Calibration Transfer

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NIR INSTRUMENTS – CRA-W

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•1976 R.Biston : CRA – Station de Haute Belgique   (Libramont)

•1979 Neotec FQA51 *(Feed Quality Analyser)*

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e

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Since 1987 9 laboratories

PSCo 4250
Perstorp 4500
NIRsystems 5000
Foss XDS

Asbl REQUASUD
Cellule de coordination
Rue de Liroux, 9
5030 GEMBLOUX

081/62.65.73
www.cra.requasud.be

John Stoner Shenk, Ph.D   25-07-1933 - 15-09-2011

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Infrared spectrometers at CRA-W

FOSS – Nirsystems (2) & Tecator (2) & InfraXaxt & XDS (2)
ProFoss DA ; (DS2500; DA1800)
~~Bran & Luebbe (2) T500 & T450~~
Perten DA7000 & DA7200
Bruker – MPA + Matrix F
Unity Scientific – spectrastar 2500
Zeiss Corona (2)
Buchi – NIRFlex 500
Thermo-Fisher Antaris

Boerhinger - microparts
Polychromix – Phasir (2)
(Brimrose Luminar)
Ocean Optics (2)
Shenk RA1630

Lactoscope (Delta Instruments)
Bruker VERTEX80 (FT-MIR+ RAMAN)
Foss WineScan

Perkin-Elmer (FT-NIR + microscope)
Spectral Dimensions Inc. NIR-Matrix
BurgerMetrics HSI

NIR APPLICATIONS developed at CRA-W

- Fertilizers (N, P, K, Humic acids)
- Soils (N, C, CEC, …)
- Seeds & Phyto-sanitary Protection (seed/seed)
- Crop monitoring (N)
- Precision Agriculture
- Nutritive value (feed & forages)
- Technology (flour, baking quality,…)
- Authenticity (orange juice, wine, olive oil, meat, honey,…)
- Fruits (apples)
- Bio-fermentation monitoring (starch→glucose→Ethanol)
- Biofuels & Biomethanisation
- NIR miscroscopy &
- Hyperspectral Imaging (animal meal)

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•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

Large data base:

File Name: D:\$DATA\6PRODUIT\MAIS\#5PE99.EQA Equation File File Date: Tue Sep 1
Master No: 00000000 Instrument Model: NIRSystem 5000 Serial No:
Lab Basis Dry Matter
Segment 1 1100 - 2498, 2

Constituent	N	Mean	SD	SEC	RSQ	SECV	1-VR
MSA	5916	93.2273	1.4512	0.5028	0.8800	0.5059	0.8785
CT	6224	4.3167	0.9695	0.4059	0.8247	0.4137	0.8189
MPT	4875	7.7373	1.1904	0.3532	0.9120	0.3575	0.9098
CEL	4266	20.7461	4.0436	0.9021	0.9502	0.9091	0.9495
Amidon	5572	27.7837	10.2633	1.6199	0.9751	1.6306	0.9748
NDF	4155	42.7243	6.6110	1.6407	0.9384	1.6549	0.9374
ADF	3184	23.8093	4.6873	1.0475	0.9501	1.0626	0.9486
ADL	3092	2.6685	0.7943	0.3798	0.7714	0.3845	0.7657
DMSrt	2005	73.5847	5.8899	1.8968	0.8963	1.9338	0.8922
DMOrt	2189	72.4042	6.0304	1.9148	0.8992	1.9487	0.8955
DMOauf	3177	67.6176	6.5700	2.2644	0.8812	2.2955	0.8779
DMSauf	3284	68.1764	6.0014	2.1665	0.8697	2.1915	0.8667
SSr	4714	5.8156	4.1260	0.9589	0.9460	0.9702	0.9447
SSt	2715	7.6885	5.5840	0.5992	0.9885	0.6127	0.9880

~ 500 000 €

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WHY TRANSFERING CALIBRATION ?

→ Use models on more than 1 instrument
- same type
- different types

→Use 'old' models with a 'new' instrument
- repairing
- lamp change
- sample presentation
- ….

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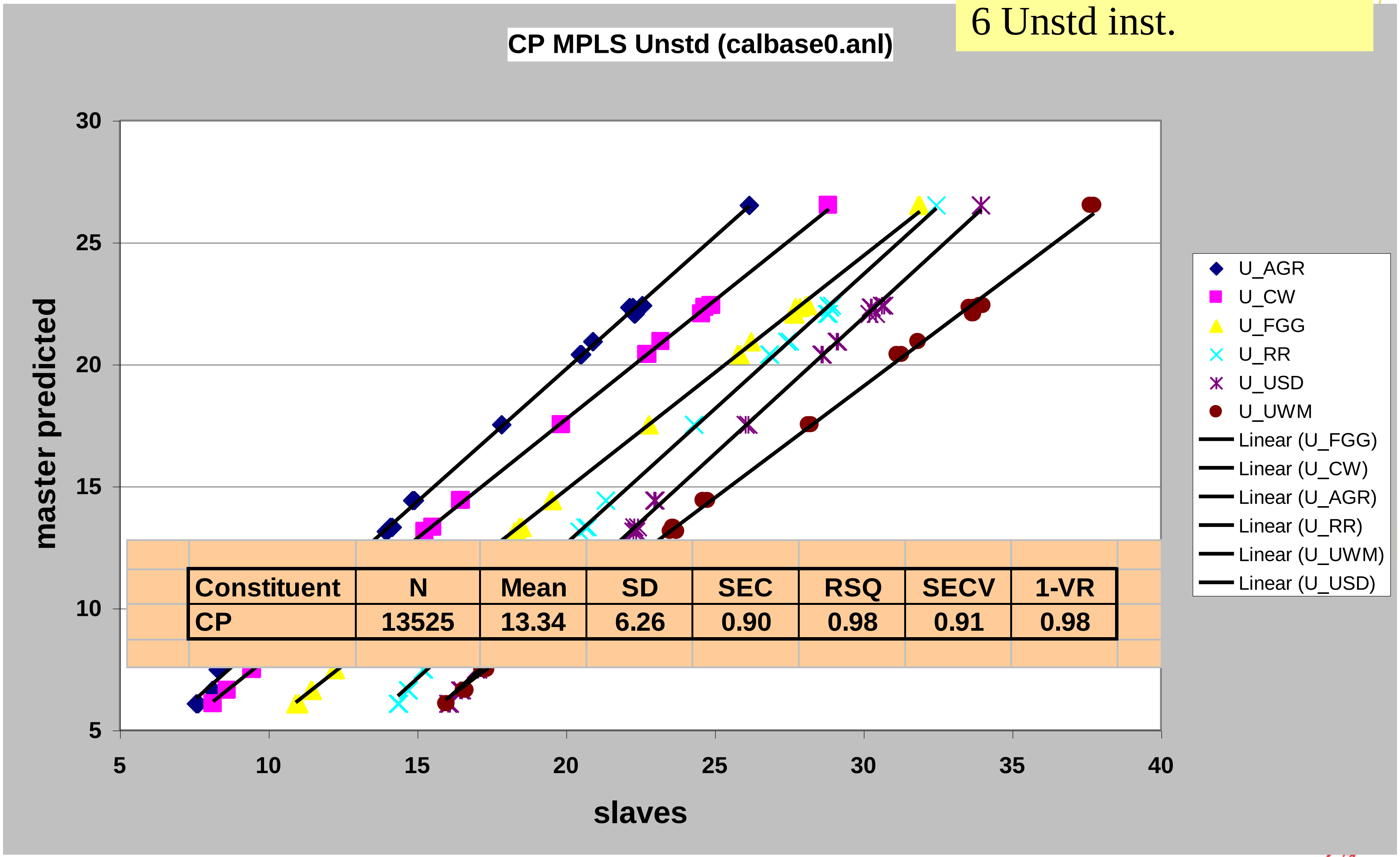
STANDARDISATION OF NIR INSTRUMENTS, INFLUENCE OF THE CALIBRATION METHODS AND THE SIZE OF THE CLONING SET, Dardenne et al., ICNIRS 2001, Kyongju.

Dried & ground forages
15 sealed cups 2 rep
6 Unstd inst.



Constituent	N	Mean	SD	SEC	RSQ	SECV	1-VR
CP	13525	13.34	6.26	0.90	0.98	0.91	0.98

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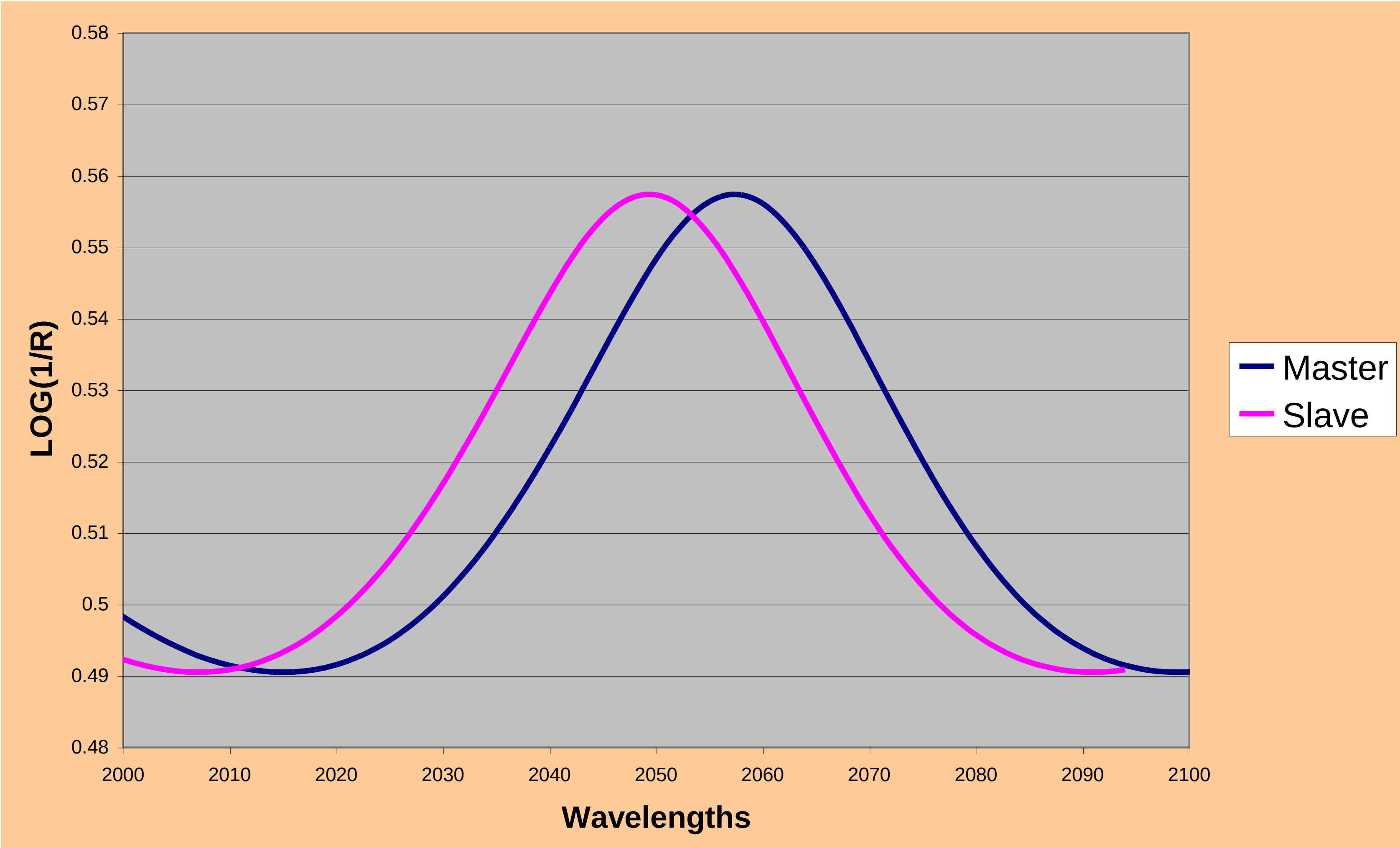
Instruments are different: wavelength axis



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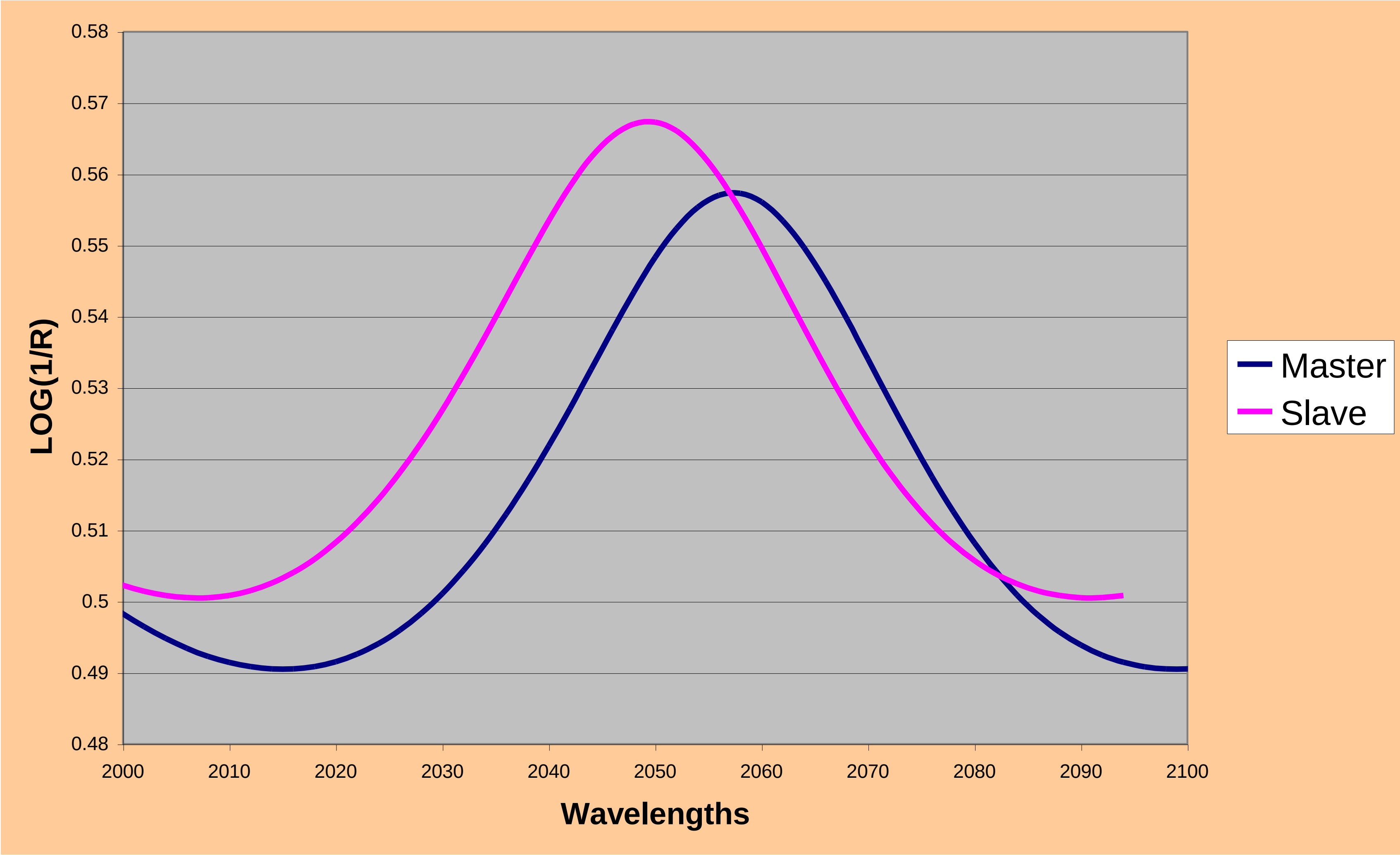
Instruments are different: absorbance axis



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TRANSFER METHODS

-Slope & bias

-Shenk & Westerhaus CLONE, *Shenk et al., 1985*

-DS Direct Standardisation, *Wang et al.,1991*

-PDS Piecewise Direct Standardisation, *Wang et al.,1991*

-FIR Finite Impulse Filter, *Blank et al., 1996*

-WT Wavelet Transform, *Walczack et al.,1997*

-OSC Orthogonal Signal Correction,
Wold et al., 1998, Sjöblom et al.,1998

-ANN, *Despagne et al., 1998, Duponchel et al.,1999*

- ***PCS Tom Fearn – Jean-Michel Roger***

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SLOPE & BIAS correction

of the predicted data from secondary instrument:

Ref values : reference method OR master predicted data

Bias ≠ 0.0 ?

