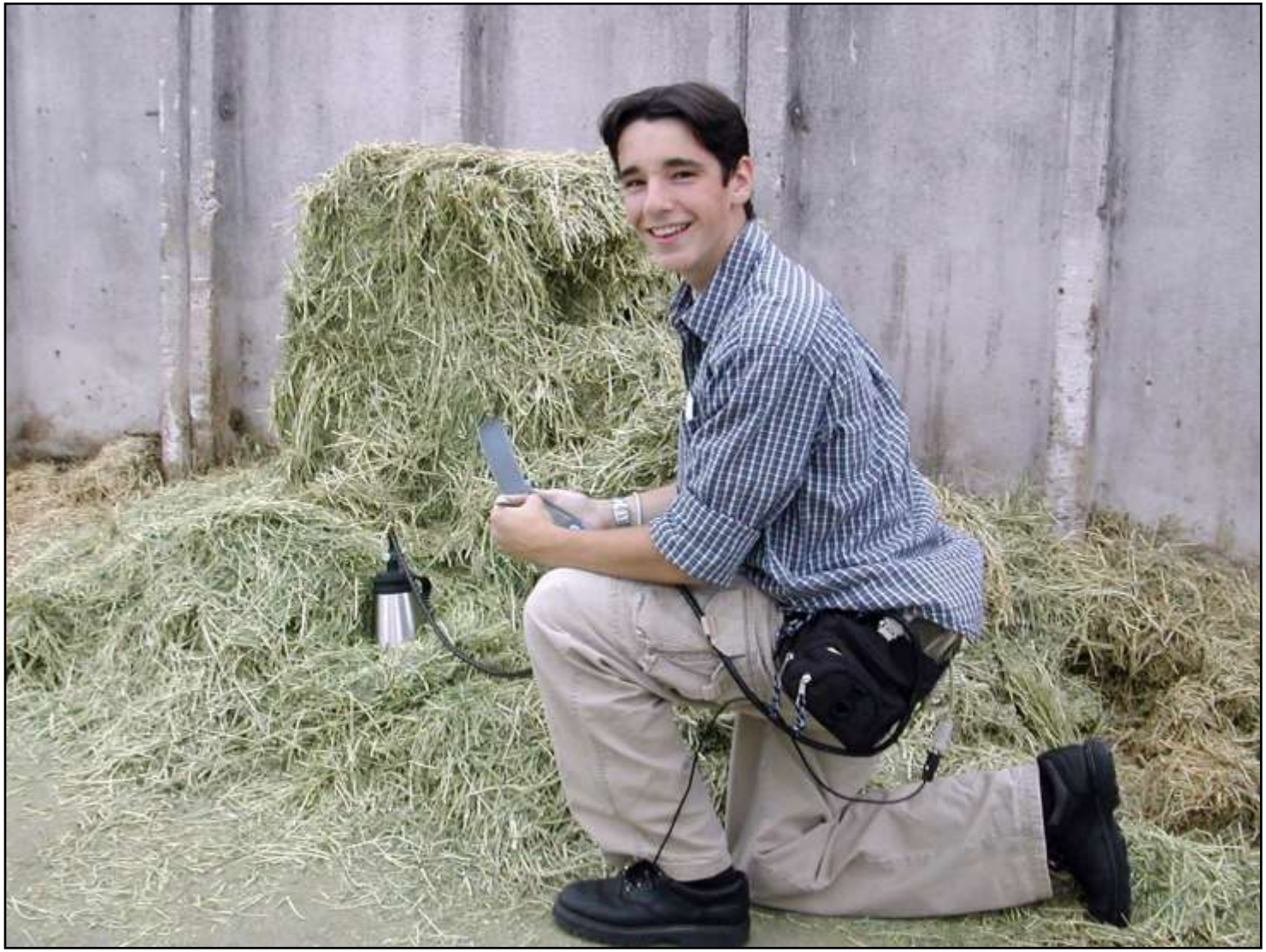
- NIRS instruments to arrive factory-calibrated

- Or user can purchase factory calibrations based on large sample sets

- NIRS instruments with no calibrations

Low cost spectrometer – farm level

INSTRUMENTATION TRENDS - MINIATURIZATION



Courtesy of Dr John Schenk

INSTRUMENTATION TRENDS - MINIATURIZATION

Figure # 1. NIR Hand-held Analyzer is taking readings for Brix, pH, TA in vineyard without removing it from vine