$$BiasConfidentLimit = \pm(t_{(1-\alpha/2)}.SEP)/\sqrt{n}$$

If SEP=1, N=20 and α=5%,

$$BCL = \pm(2.09*1)/\sqrt{20} = \pm 0.48$$

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SLOPE & BIAS correction

of the predicted data from secondary instrument:

$$SlopeConfidentLimit = b \pm t_{(1-\alpha/2)} \cdot \sqrt{RSD^2 / SSD_{\hat{y}}}$$

$$RSD = \sqrt{\frac{\sum_{i=1}^{n}\left(y-(a+b.\hat{y})\right)^2}{n-2}} \qquad SSD_{\hat{y}} = Sd\hat{y}^2.(n-1)$$

If $RSD = 1$, $Sd\hat{y} = 2$, $N = 20$ and $\alpha = 5\%$

$$SlopeConfidentLimit = b \pm 2.09 * \sqrt{1/(2^2 * 19)}$$

Slope Confident Limits : b-0.24 and b+0.24

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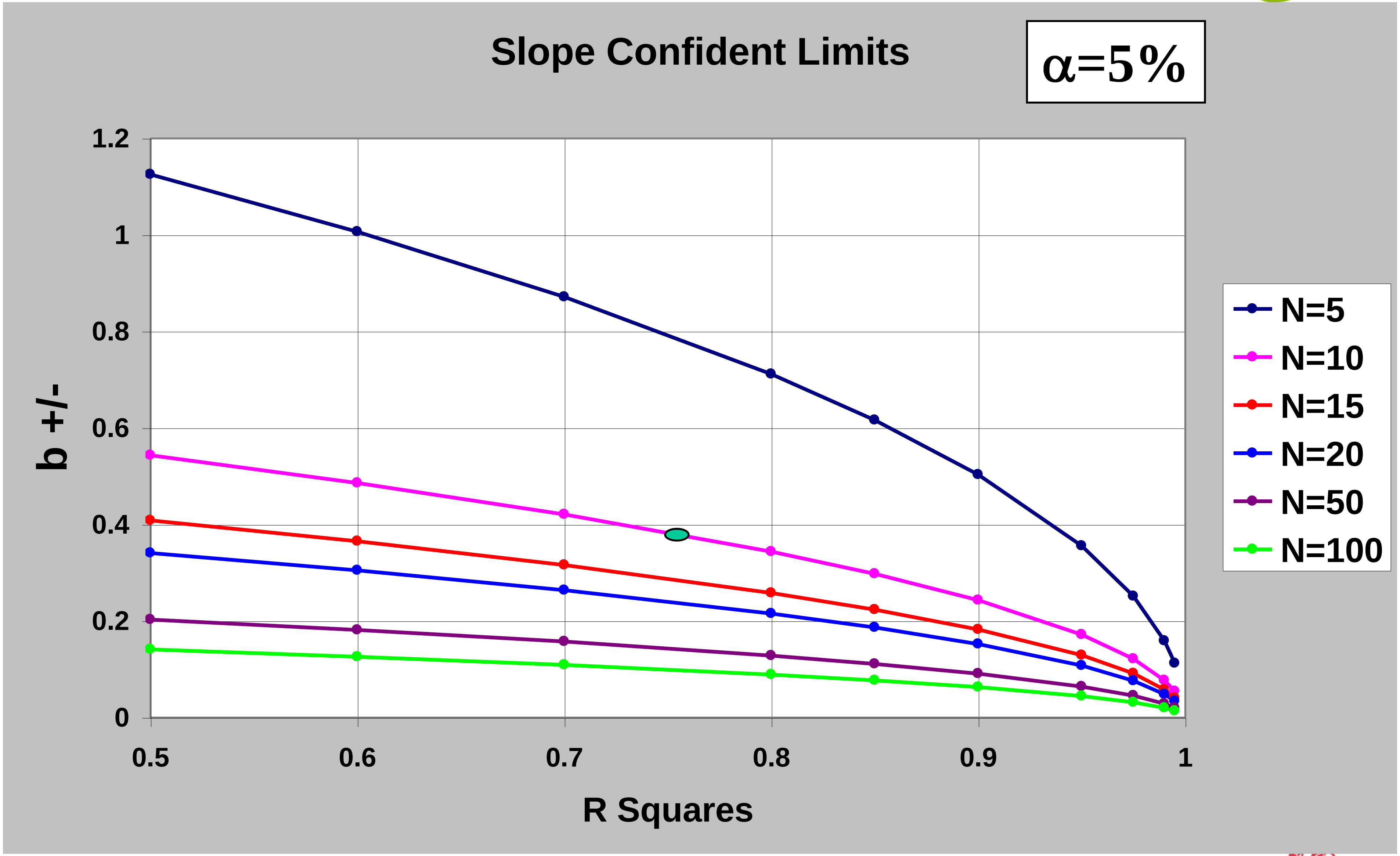
SLOPE & BIAS correction



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= Validation procedure ; (ISO 17025)

ISO 12099:2010

Animal feeding stuffs, cereals and milled cereal products -- Guidelines for the application of near infrared spectrometry

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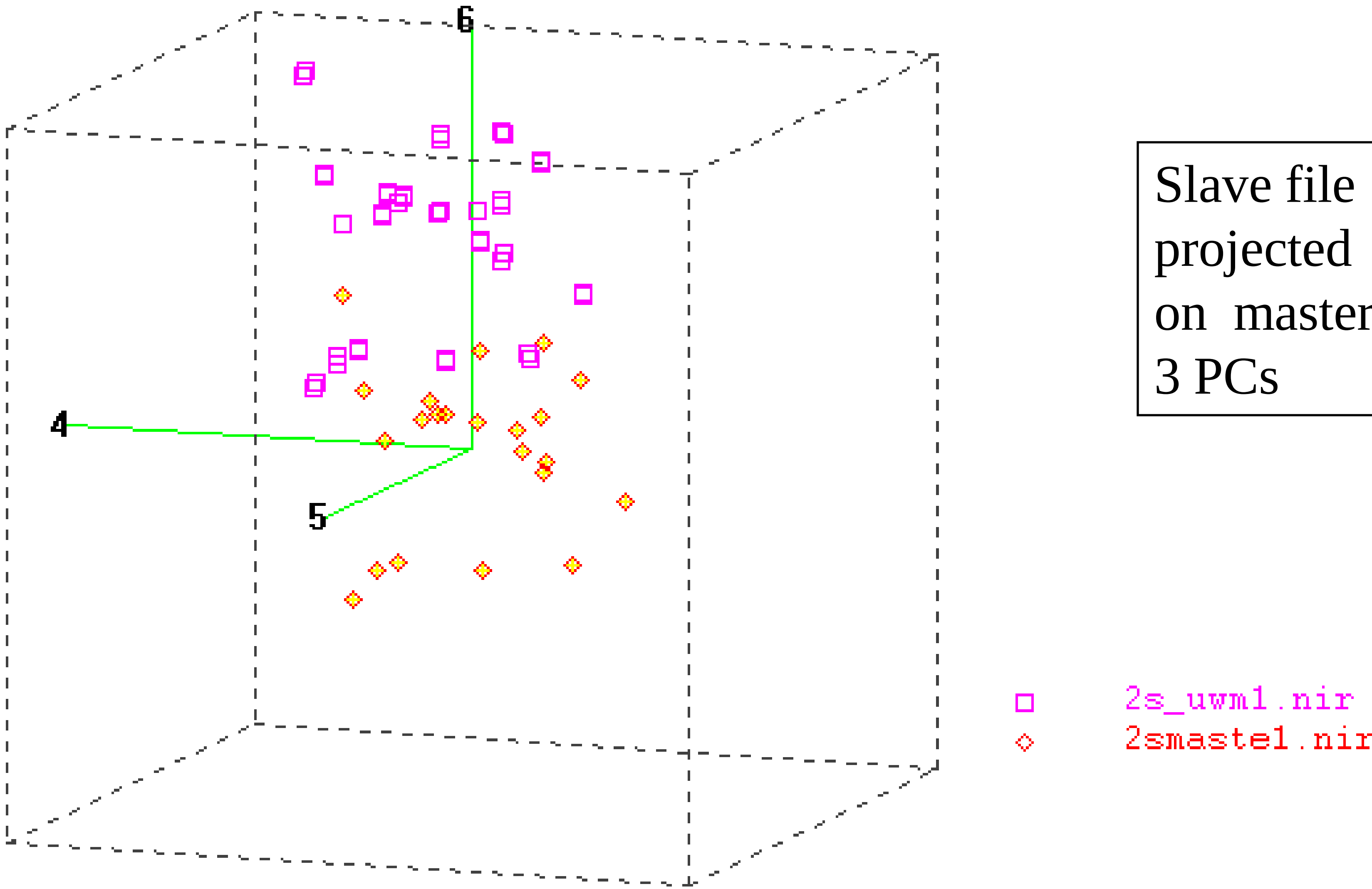
SLOPE & BIAS correction

Prediction mode:

Mahalanobis distances and Xresiduals are Unusable



Slave file projected on master 3 PCs

SLOPE & BIAS correction

OK but

- must be done /product /constituent
- impossible to merge spectra files
- spectral distances unusable

T.Fearn, JNIRS, vol9 N°4, 2001

« Its simplicity has led to widespread misuse, with perfectly good calibrations being subjected to regular small and unnecessary adjustments using biases estimated from results on one or two samples »

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Standardisation: which direction ?

Target is secondary instrument : ('forward')[a]

instrument types are different

not the same resolution and/or wl range

mono to filter

→ new models

Target is master instrument: ('backward')[a]

instrument type is the same

same models

large networks

→ same models

[a] *Campbell, 1996*

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Direct Standardisation: transfer function

$$X^{a} = b + XF$$

Wang et al.,1991
Fearn,JNIRS, 2001

$$\begin{bmatrix} X_1^a & X_2^a & X_3^a & X_4^a & X_5^a \end{bmatrix} = \begin{bmatrix} b_1 & b_2 & b_3 & b_{14} & b_5 \end{bmatrix}$$

$$+ \begin{bmatrix} X_1 & X_2 & X_3 & X_4 & X_5 \end{bmatrix} \times \begin{bmatrix} f_{11} & f_{12} & f_{13} & f_{14} & f_{15} \\ f_{21} & f_{22} & f_{23} & f_{24} & f_{25} \\ f_{31} & f_{32} & f_{33} & f_{34} & f_{35} \\ f_{41} & f_{42} & f_{43} & f_{44} & f_{45} \\ f_{51} & f_{52} & f_{53} & f_{54} & f_{55} \end{bmatrix}$$

~ calibration exercice:

- range of OD, overfitting,
- 700 dp : f (700 x 700)
- estimation of the response at 1100 nm by OD at 2498 ?

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Piecewise Direct Standardisation:

$$
\begin{bmatrix} X_1^a & X_2^a & X_3^a & X_4^a & X_5^a \end{bmatrix} = \begin{bmatrix} b_1 & b_2 & b_3 & b_{14} & b_5 \end{bmatrix}
$$

$$
+ \begin{bmatrix} X_1 & X_2 & X_3 & X_4 & X_5 \end{bmatrix} \times \begin{bmatrix} f_{11} & f_{12} & 0 & 0 & 0 \\ f_{21} & f_{22} & f_{23} & 0 & 0 \\ 0 & f_{32} & f_{33} & f_{34} & 0 \\ 0 & 0 & f_{43} & f_{44} & f_{45} \\ 0 & 0 & 0 & f_{54} & f_{55} \end{bmatrix}
$$

Moving window PLS models.

Double Window Piecewise Direct Standardization (DWPDS) (eigenvector)

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Piecewise Direct Standardisation:

Simplification to simple linear regression

X_1^a	X_2^a	X_3^a	X_4^a	X_5^a	=	b_1	b_2	b_3	b_{14}	b_5

$+$

X_1	X_2	X_3	X_4	X_5

x

f_{11}	0	0	0	0
0	f_{22}	0	0	0
0	0	f_{33}	0	0
0	0	0	f_{44}	0
0	0	0	0	f_{55}

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Shenk and Westerhaus, patented method, 1989.

CLONE procedure (backward)

$$x' = f(x)$$

$$\hat{y} = b_0 + \sum b_i x_i'$$

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CLONE procedure

Winisi, *Shenk & Westerhaus 1985*

Bouveresse et al.,1996

Conditions: n samples (sealed cups)
on master and slave (std conditions)

1. Wavelength axis correction

2. Simple regression / wavelength

→ specific file attached to the instrument

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CLONE procedure (1)

Bouveresse et al.,1996

Conditions: **n** samples (sealed cups)
on master and slave (std conditions)

1. First derivative on both files (sealed cups)
2. Search for peaks on the master file
3. Search for the highest correlation between M & S within a window

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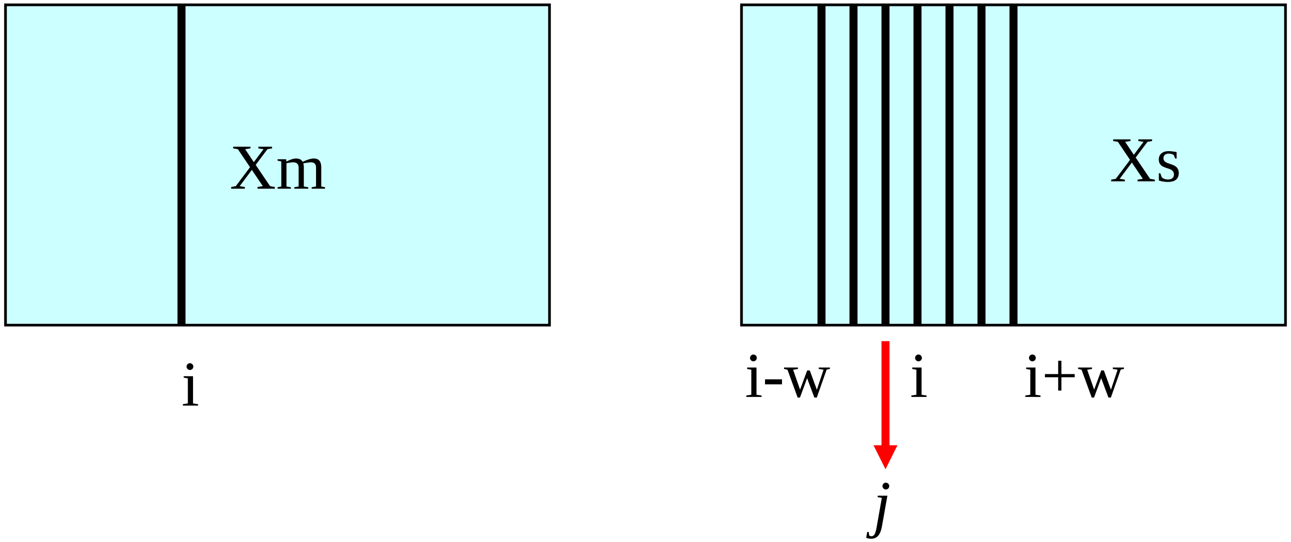
CLONE procedure (2)

First derivative spectra



Max(r) between i_m and i_s-w to i_s+w

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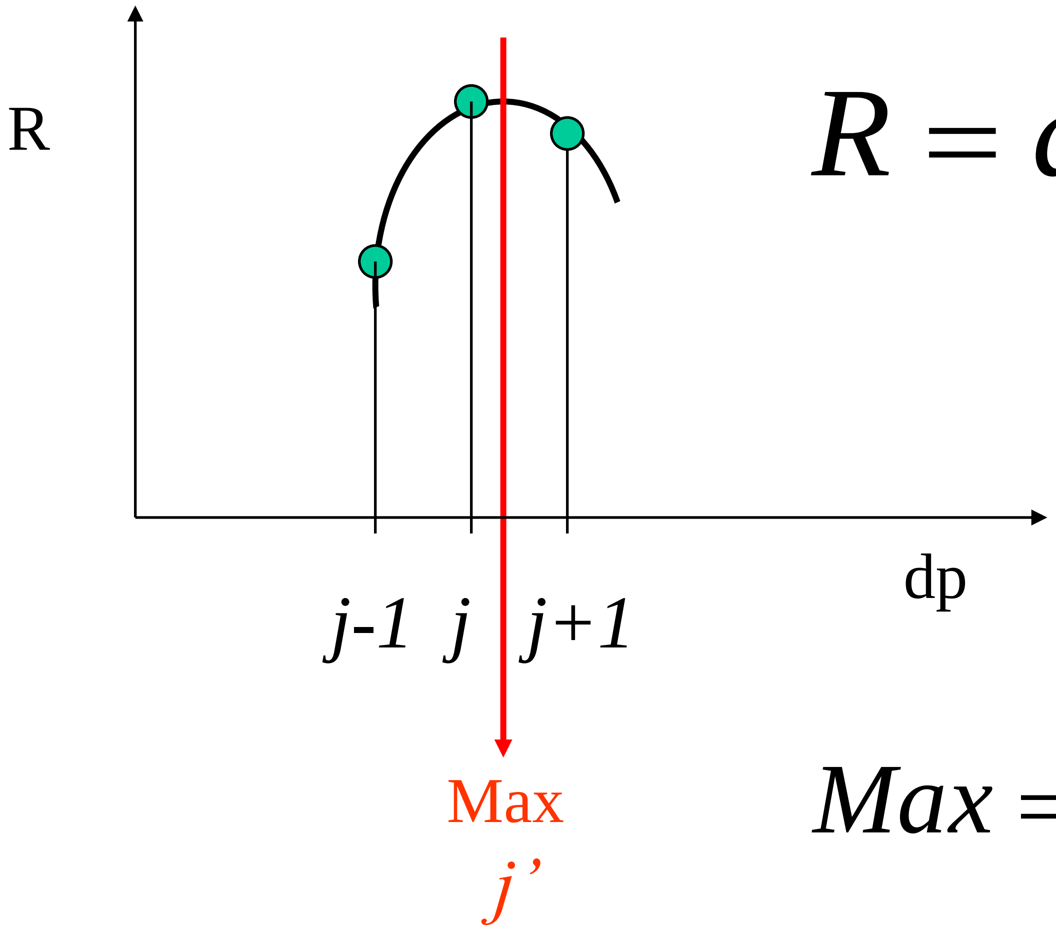
CLONE procedure (3)



$$R = a + bx + cx^2$$

$$Max = -\frac{b}{2c}$$

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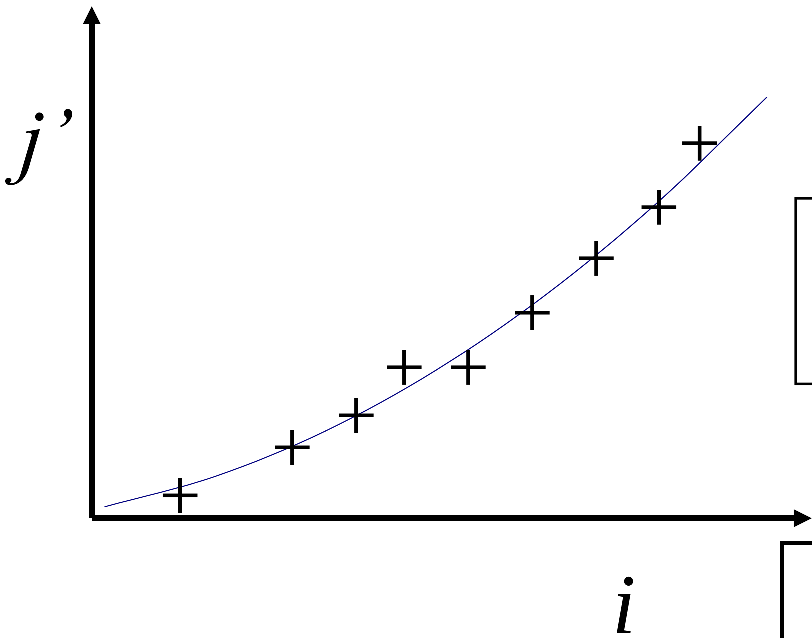
CLONE procedure (4)

Two vectors of indices:

1	***2***		***i***		***k***
			j'		



$$\hat{j}' = A + Bi + Ci^2$$

Two vectors of indices:

1	***2***		***i***		***p***
1.01	***2.02***		$\hat{j}'$		***700.1***

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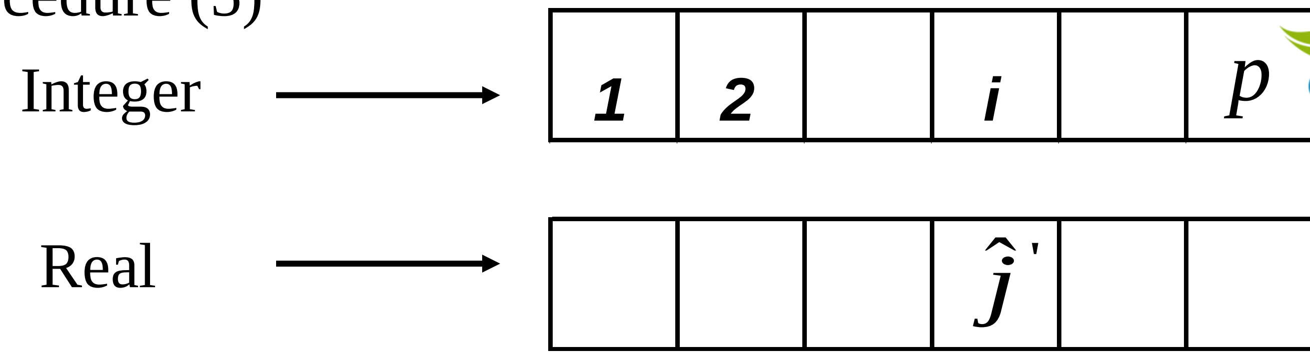
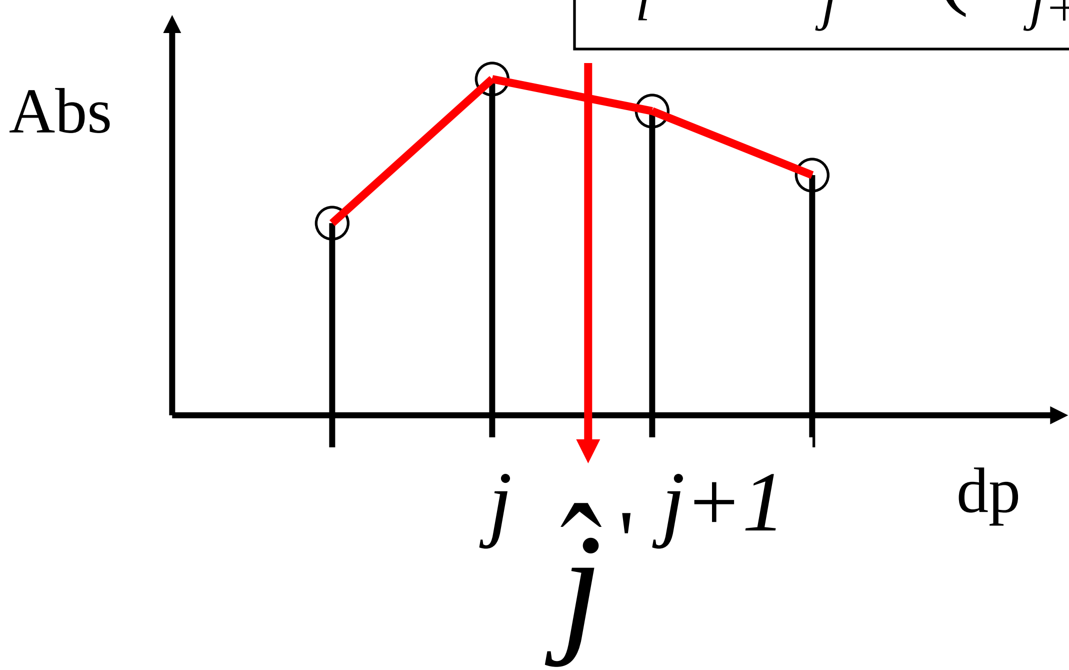
CLONE procedure (5)



Interpolation of the salves OD:

$$x_i = x_j + (x_{j+1} - x_j).(\hat{j}' - j)$$



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CLONE procedure (6)

Last step: p simple regressions (wl by wl):

$$\hat{x}_m = b_0 + b_1 x_s$$

All the information is saved in a file and attached to the instrument.

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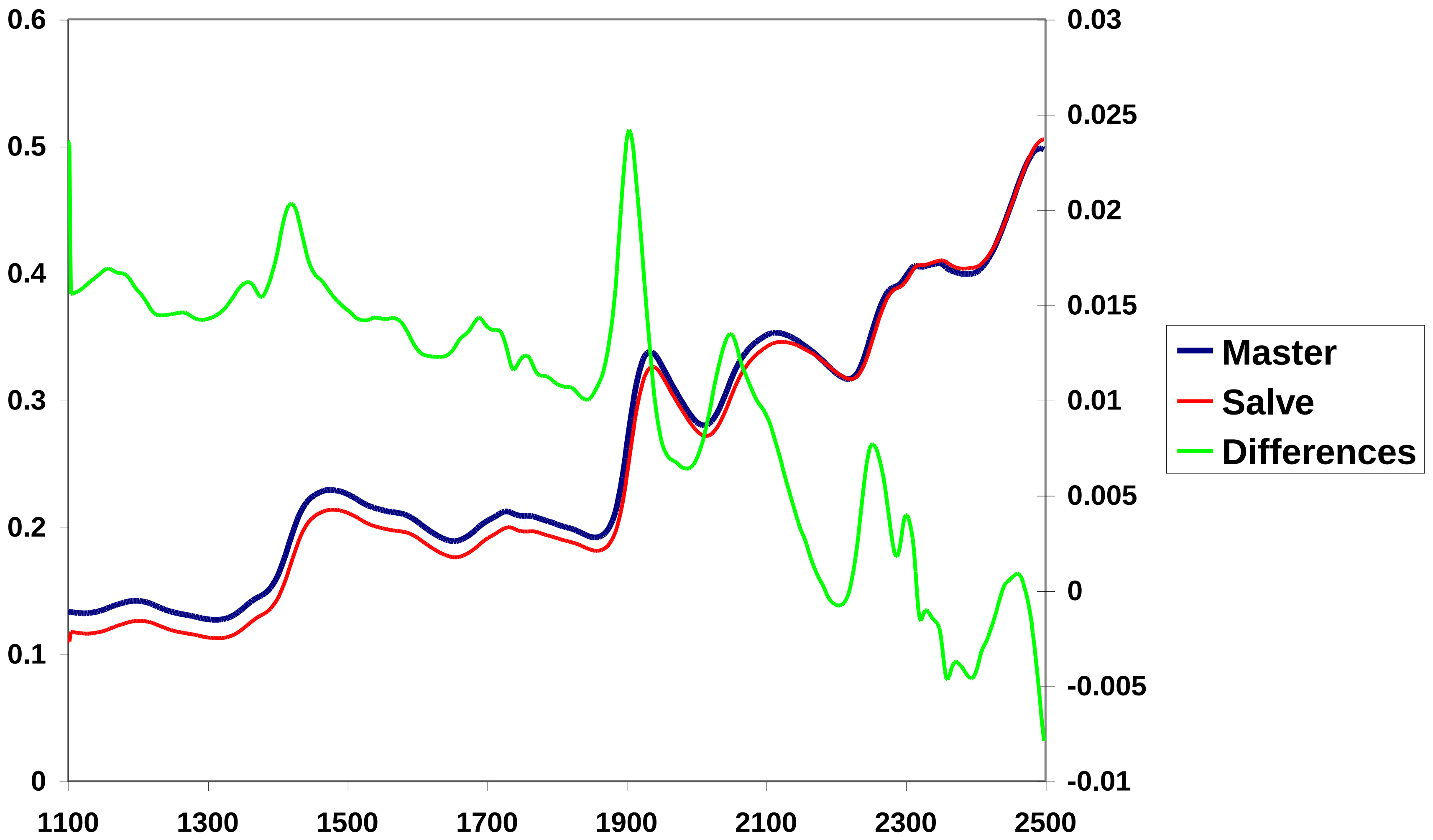
Master & salve averaged spectra and differences



RMS between spectra

$$RMS = \sqrt{\frac{\sum_{i=1}^{k}(a_{1i} - a_{2i})^2}{k}}$$

$$RMSC = \sqrt{\frac{\sum_{i=1}^{k}(a_{1i} - a_{2i} - bias)^2}{k-1}}$$

k=number of wavelengths

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Standardisation in cascade of 5 monochromators
Clone.exe - 30 sealed cups

Slave		Master	RMSC
5000	to	6500	205
6250	to	modified 5000	508
6250T	to	modified 6250	383
T500	to	modified 6250T	1149
Contrast: 6500 vs Modified T500			1109

If A=B and B=C, then A=C

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Experiment :

6 instruments + 1 ‘master’
6 sealed cups 2 rep to calculate the transfer functions
15 sealed cups 2 rep to validate
Forage models :

	N	Mean	SD	SEC	RSQ	SECV	1-VR
CP	13525	13.34	6.26	0.90	0.98	0.91	0.98
NDF	5993	50.61	12.21	2.57	0.96	2.60	0.95

2 methods:

-Clone Shenk & Westerhaus

-PDS (MatLab)

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6 instruments + 1 ‘master’

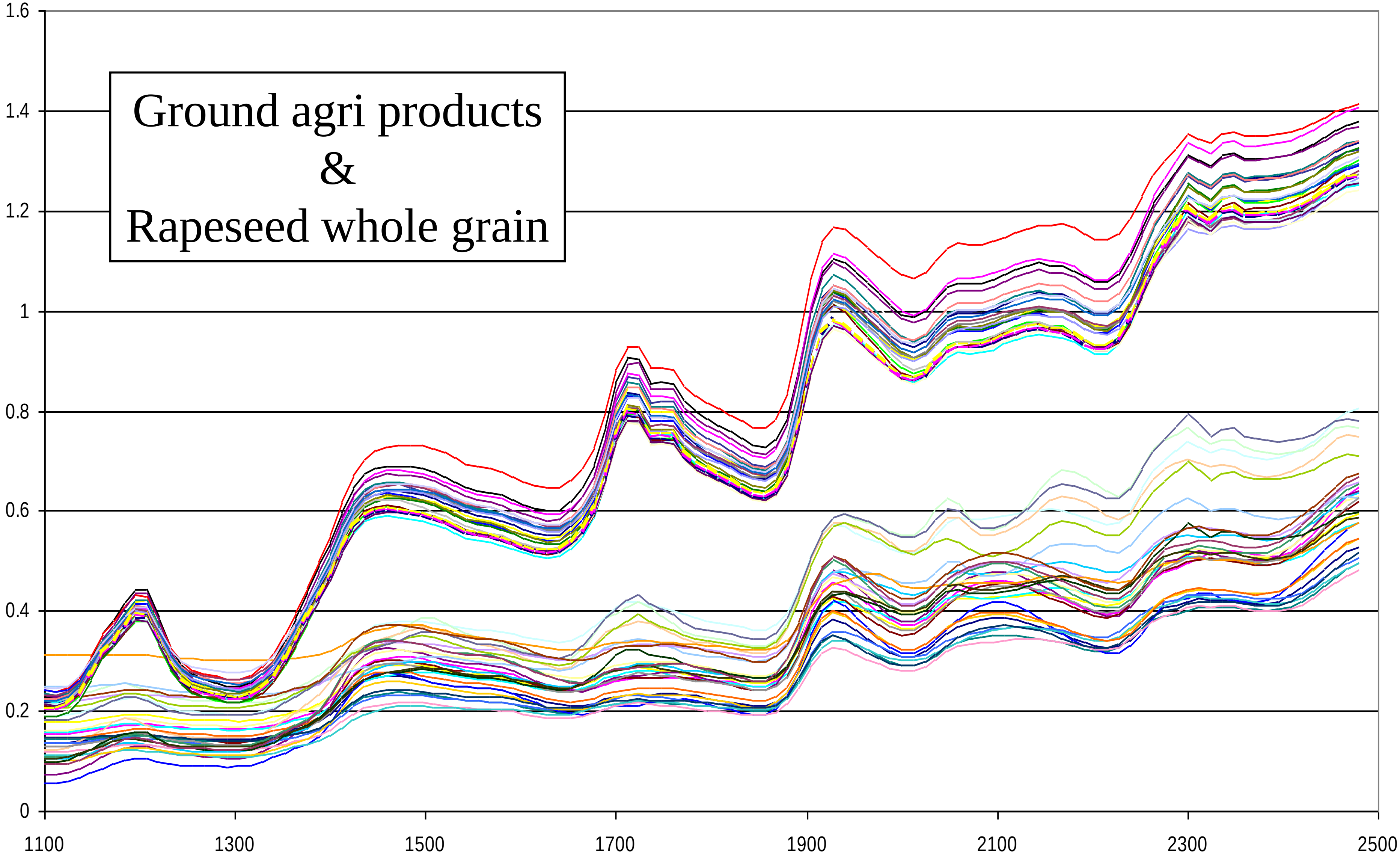
6 sealed cups 2 rep to calculate the tranfer functions