Brimrose Corporation USA

INSTRUMENTATION TRENDS - PHAZIR

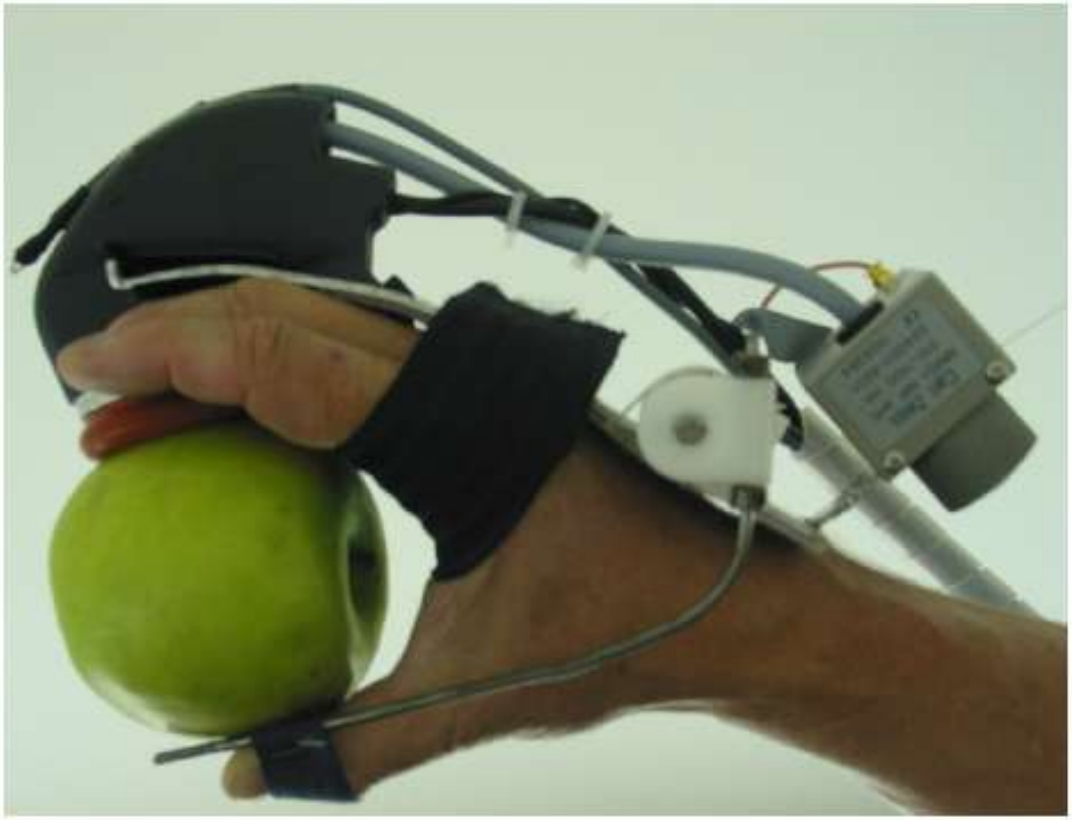
INSTRUMENTATION TRENDS

Gant instrumenté pour mesurer la qualité des fruits

GLOVE

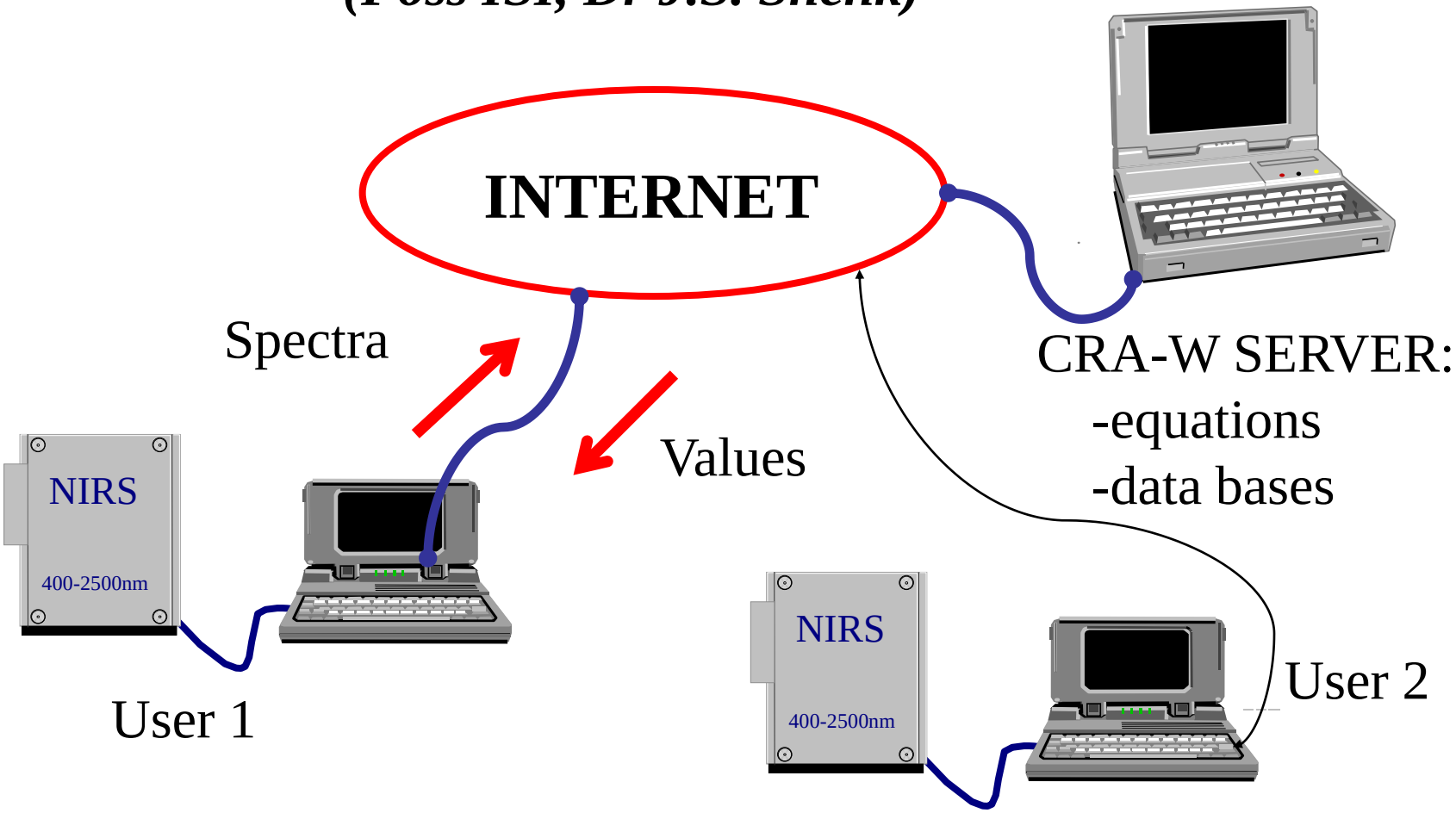
Projet Européen PL 97- 3399 (1998 - 2001)

Partenaires : (Belgique) ; APOFRUIT (Italie); Institut für Agrartechnick Bornim e. V. (Allemagne) VERHAERT (Belgique); Katholieke Universiteit Leuven - sous la coordination du CEMAGREF - UR Giqual



NETWORKS OF INSTRUMENTS

RINA® : ***Remote Instrument Near Analysis***
(Foss ISI, Dr J.S. Shenk)