15 sealed cups 2 rep to validate

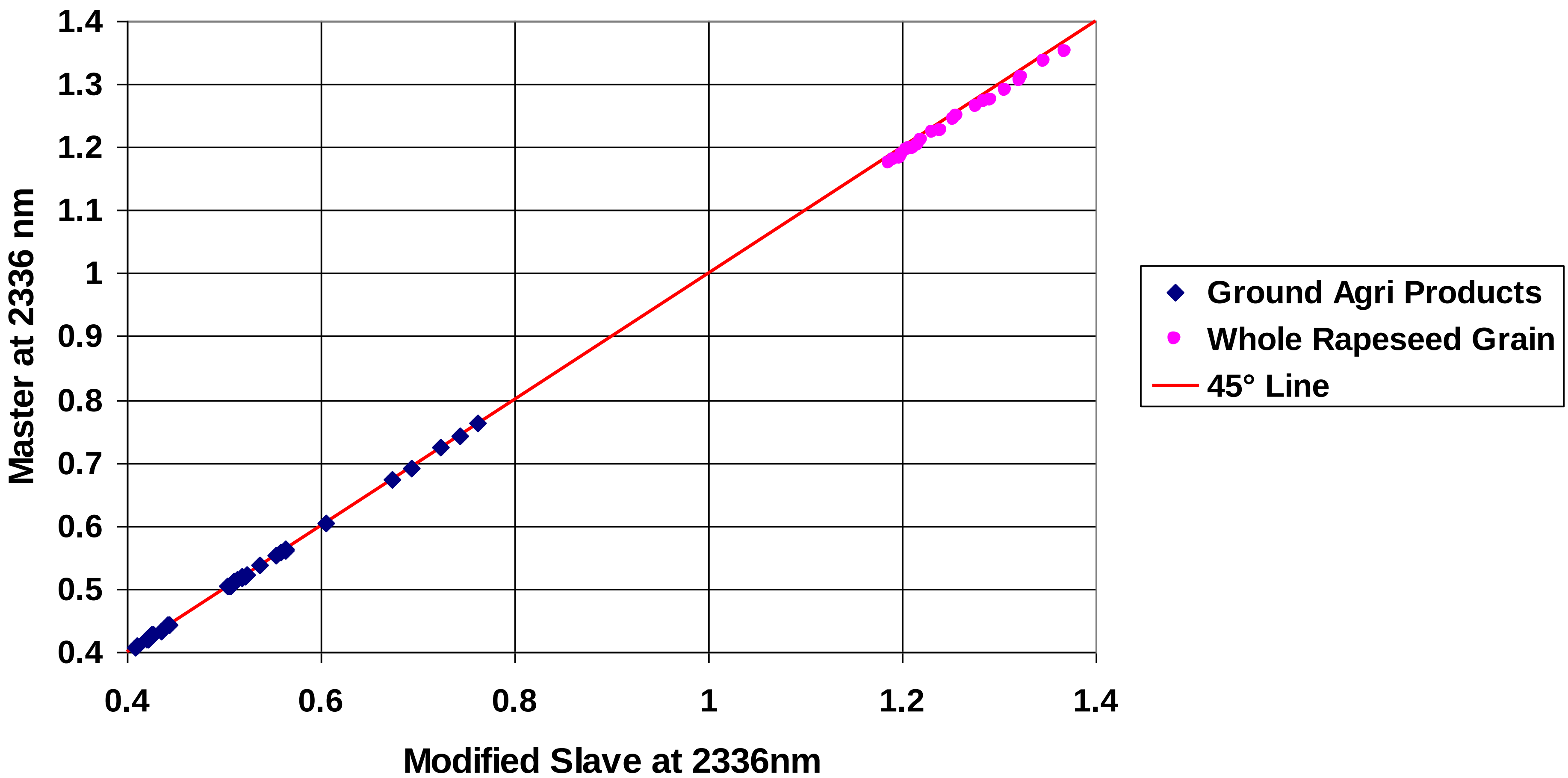
	UNSTD		CLONE		PDSBYPLS 3/1		PDSBYPLS 5/1		PDSBYPLS 5/2	
CP	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC
Inst 1	**1.036**	**6981**	**0.145**	**576**	**0.152**	**584**	**0.159**	**587**	**2.556**	**1079**
Inst 2	**0.159**	**3990**	**0.093**	**317**	**0.102**	**323**	**0.122**	**327**	**2.468**	**690**
Inst 3	**1.238**	**9238**	**0.169**	**431**	**0.153**	**435**	**0.146**	**438**	**2.653**	**711**
Inst 4	**1.382**	**7396**	**0.211**	**626**	**0.207**	**629**	**0.223**	**632**	**2.256**	**1202**
Inst 5	**0.673**	**11704**	**0.104**	**750**	**0.142**	**761**	**0.171**	**762**	**2.551**	**1540**
Inst 6	**0.484**	**12189**	**0.158**	**487**	**0.149**	**490**	**0.157**	**492**	**2.406**	**834**

	UNSTD		CLONE		PDSBYPLS 3/1		PDSBYPLS 5/1		PDSBYPLS 5/2	
NDF	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC	RMSEP	RMSC
Inst 1	**3.211**		**0.829**		**0.979**		**1.232**		**16.499**	
Inst 2	**1.807**		**0.771**		**1.061**		**1.299**		**8.815**	
Inst 3	**1.136**		**0.599**		**0.902**		**1.176**		**8.981**	
Inst 4	**4.198**		**0.704**		**0.891**		**1.161**		**22.054**	
Inst 5	**4.420**		**0.687**		**0.980**		**1.224**		**28.74**	
Inst 6	**0.604**		**0.647**		**0.841**		**1.108**		**12.314**	

Different products ?



Standardisation with Ground Agri Products
Correction of the Rape seed spectra



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RMS between SPECTRA

Two consecutive readings

Material	RMS (LOG*10^{-6})
Ceramic	30
Soya meal (0.4 od) (same cup)	200
Rape seed (0.8od) (Whole grains - same cup)	500
Soya meal (Sealed cup) Between 2 STDED instrum.	**1000**
Soya meal (refilling)	2000
Rape seed (Whole grains - refilling)	6000

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NETWORK GOAL :

« Shenk's law »

Standard deviation
(on the repeated predicted values)
between instruments
must be less
than
the sampling error

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Reproducibility: NIRS vs REF

Whole plant corn silage models:

Dried and ground samples

Var	N	SEC	R^2
Starch	1055	1.90	.97
CrudeFiber	1000	1.01	.94
NDF	502	2.05	.94
CrudeProt.	1433	0.38	.87

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EVALUATION OF THE REPRODUCIBILTY OF 5 STANDARDISED NIR INSTRUMENTS
60 samples measured

Evaluate files using: MAIS.EQA

Samp	STARCH	CrudeFib	NDF	CrudePro
1	0.72	0.30	0.67	0.18
2	1.23	0.44	0.75	0.19
3	0.53	0.38	0.55	0.13
59	0.64	0.32	0.37	0.07
60	0.52	0.27	0.15	0.07
Std	0.73	0.40	0.64	0.15
SEC	1.90	1.01	2.05	0.38
Bipea, nov 2000	2.00	1.43	4.00	0.50

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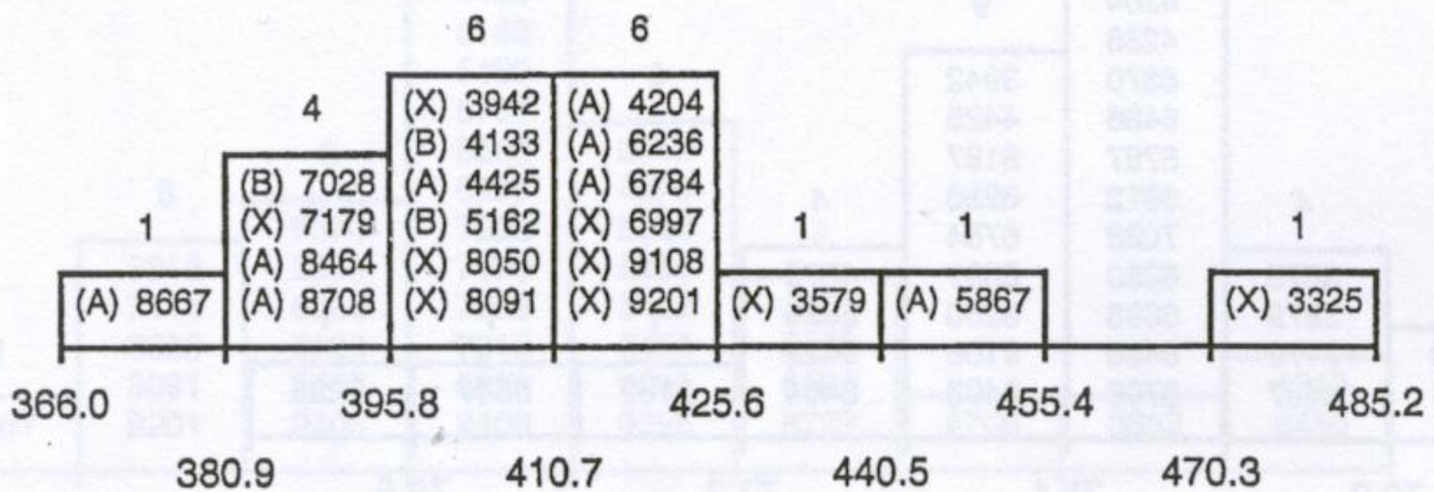
BIPEA, NOVEMBRE 2000

FOURRAGES 14

MAIS VERT SECHE

NDF – CONSTITUANTS PARIETAUX : N.D.F

REFERENCE :	407.6
TOLERANCE :	40.0
MAXIMUM :	447.6
MINIMUM :	367.6



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SEALED CUPS

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Centre wallon de Recherches agronomiques

Since 1987 9 laboratories

PSCo 4250
Perstorp 4500
NIRsystems 5000
Foss XDS

Asbl REQUASUD
Cellule de coordination
Rue de Liroux, 9
5030 GEMBLOUX

081/62.65.73
www.cra.requasud.be

EUROPEAN CRA-W CONTACTS

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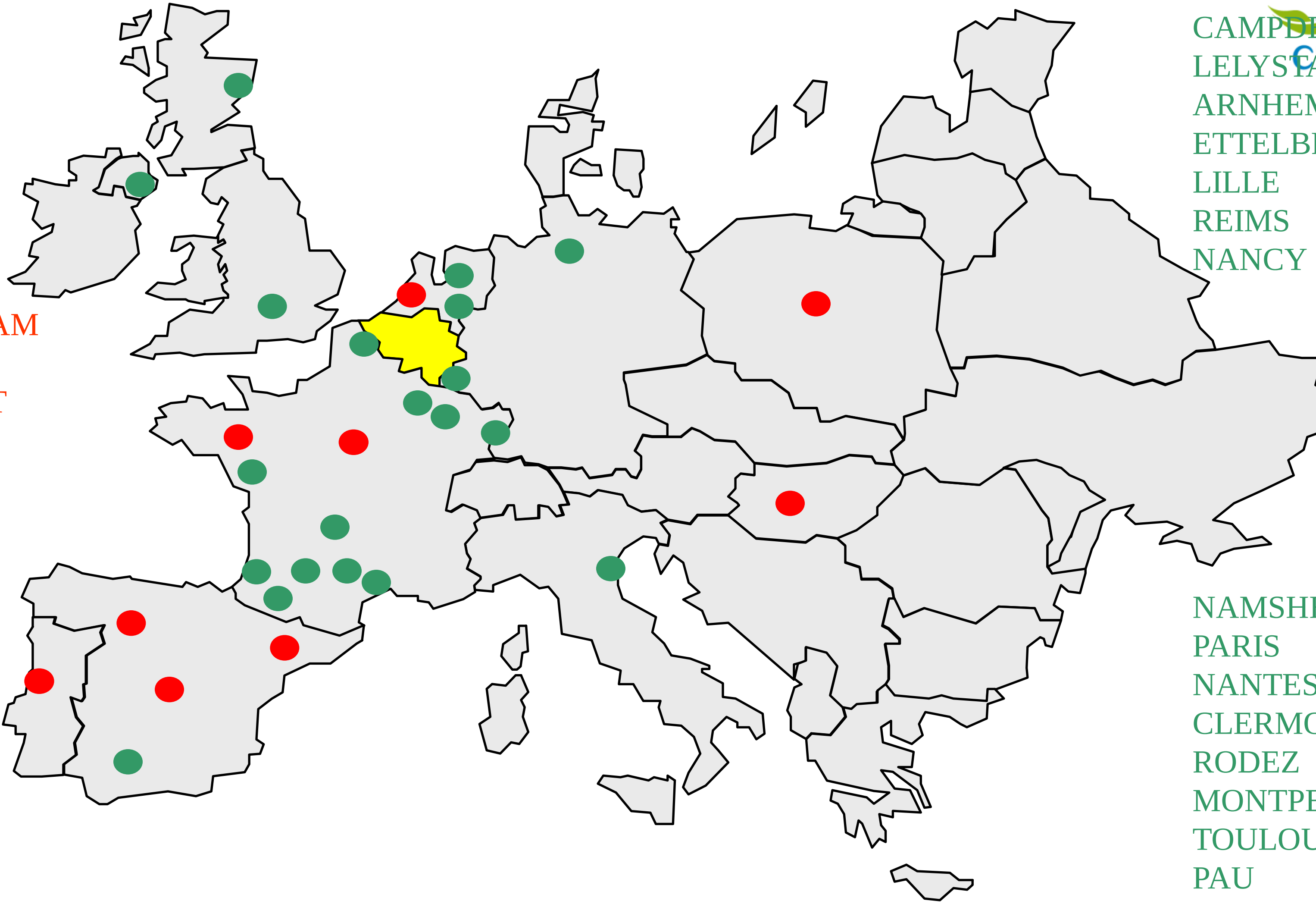
FRAGA
MADRID
LISBONNE



NAMSHEIM
PARIS
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CLERMONT-F
RODEZ
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EUROPEAN PROVIMI NETWORK

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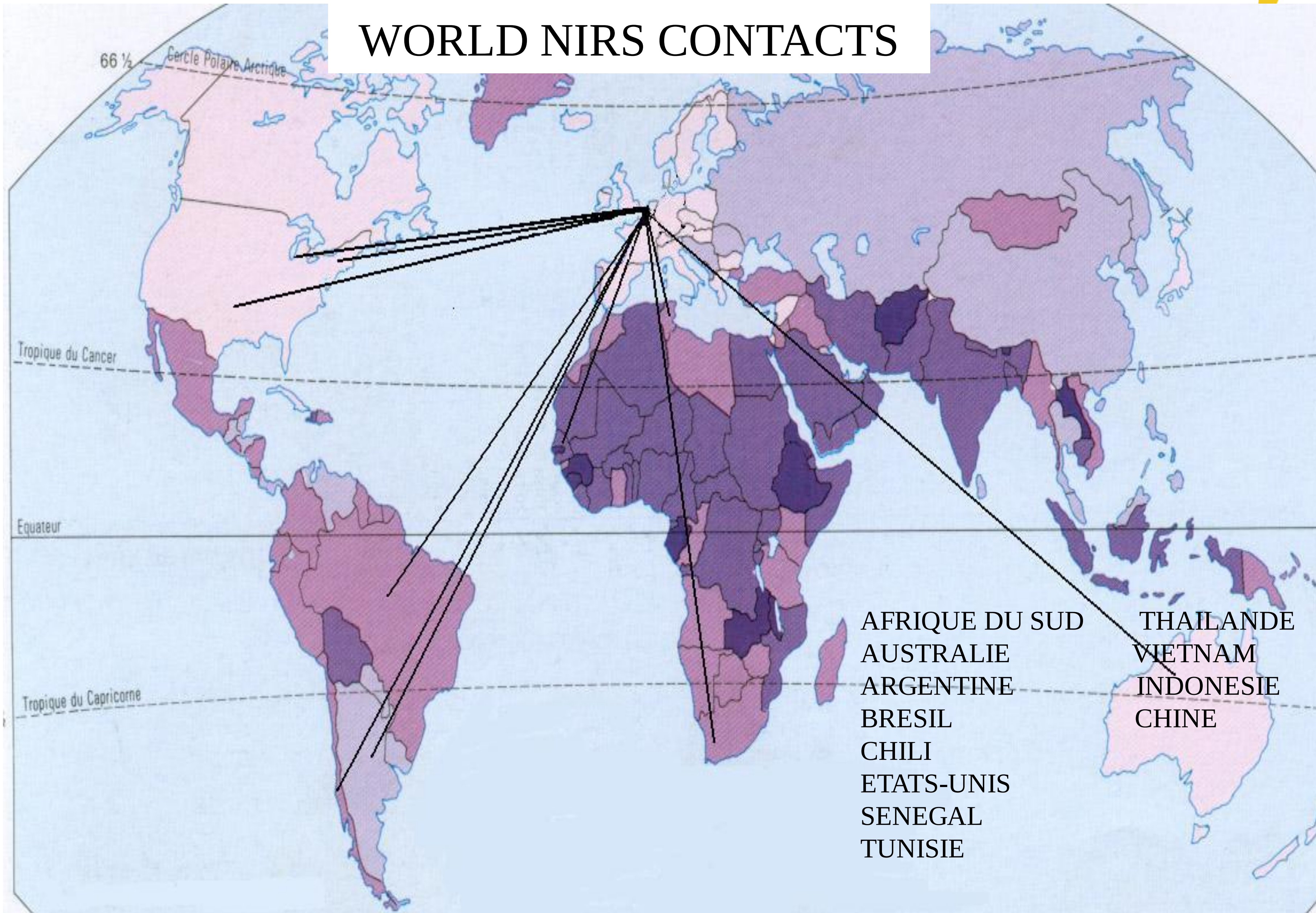
WORLD NIRS CONTACTS



AFRIQUE DU SUD
AUSTRALIE
ARGENTINE
BRESIL
CHILI
ETATS-UNIS
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TUNISIE

THAILANDE
VIETNAM
INDONESIE
CHINE

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Wallonie

Standardisation: which direction ?

Target is master instrument: ('backward')

instrument type is the same

→ same models

CLONING, STANDARDISATION,

Target is secondary instrument : ('forward')[a]

instrument types are different

not the same resolution and/or wl range

mono to filter

→ new models

CALIBRATION TRANFER →DATA BASE TRANSFER & RECALIBRATION

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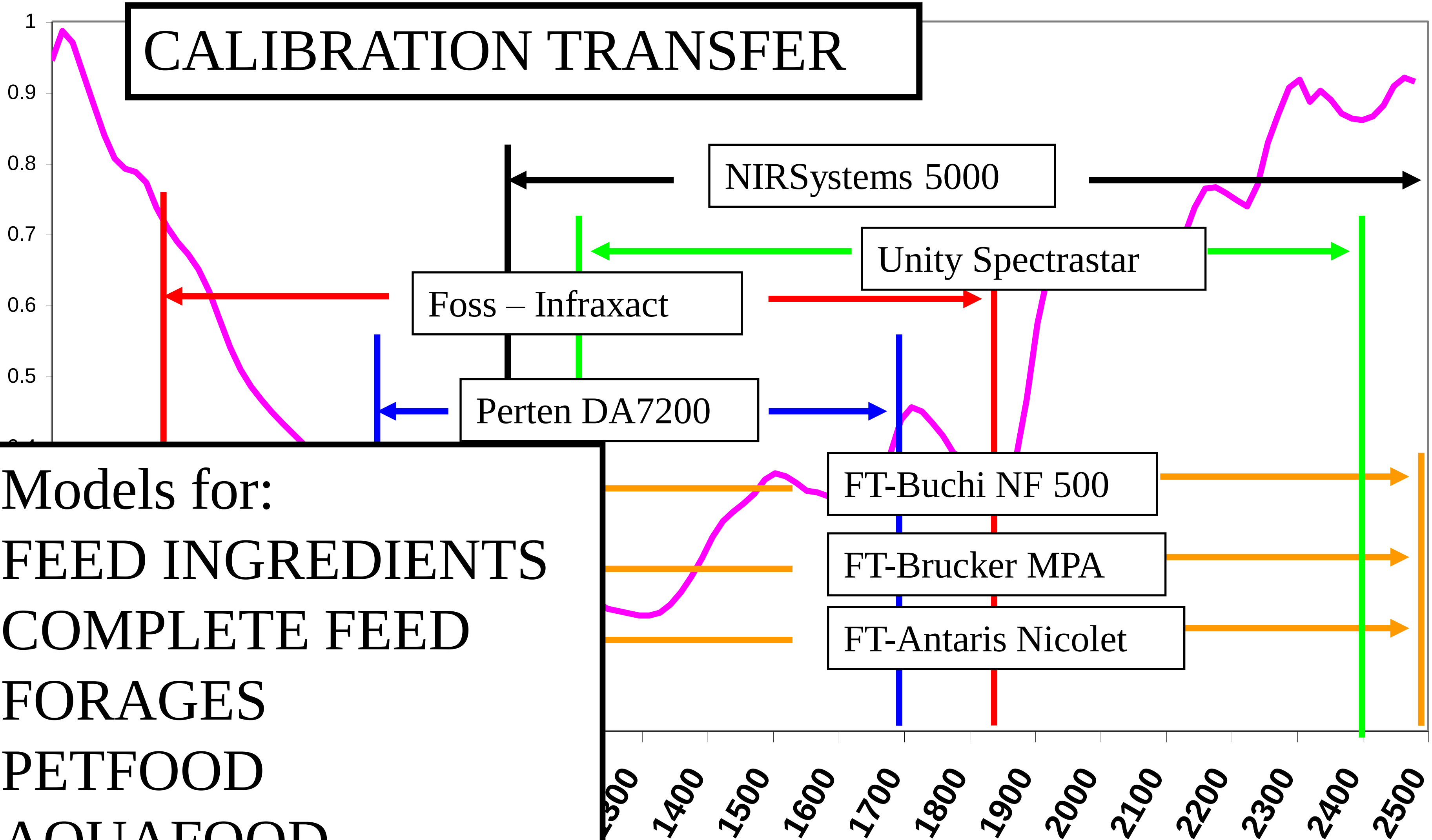
INSTRUMENTS POWERED BY INGOT®

http://www.aunir.co.uk/



Models for:

FEED INGREDIENTS

COMPLETE FEED

FORAGES

PETFOOD

AQUAFOOD

FLOURS

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tural Products Department
ardenne@cra.wallonie.be

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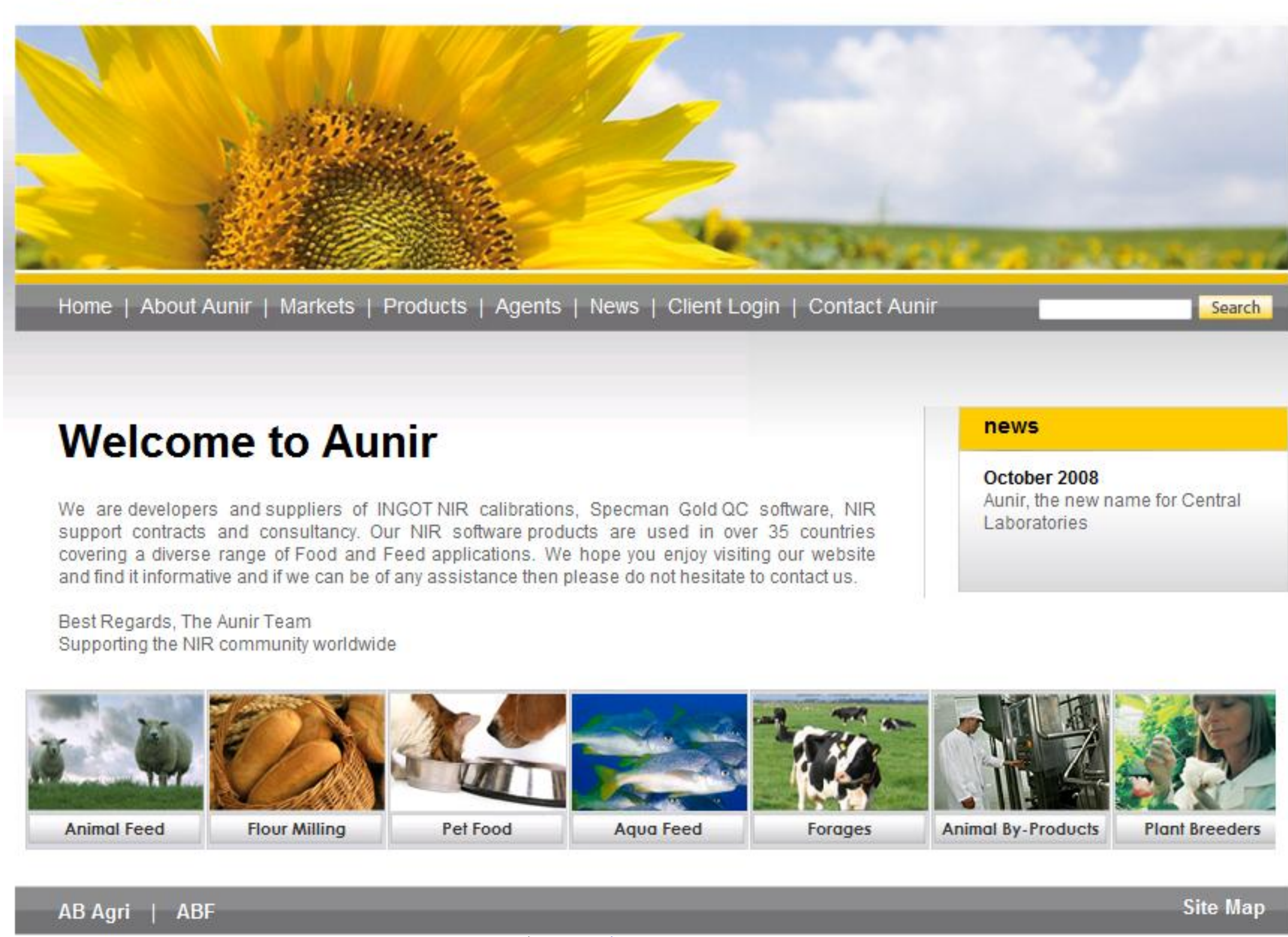
Aunir http://www.aunir.co.uk/ INGOT SPECMAN SPECNET




MPA


FOSS
InfraXact

Pierre Dardenne, dardenne@cra.wal

cra-w

Phazir, Polychromix

Polychromix
30 Upton Drive
Wilmington, Massachusetts
USA 01887
Tel: +1 (978) 284-6000
Fax: +1 (978) 284-6060

Centre w

Wallonie

Transfer Requirements

Instrument 1 (Current)

Calibration data sets (historical data sets)
Sealed cup (30)
Test set (27 feed)

Instrument 2, 3, 4,… (Target)
Between cup correction
Sealed cup (30)
Test set (27 feed)

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SEALED CUPS

Dr. J.S. Shenk, mid 80'

http://www.terraceassembly.com/

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Contrast Output

brboxb4a.nir vs. brboxb4b.nir:

Pos.	Sample No.	R^2	RMS	Standard Bias	RMSC
16	BRB4-16	1.0000	3034	-2976	590
17	BRB4-17	1.0000	410	276	303
18	BRB4-18	1.0000	1213	959	743
19	BRB4-19	1.0000	3693	3583	893
20	BRB4-20	1.0000	955	-770	565
21	BRB4-21	1.0000	656	-317	575
22	BRB4-22	1.0000	523	-399	339
23	BRB4-23	1.0000	1483	-1363	585
24	BRB4-24	1.0000	729	574	450
25	BRB4-25	1.0000	649	464	454
26	BRB4-26	1.0000	1189	121	1184
27	BRB4-27	1.0000	6155	5910	1719
28	BRB4-28	1.0000	1577	1161	1068
29	BRB4-29	1.0000	514	29	513
30	BRB4-30	1.0000	1032	827	618
	Overall Aves:	1.0000	1944	425	892

Contrast Output

5b4a.nir vs. 5b4b.nir:

Pos.	Sample No.	R^2	RMS	Standard Bias	RMSC
16	$7B4-16	1.0000	867	-858	122
17	$7B4-17	1.0000	1076	-1075	54
18	$7B4-18	1.0000	911	-910	41
19	$7B4-19	1.0000	1079	-1074	96
20	$7B4-20	1.0000	949	-946	76
21	$7B4-21	1.0000	438	-413	145
22	$7B4-22	1.0000	287	-269	101
23	$7B4-23	1.0000	303	-289	94
24	$7B4-24	1.0000	399	-396	46
25	$7B4-25	1.0000	634	-630	72
26	$7B4-26	1.0000	530	-510	141
27	$7B4-27	1.0000	93	-26	89
28	$7B4-28	1.0000	944	-940	84
29	$7B4-29	1.0000	163	161	28
30	$7B4-30	1.0000	638	608	196
	Overall Aves:	1.0000	667	-490	156

FT1

Static cup

DISP

Rotative cup

Contrast Output

#b4_5000.nir vs. brboxb4m.nir:

Pos.	Sample No.	R^2	RMS	Standard Bias	RMSC
16	16	0.9998	57248	-56475	9379
17	17	0.9994	54105	-53631	7152
18	18	0.9996	55968	-55381	8090
19	19	0.9998	60404	-59504	10393
20	20	0.9997	54860	-54264	8068
21	21	0.9989	58355	-58050	5958
22	22	0.9993	54308	-53873	6864
23	23	0.9999	56899	-56346	7921
24	24	0.9997	54603	-54127	7202
25	25	0.9994	51152	-50804	5959
26	26	0.9997	57477	-56796	8823
27	27	0.9997	50555	-49989	7551
28	28	0.9997	55822	-55237	8060
29	29	0.9996	59654	-58972	9004
30	30	0.9997	54929	-54258	8560
	Overall Aves:	0.9996	56001	-55280	8350

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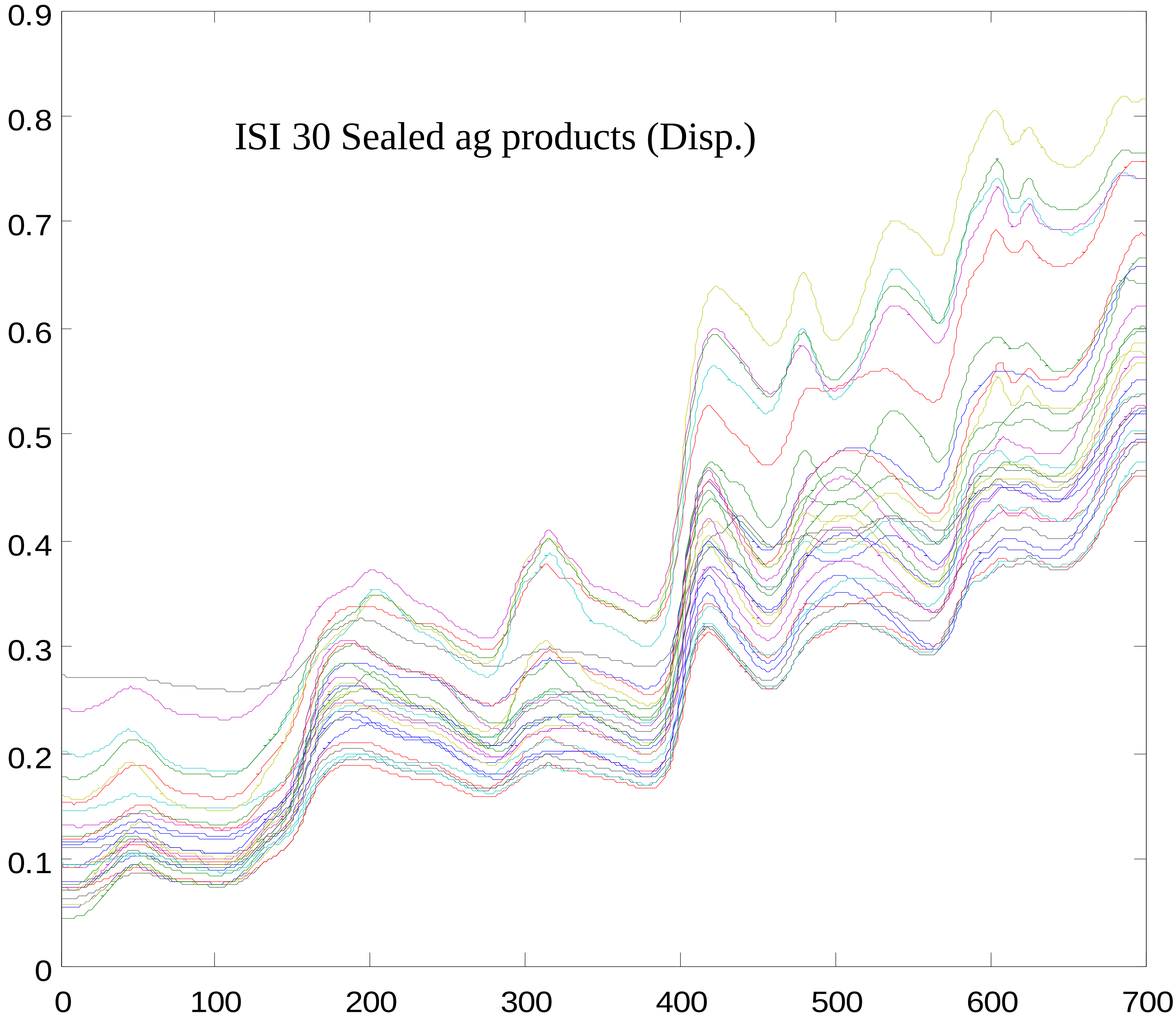