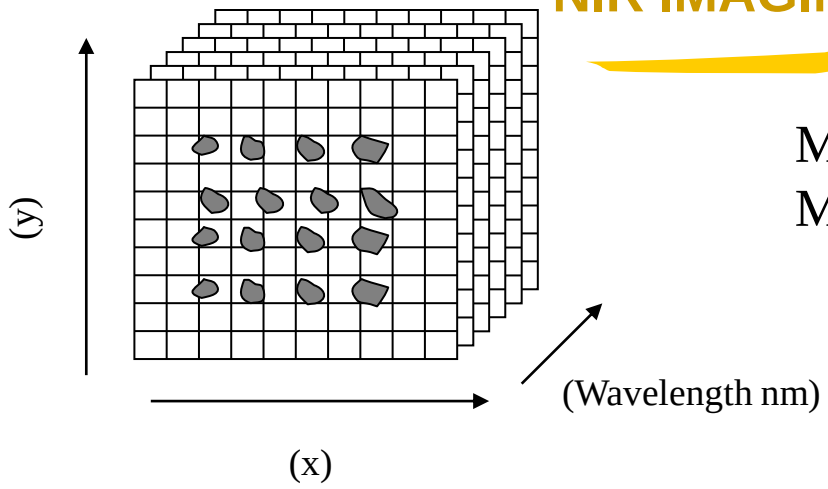


IMAGING

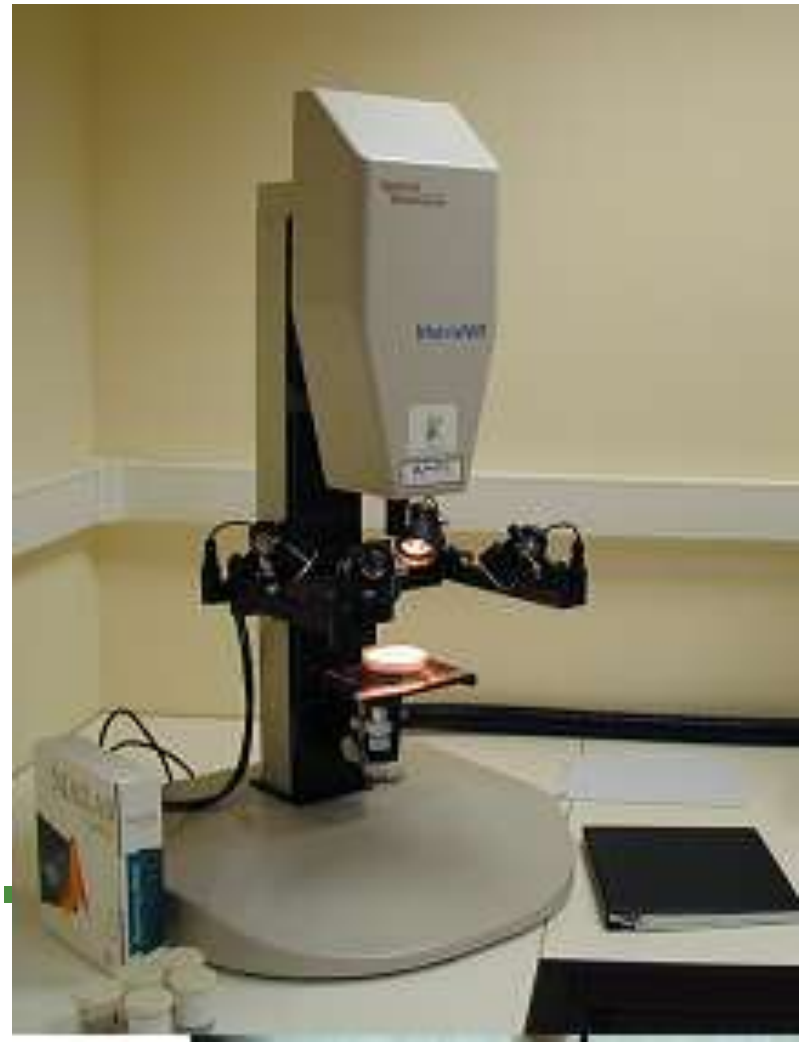
Dedicated session at NIR 2007
Umeå, Sweden
organized by Jim Burger

http://www.nir2007.com/

NIR IMAGING SYSTEM



Matrix NIR,
Malvern Instruments Ltd, Malvern, UK



- **Camera InGaAs**
- **900 - 1700 / 10 nm**
- **240 x 320 pixels**
- **Each pixel: 70 µm*70 µm**
- **Analyzed surface : 5 cm²**
- **76 800 spectra 24 MB**
- **Analysis time : +/- 10 min**

Instrumentation

Chemometrics

Applications

Big gap between published algorithms and what the manufacturers can propose

Quantification

MLR
PLS
ANN
LS-SVM
…

Variable selection

UVE-PLS
IVE-PLS
AVS-PLS
…

Classification

PLS-DA
ANN
SVM
SIMCA
k-NN
…

Outlier detection

Leverage
Residuals
Convex hull
Robust techniques
…

CHEMOMETRIC NEEDS

Rapid & specific methods

- **Local**
- **SVM …**

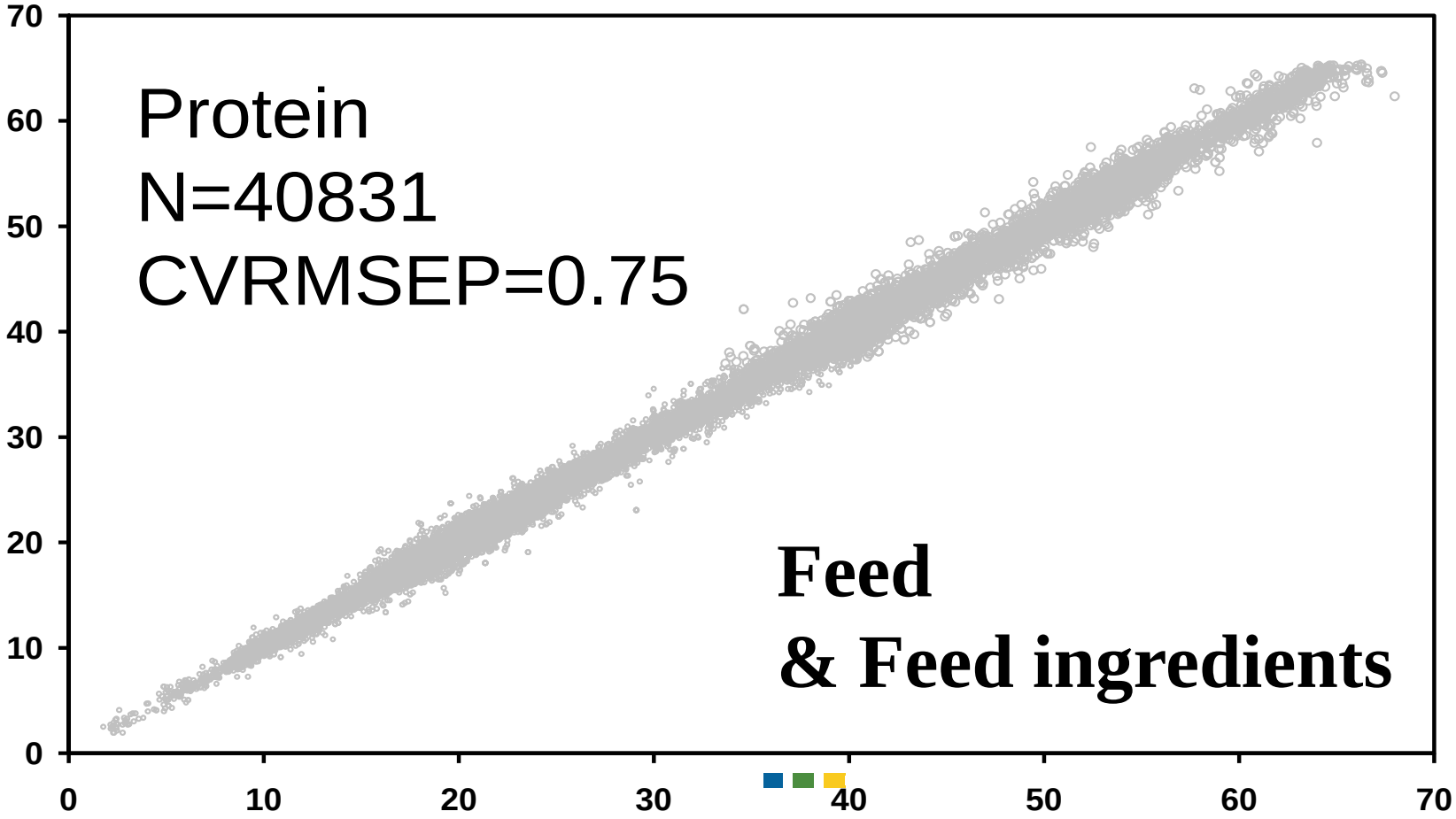
Methods able to deal with:

- **large databases**
- **Uncertainty determination**
- **Noise reduction …**

Dealing with…large data bases and rapid methods

Merging data base: CRA-W & Central Laboratories, UK

Example : PROTEIN
N=40831 by LOCAL WinISI III®
Neighbours samples = 250, Factors ignored=3,
Max factors=33, SNVD 1,4,4 1100-2498/12



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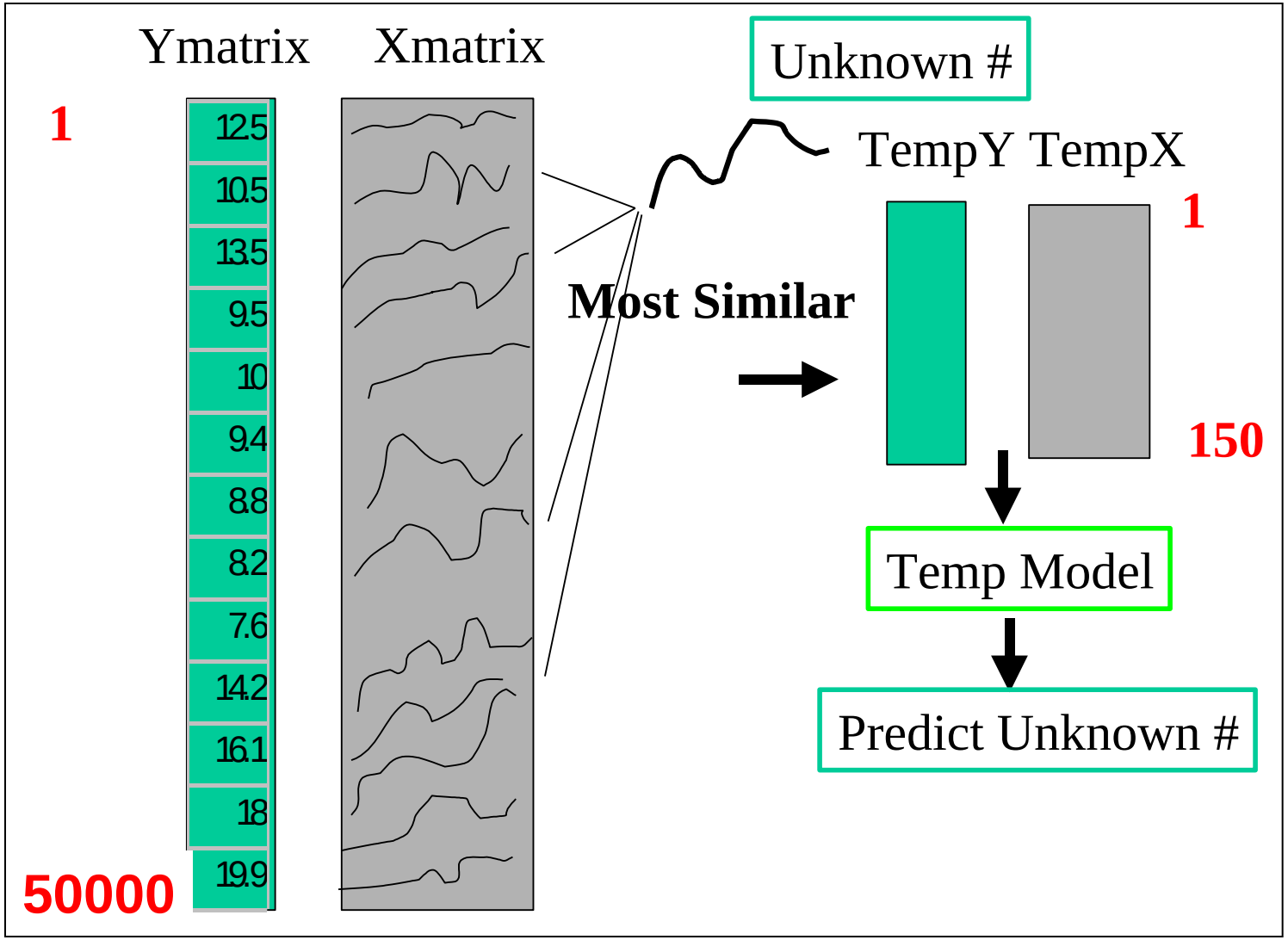
Dealing with…large data bases and rapid methods

LOCAL



LOCAL concept, Dr. J. Schenk, Infrasoft International LLC

Dealing with…large data bases and rapid methods

LOCAL

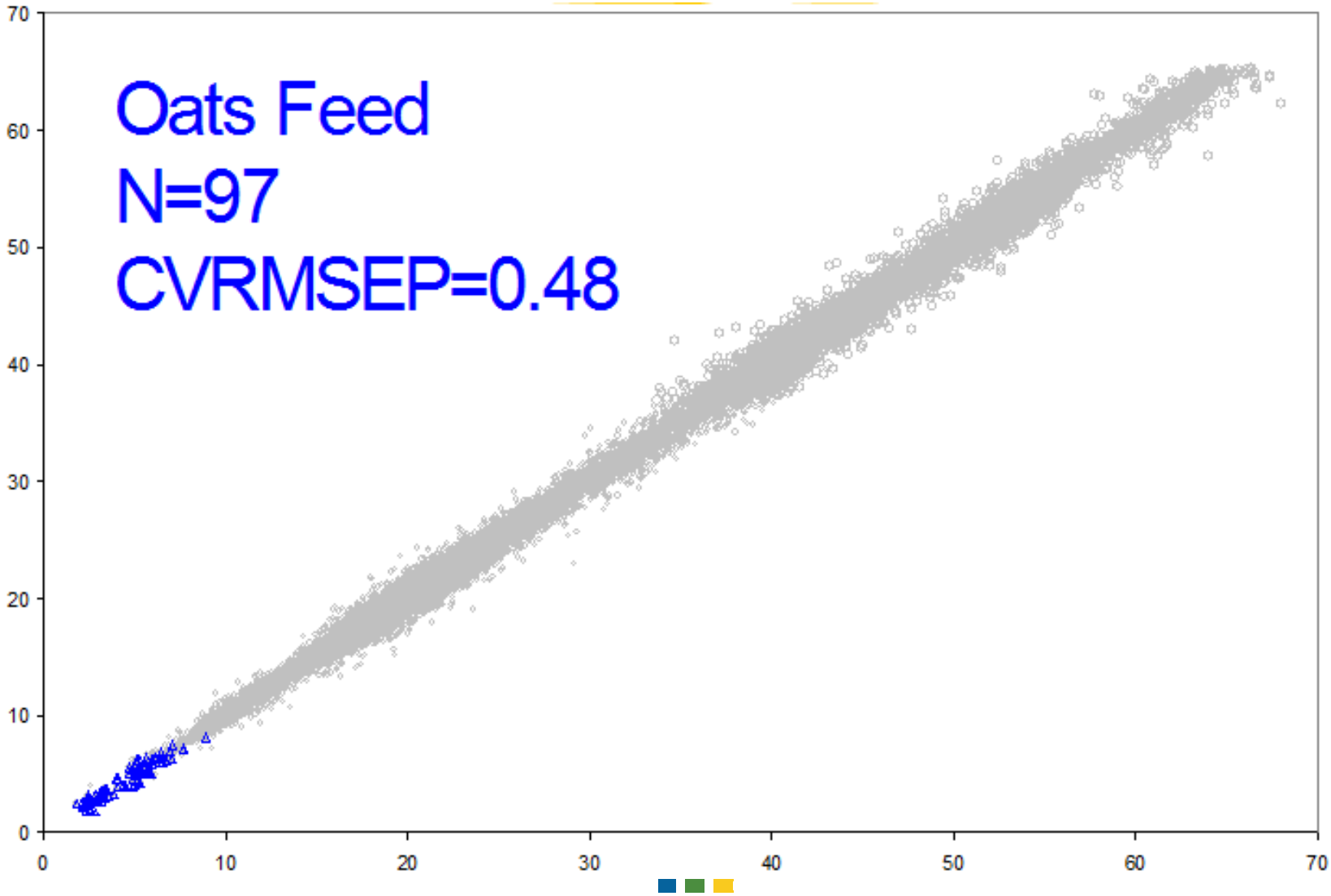
3 parameters: number (N) of closest samples, the maximum number of PLS factors (Fmax) and the minimum number of PLS factors (Fmin).