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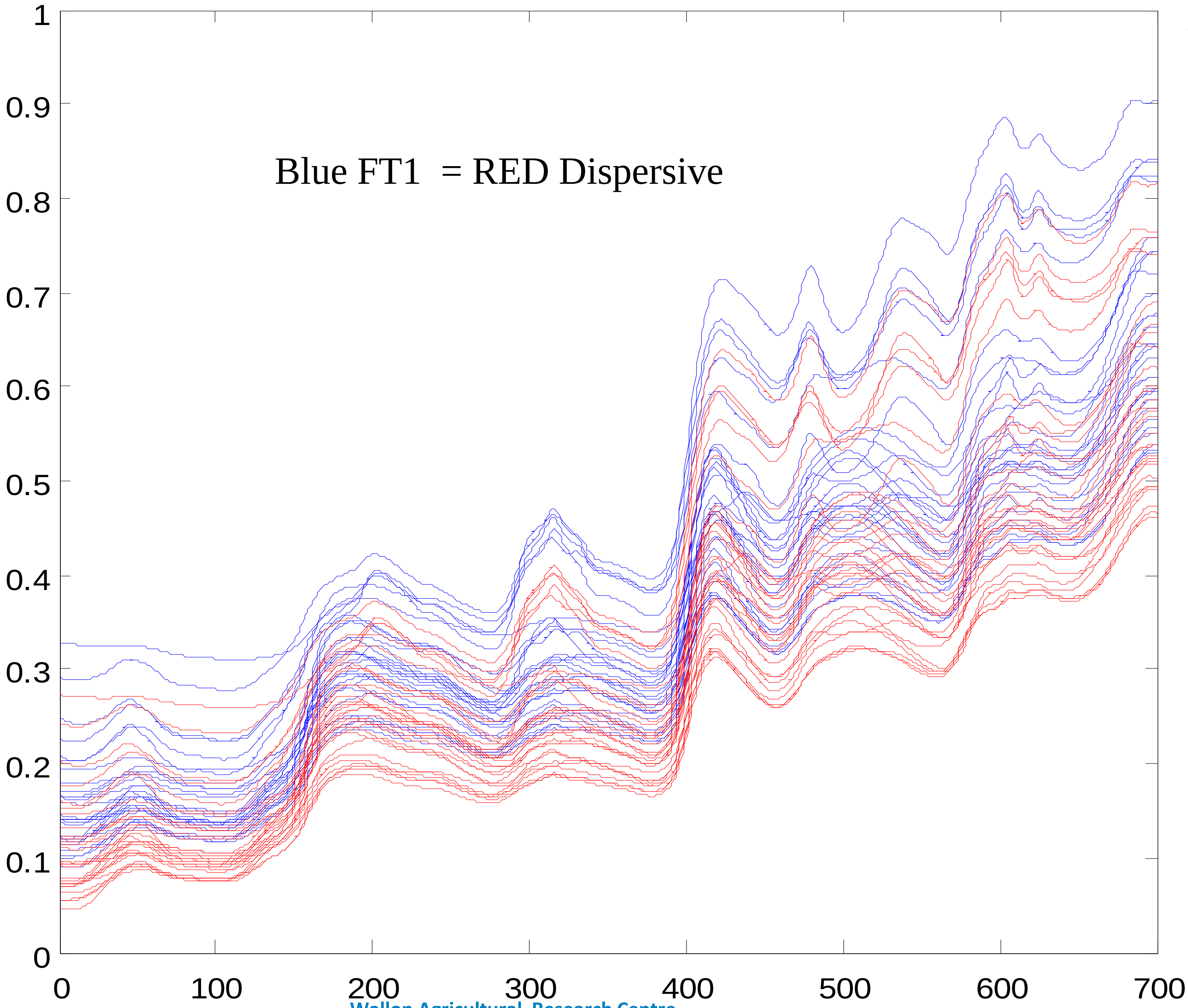

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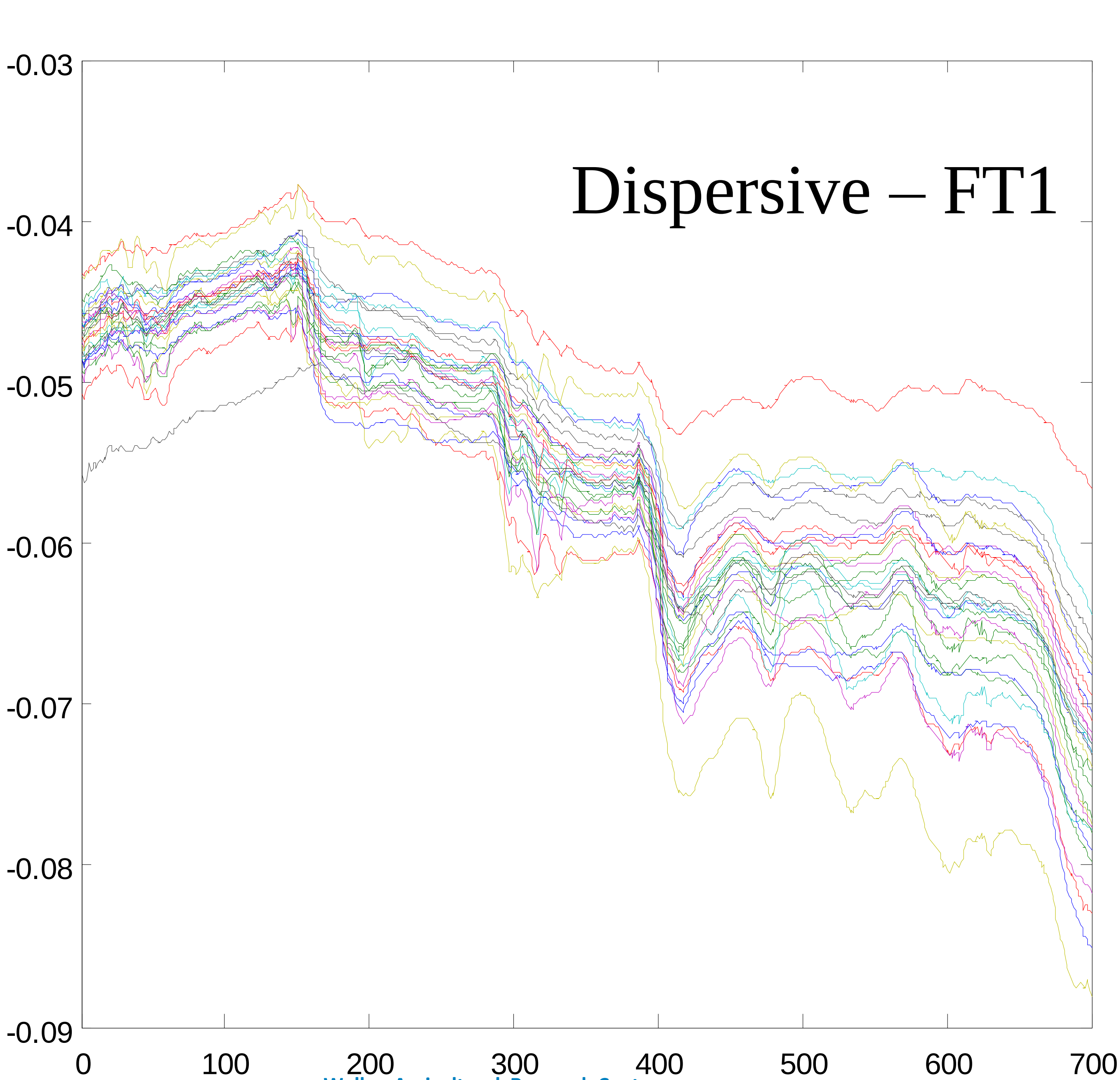

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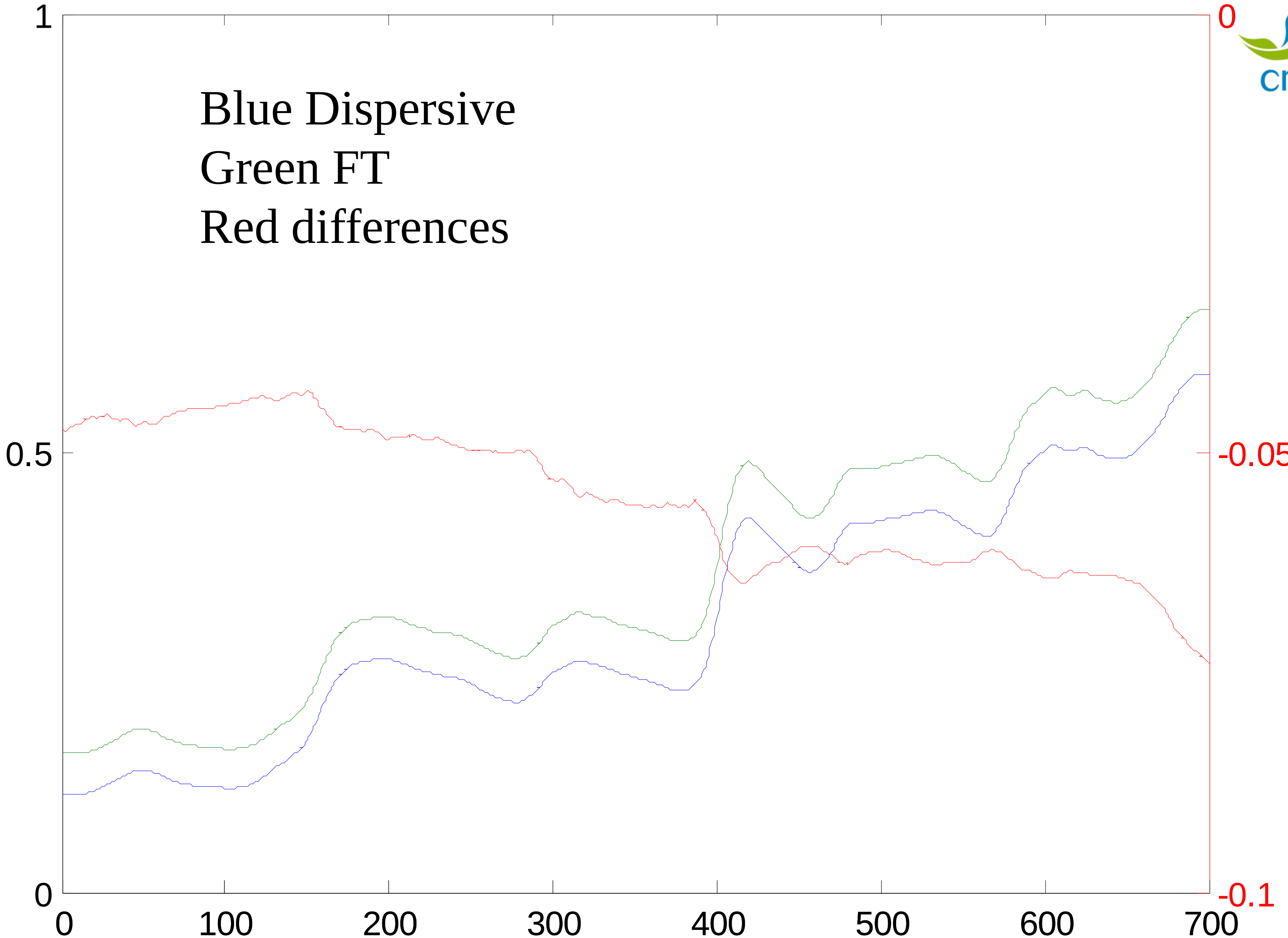

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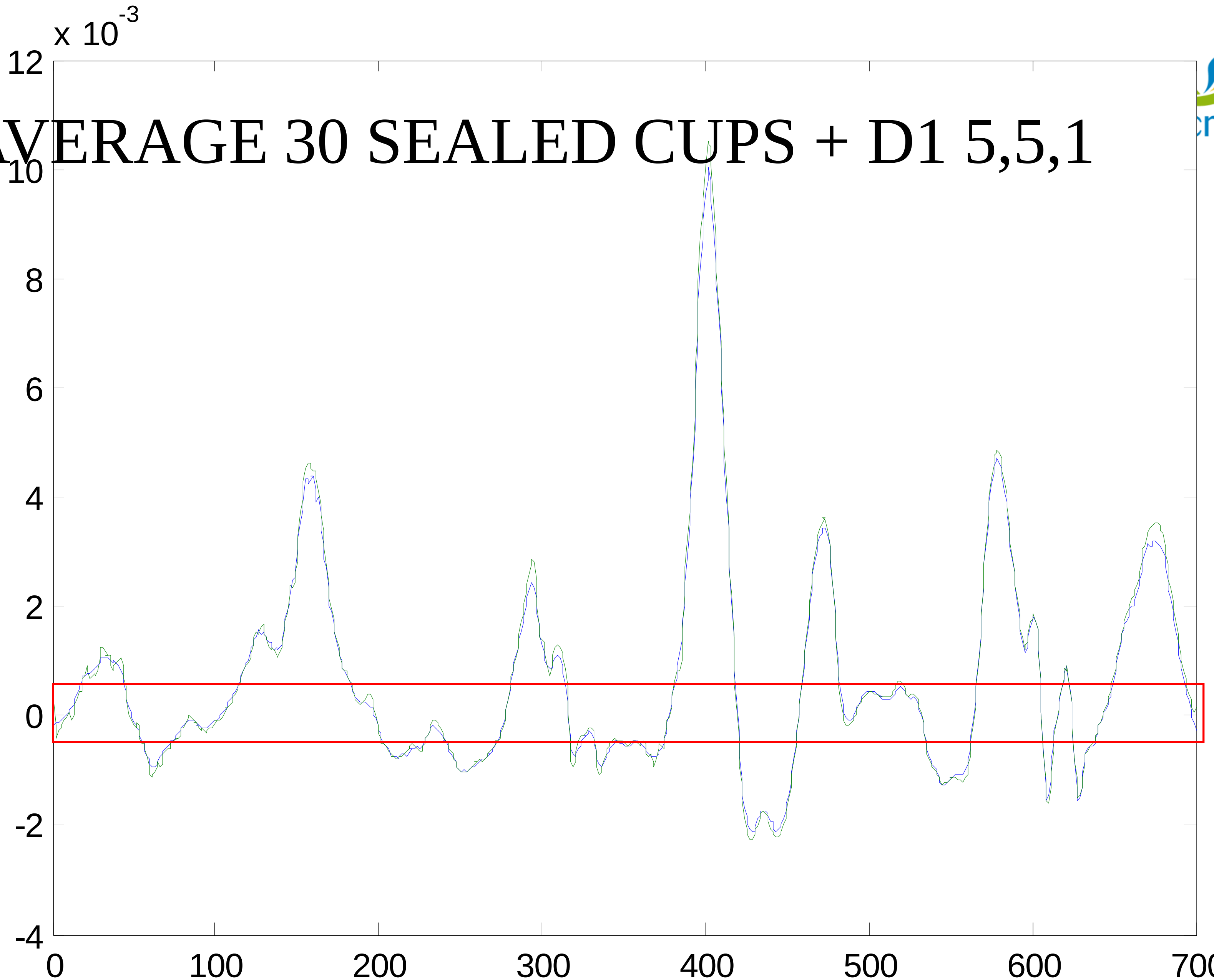
AVERAGE 30 SEALED CUPS + D1 5,5,1