The final predicted result is a weighted sum of the predicted values from all the models between Fmin and Fmax, values which are weighted according to the standard deviation of the Bcoefficients and to the size of the Xresiduals.

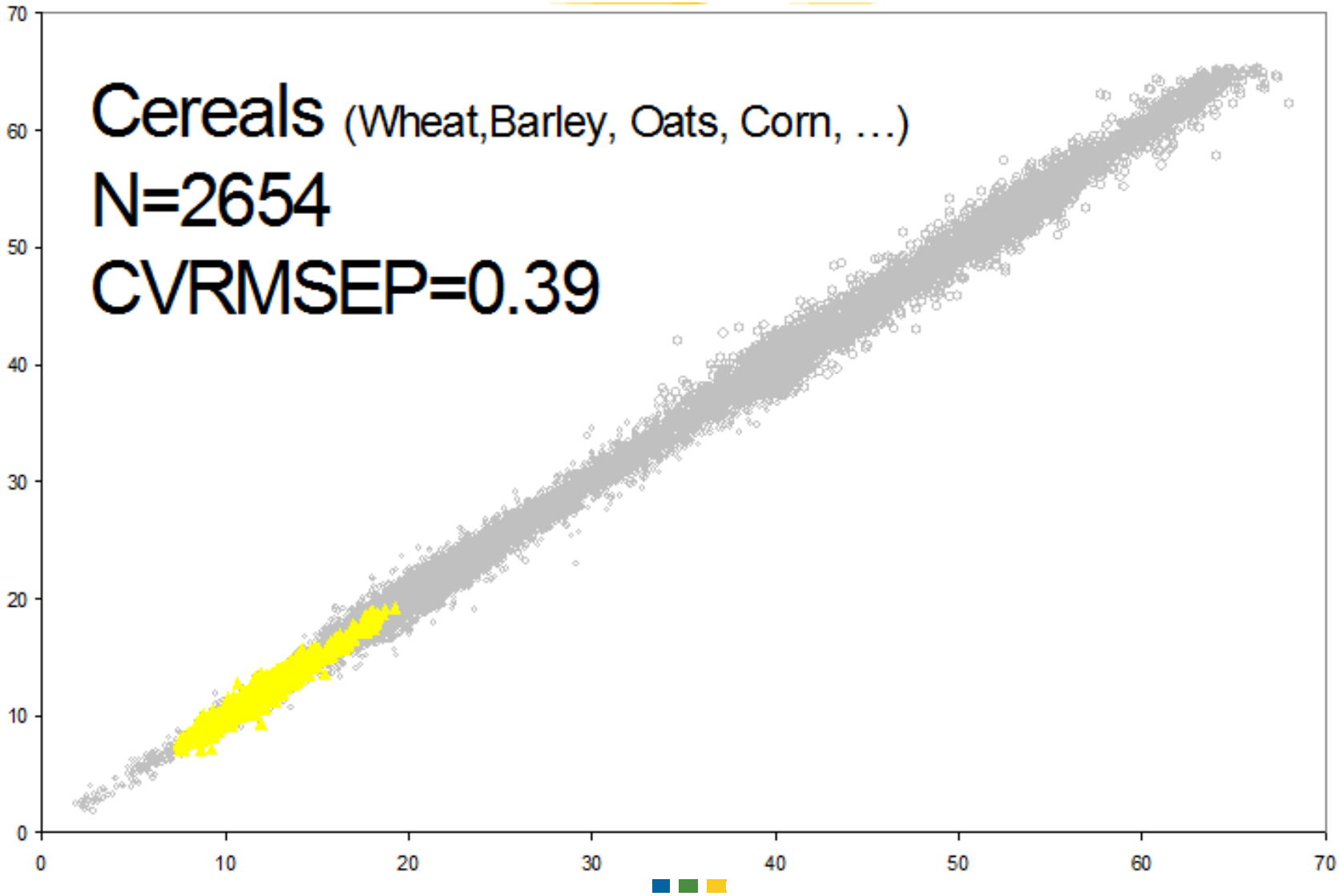
This method is the only one (that we know) which takes information of the unknown sample (the spectrum itself with the use of the Xresiduals) to weigh the predicted values and so to improve the accuracy.

G. Sinnaeve, P. Dardenne, R. Agneessens. Global or local? a choice for NIR calibrations in analyses of forage quality. *Journal of near infrared spectroscopy, vol.2, 163-175, 1994.*