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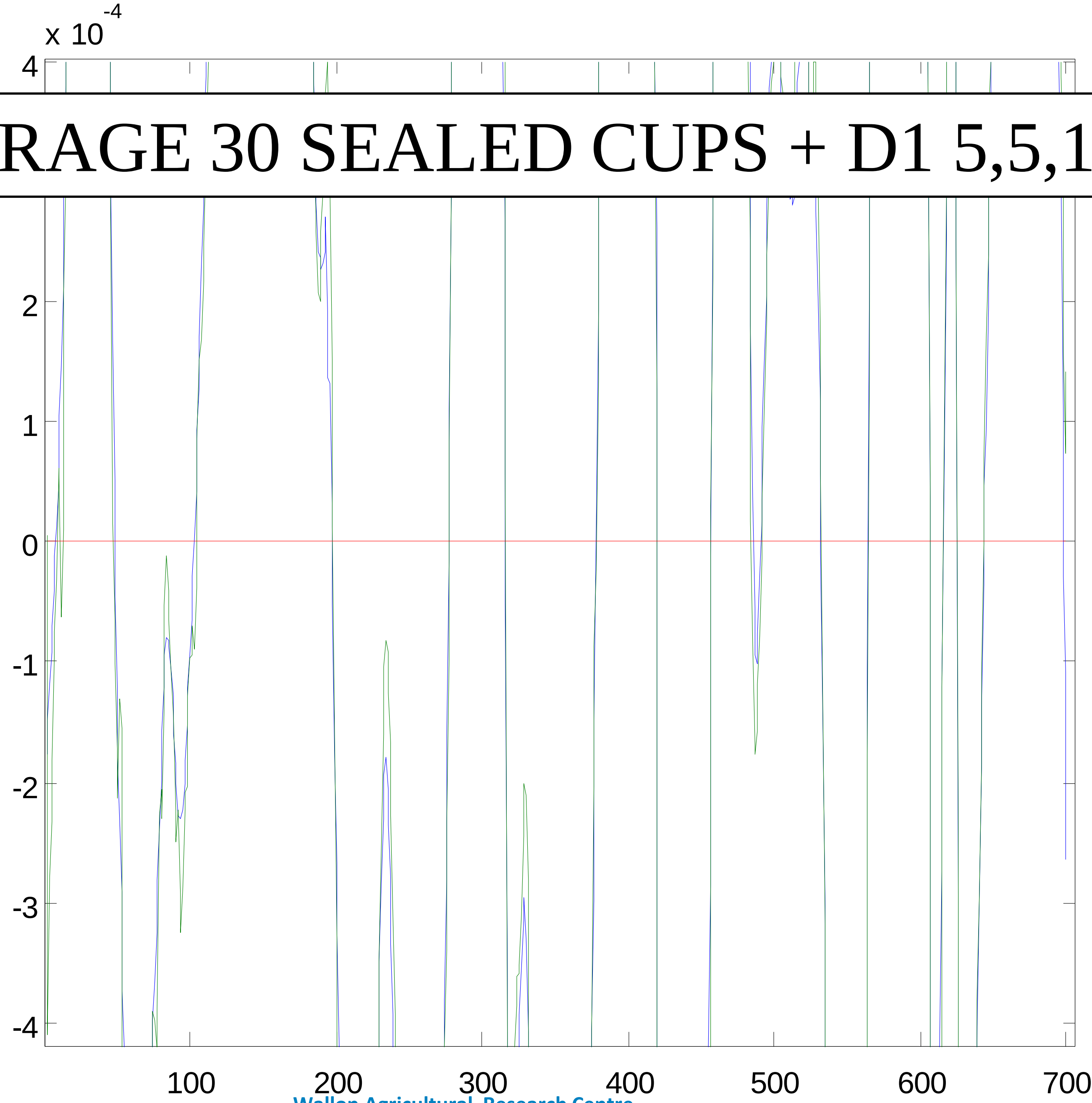
AVERAGE 30 SEALED CUPS + D1 5,5,1



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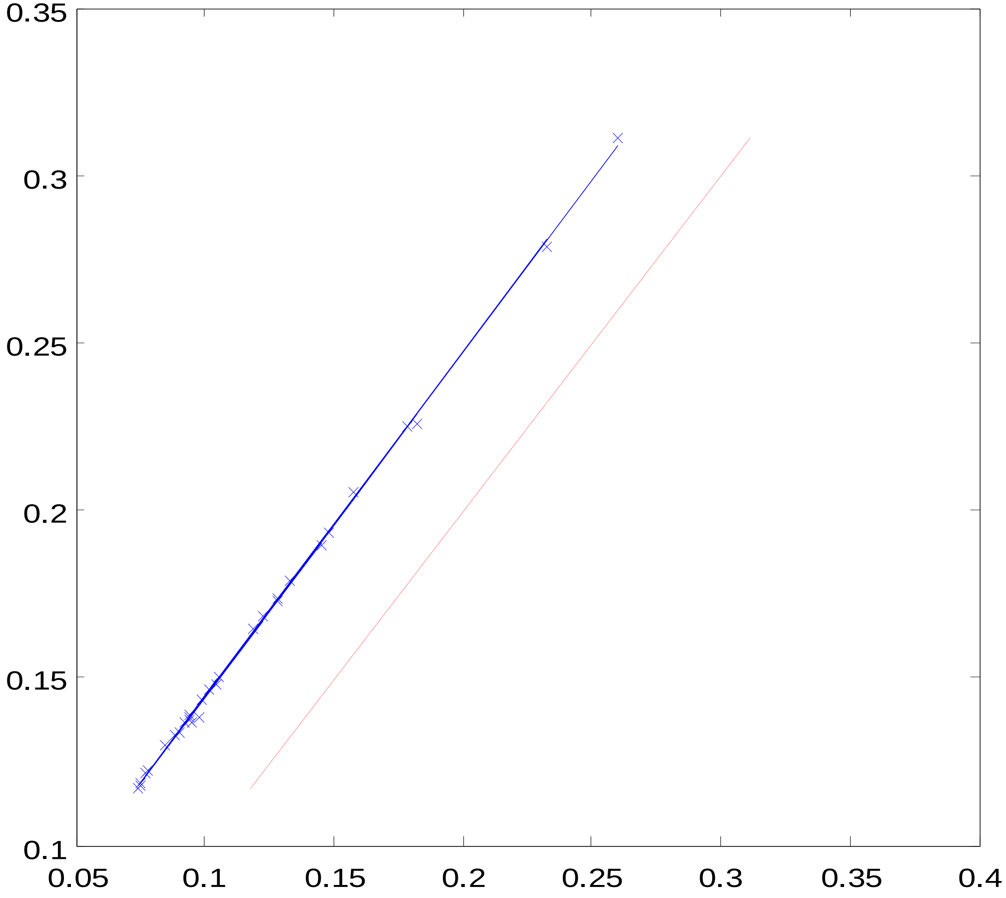

N= 30
y= 0.041+1.03x
biais= -0.044597
R2= 0.99909
RMSE= 0.044639
SEP= 0.0019836
SDyx= 0.0014458

ABS_FT vs ABS_Disp at 1300 nm

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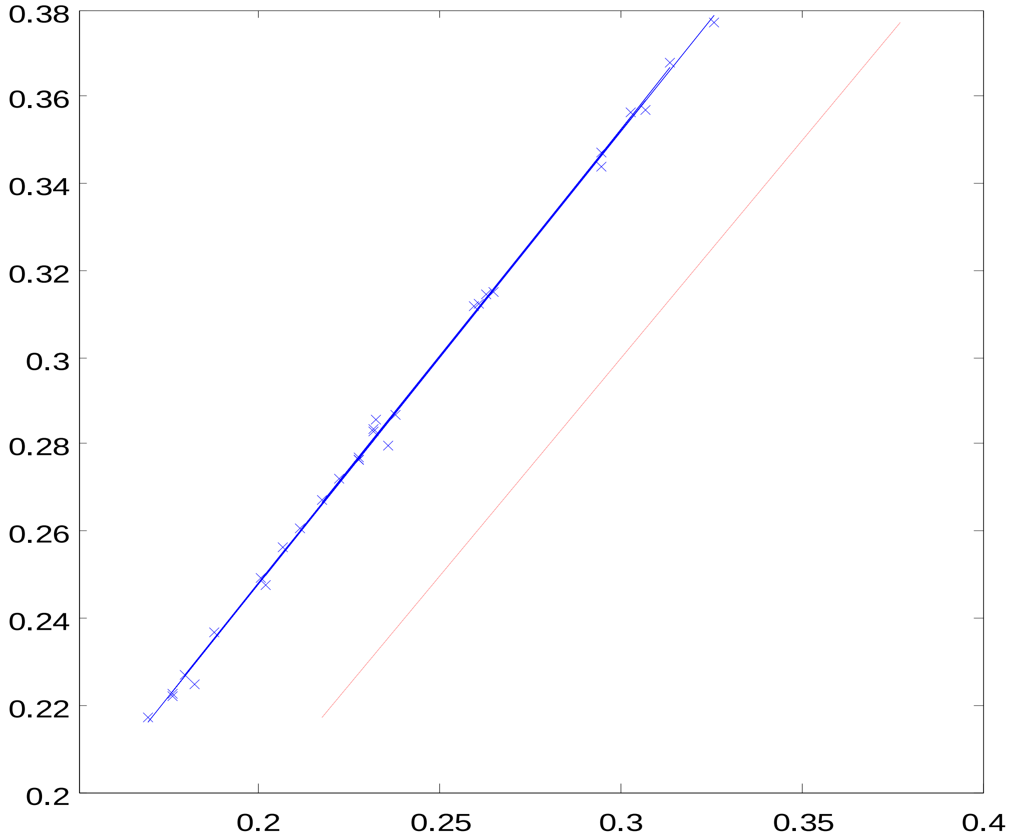

N= 30
y= 0.041+1.038x
biais= -0.049593
R2= 0.99804
RMSE= 0.049663
SEP= 0.0026622
SDyx= 0.0020949

ABS_FT vs ABS_Disp at 1600 nm

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1. Correction of the Disp spectra to be equal to FT spectra

- PDS (stdgen and stdize in Eigenvectors tools – Matlab)

  (installed into OPUS – Bruker)

- CLONE from Foss – ISI

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CLONE ISI - FT1

Quadratic Wavelength Shift Between Host and Master

Host position before = 0.125 + 1.0004M − 0.000004M^2

Standard error before = 0.505

Individual Adjustment Equations for Each Data Point or Wavelength

Data Pt	Intercept	Coefficient	Explained Var
1	b(0) = 0.0441	b(1) = 1.0285	RSQ = 0.9991
2	b(0) = 0.0442	b(1) = 1.0298	RSQ = 0.9991
3	b(0) = 0.0441	b(1) = 1.0296	RSQ = 0.9990
4	b(0) = 0.0440	b(1) = 1.0286	RSQ = 0.9990
5	b(0) = 0.0441	b(1) = 1.0269	RSQ = 0.9991
6	b(0) = 0.0439	b(1) = 1.0270	RSQ = 0.9991
7	b(0) = 0.0439	b(1) = 1.0273	RSQ = 0.9990
• • •			
694	b(0) = 0.0443	b(1) = 1.0486	RSQ = 0.9982
695	b(0) = 0.0441	b(1) = 1.0493	RSQ = 0.9982
696	b(0) = 0.0441	b(1) = 1.0492	RSQ = 0.9982
697	b(0) = 0.0451	b(1) = 1.0478	RSQ = 0.9982
698	b(0) = 0.0453	b(1) = 1.0477	RSQ = 0.9982
699	b(0) = 0.0453	b(1) = 1.0480	RSQ = 0.9982
700	b(0) = 0.0457	b(1) = 1.0478	RSQ = 0.9982

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CLONE ISI - FT2

Quadratic Wavelength Shift Between Host and Master

Host position before = 0.189 + 1.0006M – 0.000006M²

Standard error before = 0.478

Individual Adjustment Equations for Each Data Point or Wavelength

Data Pt	Intercept	Coefficient	Explained Varia
1	b(0) = 0.0338	b(1) = 1.0334	RSQ = 0.9891
2	b(0) = 0.0332	b(1) = 1.0334	RSQ = 0.9891
3	b(0) = 0.0337	b(1) = 1.0332	RSQ = 0.9891
4	b(0) = 0.0335	b(1) = 1.0332	RSQ = 0.9891
5	b(0) = 0.0333	b(1) = 1.0331	RSQ = 0.9891
	. . .	. . .	
695	b(0) = -0.0060	b(1) = 1.0553	RSQ = 0.9886
696	b(0) = -0.0057	b(1) = 1.0546	RSQ = 0.9885
697	b(0) = -0.0048	b(1) = 1.0531	RSQ = 0.9885
698	b(0) = -0.0044	b(1) = 1.0523	RSQ = 0.9885
699	b(0) = -0.0041	b(1) = 1.0516	RSQ = 0.9885
700	b(0) = -0.0038	b(1) = 1.0509	RSQ = 0.9886

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Contrast Output

brboxb4m.nir vs. mob4_5.nir:

Pos.	Sample No.	R^2	RMS	Standard Bias	RMSC
16	16	1.0000	703	299	636
17	17	1.0000	1348	1308	329
18	18	1.0000	2228	2116	697
19	19	1.0000	1142	-707	898
20	20	1.0000	361	223	284
21	21	0.9999	1786	1548	891
22	22	1.0000	745	679	307
23	23	1.0000	4372	-3513	2604
24	24	1.0000	2857	-2253	1758
25	25	1.0000	1976	-1726	962
26	26	1.0000	1643	1479	716
27	27	1.0000	5591	-5441	1290
28	28	1.0000	830	787	264
29	29	1.0000	4817	4491	1742
30	30	1.0000	573	-364	444
	Overall Aves:	1.0000	2637	0	1163

CONTRAST FT and MODIFIED DISP : 1163 µlog

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2. CORRECTION FOR THE CUP TYPE

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USING A SIMPLE BIAS CORRECTION wl/wl

a. 20 times one sample using both cups on the FT instrument (target)

b. Average both files

c. Substract : FT Cup - ISI ring Cup

d. Add this difference to the standardized data base:

FT cal data = Modified ISI cal data + (FT Cup – ISI ring Cup)

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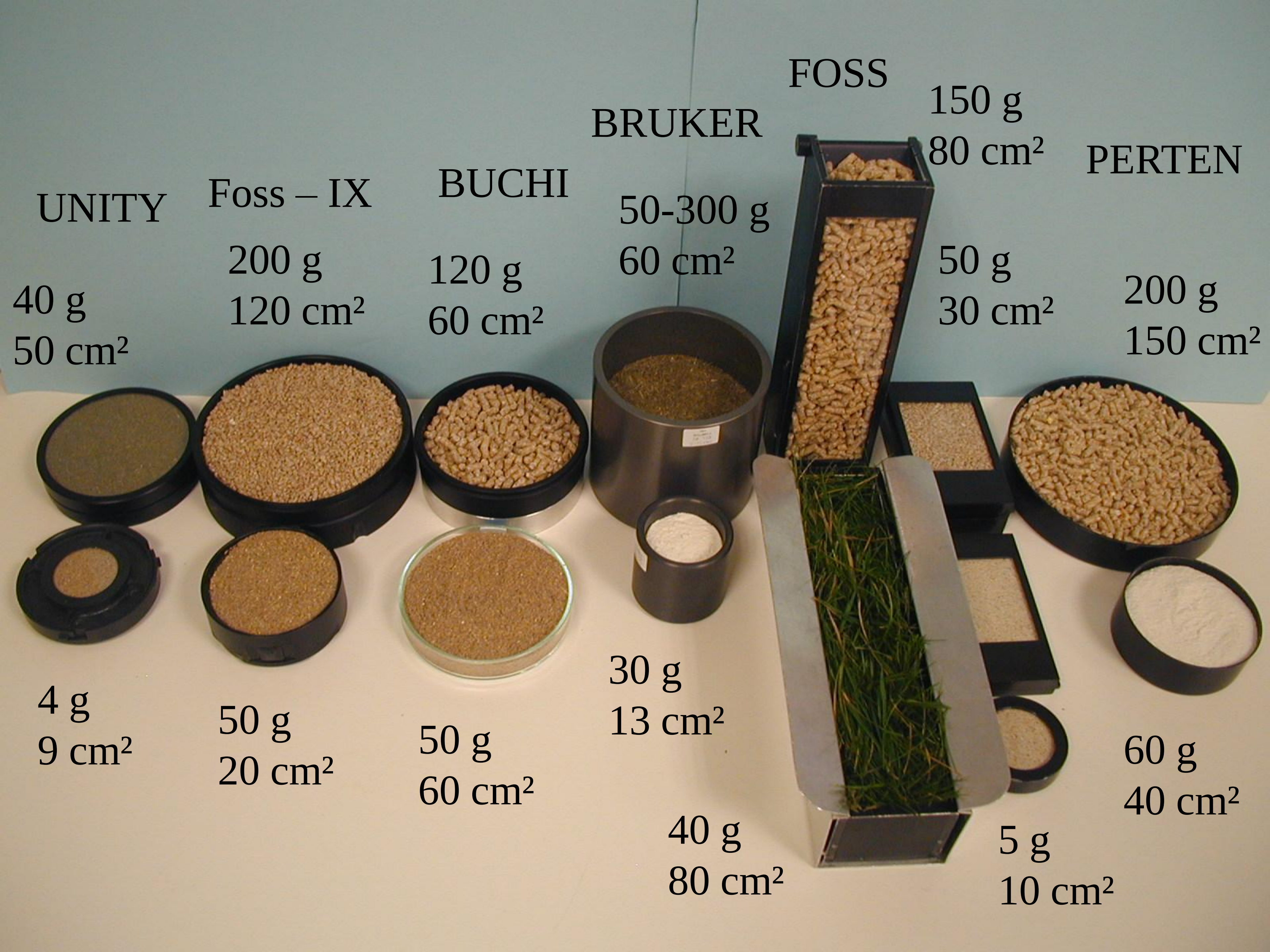
UNITY
40 g
50 cm²
4 g
9 cm²
Foss – IX
200 g
120 cm²
50 g
20 cm²
BUCHI
120 g
60 cm²
50 g
60 cm²
BRUKER
50-300 g
60 cm²
30 g
13 cm²
40 g
80 cm²
FOSS
150 g
80 cm²
50 g
30 cm²
5 g
10 cm²
PERTEN
200 g
150 cm²
60 g
40 cm²

when the data base is corrected,

3. export the data base into the specific software format

BRUKER = OPUS
BUCHI = NIRCAL
UNITY = Calibration Workshop (Sensologic Gmbh) - **Ucal**
PERTEN = Unscrambler (Grams)
Thermo Antaris (NICOLET) = Unscrambler (Grams)
Q-Interline = Grams.
.