Dealing with…large data bases and rapid methods



Dealing with…large data bases and rapid methods



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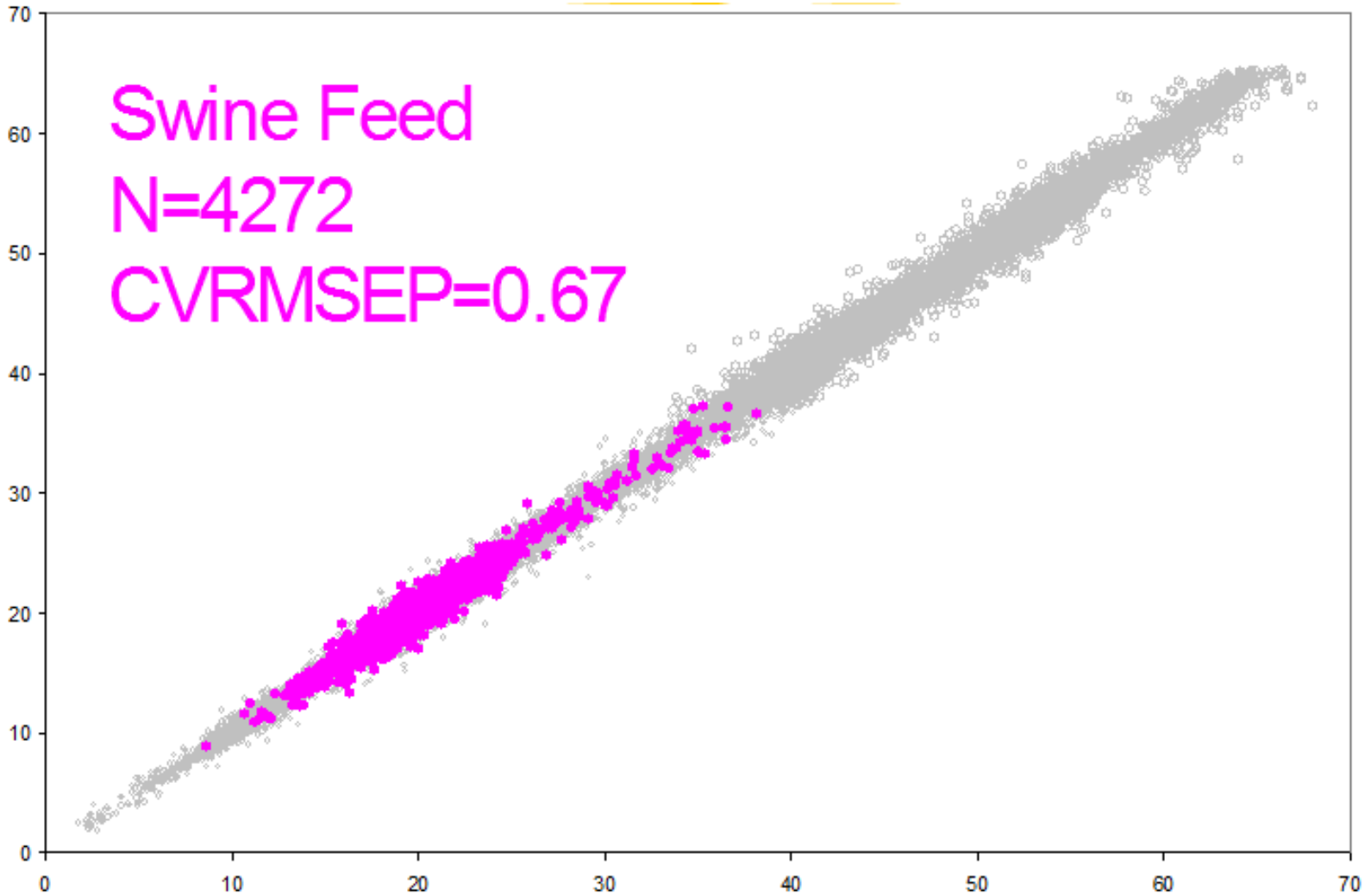
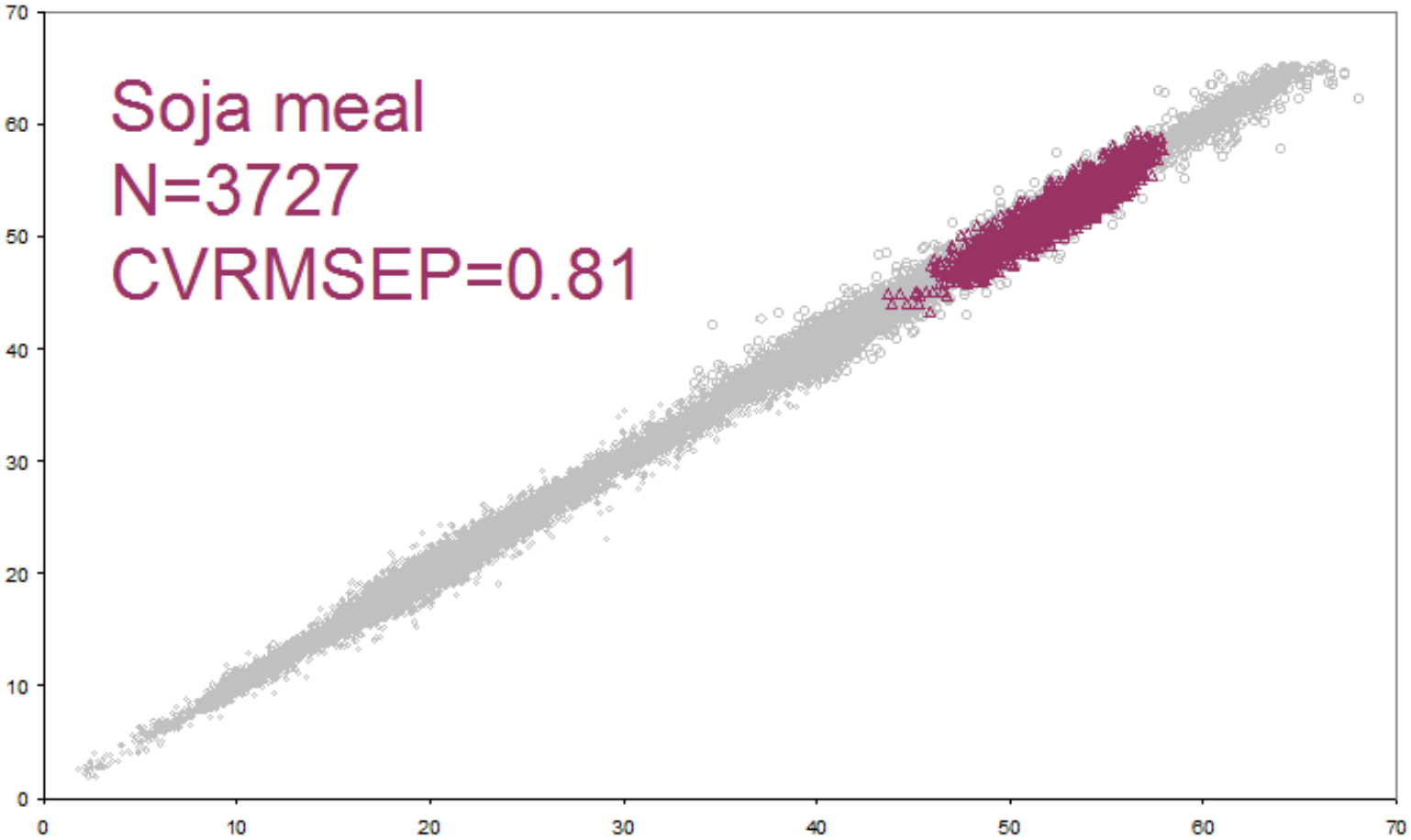
Dealing with…large data bases and rapid methods



Dealing with…large data bases and rapid methods



Dealing with…uncertainty

The uncertainty of a calculated value is statistically defined as the interval around that value such that any repetition of the calculation will produce a new result that lies within this interval with a given probability

Klaas Faber
'Estimating Uncertainty in Multivariate Calibration'

Dealing with…uncertainty

$$\text{RMSEP} = \sqrt{N^{-1}\sum_{n=1}^{N}\left(\hat{y}_n - y_{n,\text{ref}}\right)^2}$$

$\hat{y}_n$ = prediction for sample n

$y_{n,\text{ref}}$ = associated reference value

Dealing with…uncertainty

The result (RMSEP) is a constant measure for prediction uncertainty that cannot lead to prediction intervals with correct coverage probabilities (say 95%).

A crucial assumption is that the reference values are sufficiently precise; this is certainly not always true (octane rating, classical Kjeldahl) - often the prediction is even better than the reference value.

High intrinsic variability of RMSEP estimate requires *N* to be large.

Lecture of Ornella Preisner, IBB: Bootstrapping…

Sample-specific prediction uncertainty

of the NIR analyses

$$s(\hat{y}_i - y_i) = \left[(1+h_i).SEC^2 - S_{ref}^2\right]^{1/2}$$

Faber and Bro, *Chemom., Intell. Lab. Syst.* 61, 133 (2002)
Fernandez Pierna & *al., Chemom., Intell. Lab. Syst.* 65,281 (2003)

$$SEP_{actual}^2 = SEP_{observed}^2 - SEL_{ref}^2$$

Dealing with…noise

Regression model $$y = Xb + e$$

$$b = (X^T X)^{-1} X^T y$$

A good estimate for ***b*** is required
It must provide:
- A good fit to y
- good predictions for unknown samples

Dealing with…noise

The accuracy of b (and therefore the accuracy of $\hat{y}$) estimated by NIR models depends on the quality of the reference method.

The performance of the reference laboratory methods limits the reliability of the NIR calibrations.

A crucial assumption in multivariate calibration is that the reference values are sufficiently precise. This is not always true!

Dealing with…noise

L. Munck, Univ. Copenhagen

"*Data is 'the king' that rules chemometric modelling*"

Phil Williams, PDK Grain, Canada

"Just as the spectra are the heart of NIRS technology, the reference test is the heart of NIR applications"

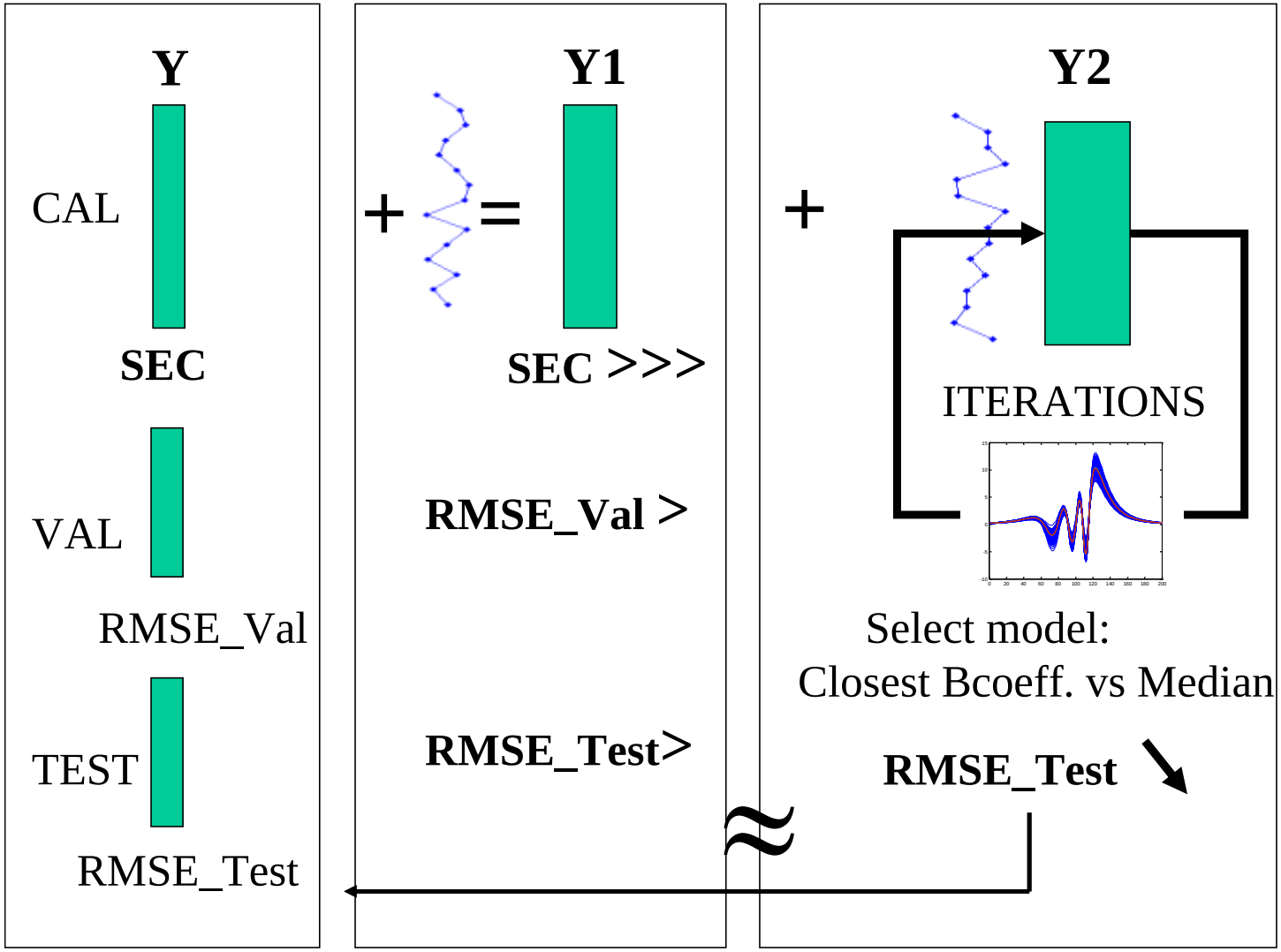
Dealing with…noise

We aim to prove that one can still have good calibrations with quite poor reference values or with a large quantity of noise added.

NAPLS

Dardenne P. & Fernández Pierna J. A. 'A new method to improve the accuracy of the NIRS models: NAPLS: Noise addition PLS method'
J. Near Infrared Spectrosc. 14, 349-355 (2006)

NAPLS



Dardenne P. & Fernández Pierna J. A. ‘A new method to improve the accuracy of the NIRS models: NAPLS: Noise addition PLS method, J. Near Infrared Spectrosc. 14, 349-355 (2006)

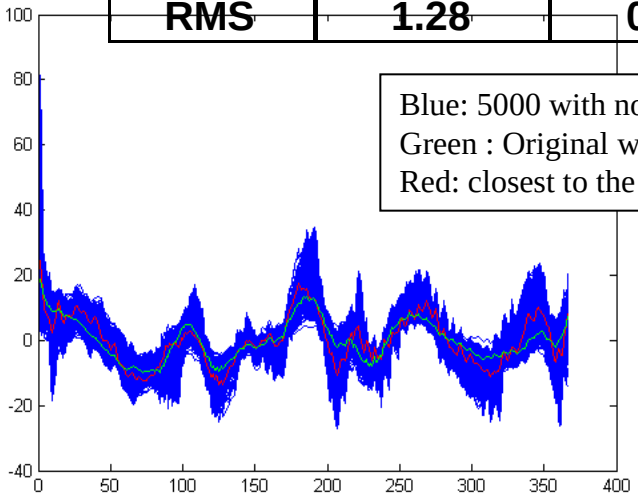
NAPLS – FORAGE DATA SET

Run	RMScal_noise	RMSval	RMStest	RMStest_final	% diference test
1	1.65	0.77	0.86	0.59	31.61
2	1.52	0.68	0.82	0.67	17.39
3	1.41	0.71	0.80	0.62	22.36
4	1.62	0.68	0.86	0.62	28.12
5	1.67	0.91	1.02	0.80	21.41
6	1.49	1.05	0.97	0.68	30.02
7	1.64	0.80	0.80	0.58	26.88
8	1.50	0.77	0.75	0.55	27.47
9	1.68	0.76	0.77	0.60	22.43
10	1.67	0.67	0.64	0.56	12.30
RMS	1.59	0.79	0.84	0.63	24.43

RMStest_orig=0.60

NAPLS – WHEAT DATA SET

Run	n=100 RMScal_noise	n=100 RMSval_noise	n=2450 RMStest_noise	RMStest_final	% diference test
1	1.34	0.50	0.47	0.39	15.51
2	1.28	0.57	0.50	0.42	16.43
3	1.25	0.63	0.53	0.36	32.70
4	1.24	0.69	0.59	0.42	28.71
5	1.27	0.64	0.55	0.41	26.22
6	1.27	0.65	0.55	0.37	33.67
7	1.36	0.59	0.53	0.36	30.94
8	1.23	0.62	0.55	0.37	32.04
9	1.21	0.53	0.47	0.38	19.64
10	1.31	0.57	0.50	0.40	20.15
RMS	1.28	0.60	0.53	0.39	26.05



Blue: 5000 with noise
Green : Original without noise
Red: closest to the median

RMStest_orig=0.50

Near Infrared Spectroscopy (NIRS)

Instrumentation

Chemometrics

Applications

APPLICATIONS DEVELOPED AT CRA-W

- Fertilizers
- Soils
- Seeds & Phyto-sanitary Protection
- Crop monitoring (N)
- Precision Agriculture
- Nutritive value (feed & forages)
- Technology (flour, baking quality,…)
- Authentication (olive oil, meat, honey,…)
- Fruits
- Transformed Products (meat, dairy, juices,…)
- Bio-fermentation monitoring

•NUTRITIVE VALUE OF FEED

CHEMICAL COMPOSITION & DIGESTIBILITY

- **Moisture – DM**
- **Ashes – OM**
  + P, Ca, K, Mg
- **Fat**
  + FA profile
- **Proteins (N)**
  + AA profile
- **Fibres**
  (cellulose, NDF,ADF,ADL)
- **Starch**
  + amylose - amylopectin
- **Total Sugar**
  + sugar profile
- **OMD**
  in vivo, *in vitro*, enzymatic

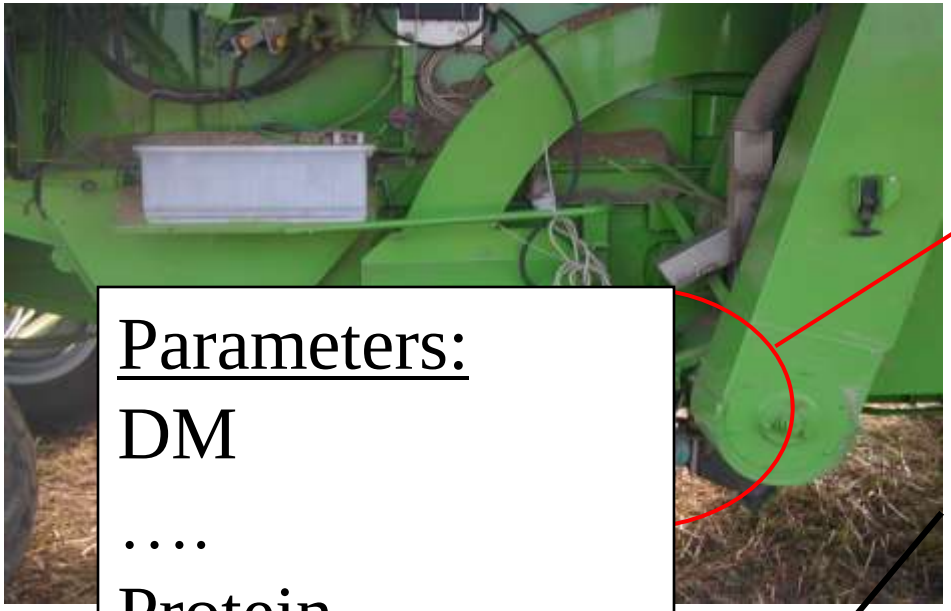
Feed Ingredients

Cereals & by-products
Wheat bran
Soyameal
Sugarbeet pulp
Animal protein (MBM)
.....

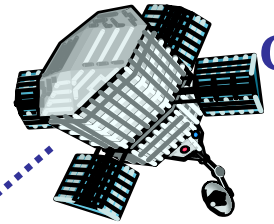
Complete feed

Cattle
Swine
Poultry
Pet food

PRECISION AGRICULTURE



NIR Spectrometer



GPS

<u>Parameters:</u>

DM

….

Protein

Fibre

OMD

.

.

CONCLUSION

- use of ‘universal’ and recognized data bases (models) (+ wireless & internet)

- chemometrics (new algorithms & computing power)

- increase of on-line installations/measurements

- new low cost portable spectrometers

- new applications for imaging spectroscopy

EVENTS

Belgian Chemometrics Society

Workshop on Multivariate Image Processing

November 8, 2007
Gembloux - Belgium

9th Belgian Chemometrics Symposium and presentation of the D.L. Massart Award in Chemometrics 2008

April 11, 2008, Brussels

http://www.chemometrie.kvcv.be

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FEED SAFETY
International Conference 2007
Methods and Challenges
27th and 28th November 2007

Centre de Congrès du Beffroi
Namur - Belgium

http://safeedpap.feedsafety.org/fs2007/

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