4. Add some real spectra from the target instrument into the data base; (ref. from the master or ref. from lab)

5. Recalibrate and

6. Validate with new measurements

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27 complete feed

SEDC : standard deviation of the residuals between original instrument and target instrument predicted values (n=27)

	DISP		FT1		FT2		Disp1	
CONST.	N	SECV	SEDC	R2	SEDC	R2	SEDC	R2
FAT	8700	0.45	0.21	0.991	0.19	0.993	0.33	0.978
FIBRE	5700	0.75	0.33	0.993	0.35	0.994	0.63	0.983
PROTEIN	19000	0.85	0.57	0.986	0.70	0.985	0.78	0.971

0.22

0.54
0.70
0.84

SEDC << 0.50 SECV

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- A transfered model will never be better than a specific instrument model (using the same sample set)

- A large transfered data base will predict better than a limited specific instrument model

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Wallonie

Prof. Tom Fearn: Orthogonalisation ~~ OSC

EPO-PLS, external parameter orthogonalisation of PLS, JM Roger, 2003

Chemometrics and Intelligent Laboratory Systems
Volume 66, Issue 2, 28 June 2003, Pages 191-204

Worldwide STD trial – Foss-Tecator & ISI

Poster 4.27 2001 ICNIRS South-Corea

Spectral standardisation methods and modelling techniques applied to a diverse population of forage samples.

P. Dardenne,[a] I.A. Cowe[b] and M. Lagerholm[b]

[a] ***Agricultural Research Center (CRA), 24 Chaussee de Namur, B-5030 Gembloux, Belgium***

[b] ***Foss Tecator AB, Box 70, S-26121, Hoganas, Sweden***

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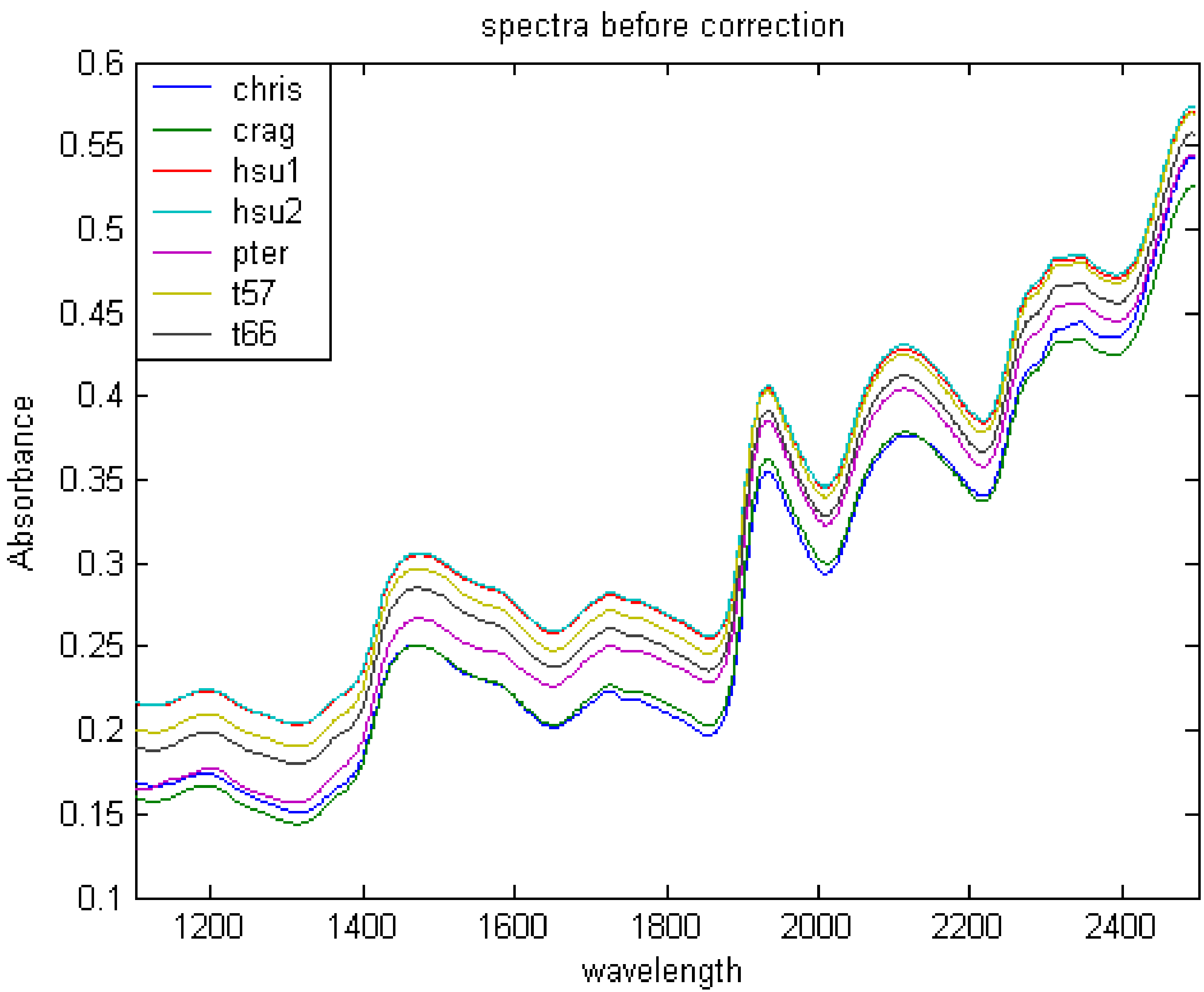
Average Spectra from 10 samples scanned 7 instruments



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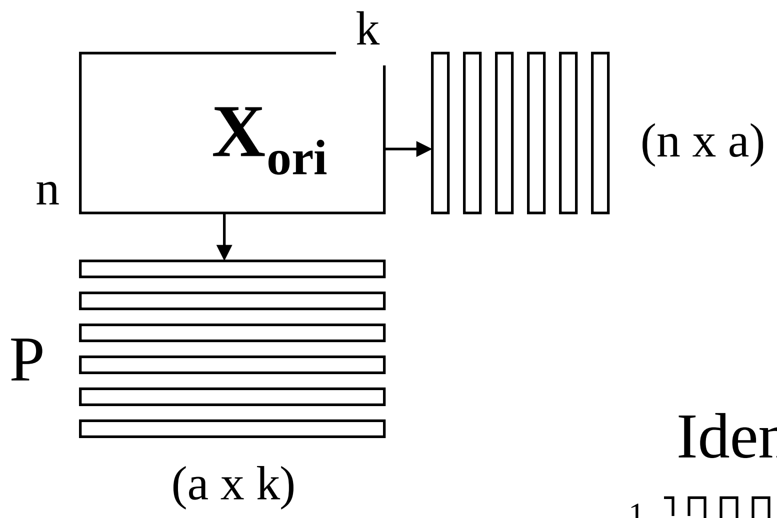
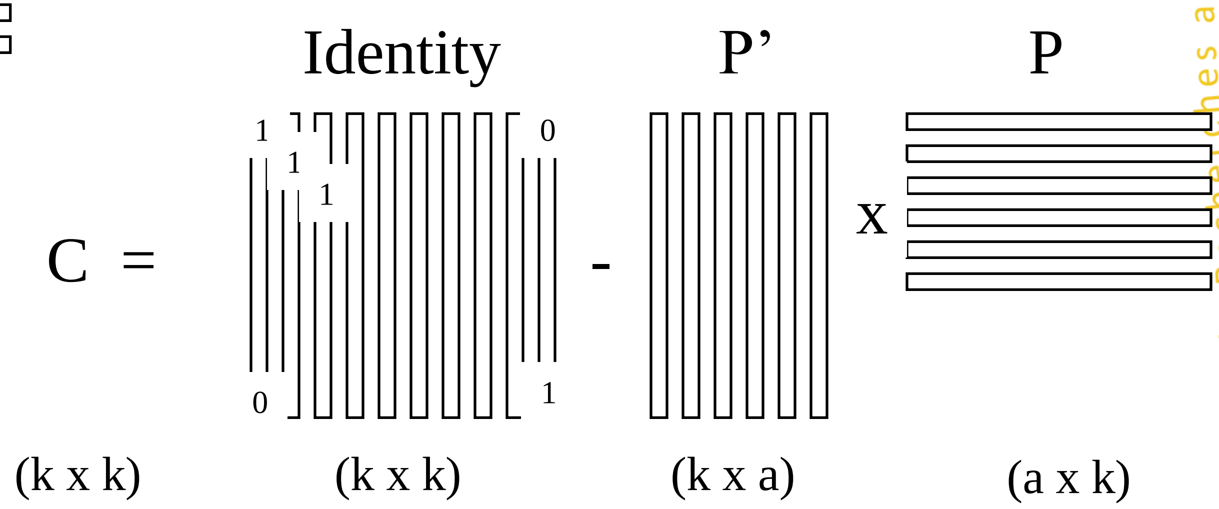
Tom Fearn's Standardisation (= orthogonalisation)





$$X_{cor} = X_{ori} * C \quad \textit{or} \quad X_{cor} = X_{ori} - X_{ori} * P' * P$$

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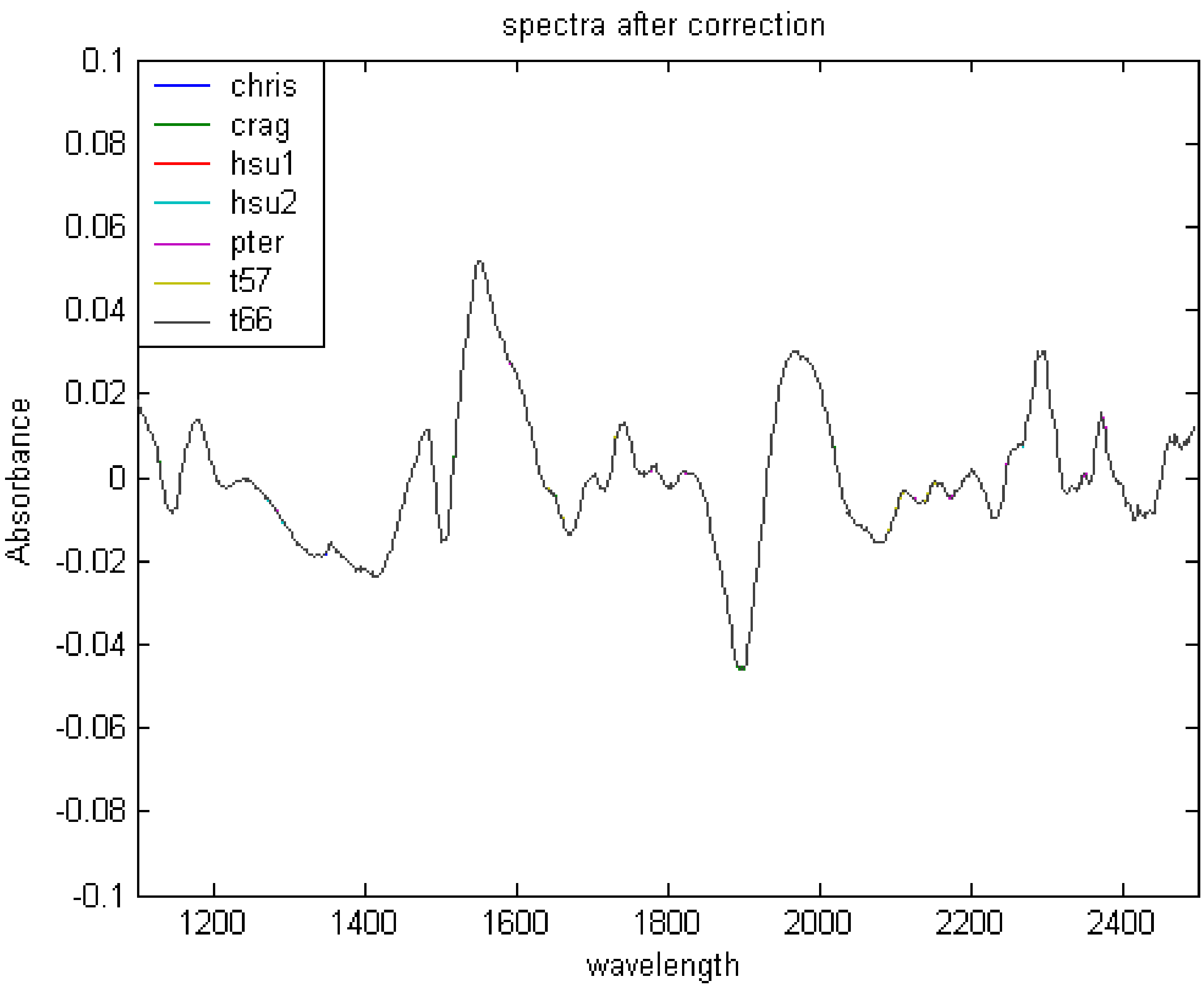
Average Spectra from 7 instruments (10 samples) after orthogonalisation



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CONCLUSIONS

ADVANTAGES OF CLONING MATCHING STANDARDISATION

1 → Share models from large and expensive data sets
-same type of instrument & different types
-keep efficient the outlier detection in routine mode

2 → Merge spectra from several instruments
- improve robustness
- share costs of reference analyses

3 → Keep instruments constant overtime (repairing)

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CRA-W NIR team

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Dr Vincent Baeten

Dr Juan-Antonio Fernandez

Ir Pilippe Vermeulen

Ir Bernard Lecler

Ir Olivier Minet

Anne Mouteau

Claudine Clément

Emma-Marie Mukandoli

Geoffrey Pletinckx

Marianne Flahaux

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Chimiométrie 2011 - Spécial Applications

Accueil

Accueil
Journée de formation
Inscription : marche à suivre
Tarifs 2011
Appel à communication
Thèmes
Comité scientifique
Comité d'organisation
Lieu de l'événement
Programme scientifique
Partenaires
Challenge2011
Les Winners de Chimiométrie2011
ACCES aux COMs
Actes du colloque

Publication dans CHEMOLAB

Challenge 2011

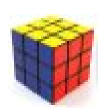
Les challenges organisés par le GFC sous l'autorité de Pierre Dardenne et Juan Antonio Fernández Pierna du centre Wallon de Recherhes Agronomiques, CRA-W (http://cra.wallonie.be/),se présentent sous la forme d'une énigme. Il s'agit de trouver les réponses d'un ou de plusieurs fichiers-tests à partir d'un fichier d'étalonnage. Les données de ce dernier fichier peuvent être polluées (données manquantes, données aberrantes, etc.).

Le fichier d'étalonnage et les fichiers-tests sont mis à la disposition de tous sur le site du GFC. L'analyse des solutions se fait au cours du congrès du GFC et la meilleure solution est primée. Un article parait dans la revue Chemolab pour faire la synthèse des solutions.

Voici ci-dessous les fichiers du **challenge 2011 :**

Les données : cliquez ici (.XLS) **ou** ici (.XLSX)

La description des données et les objectifs :



Pour accéder aux Challenges des années précédentes : cliquez ici

http://www.chimiometrie.fr/chimiometrie2011

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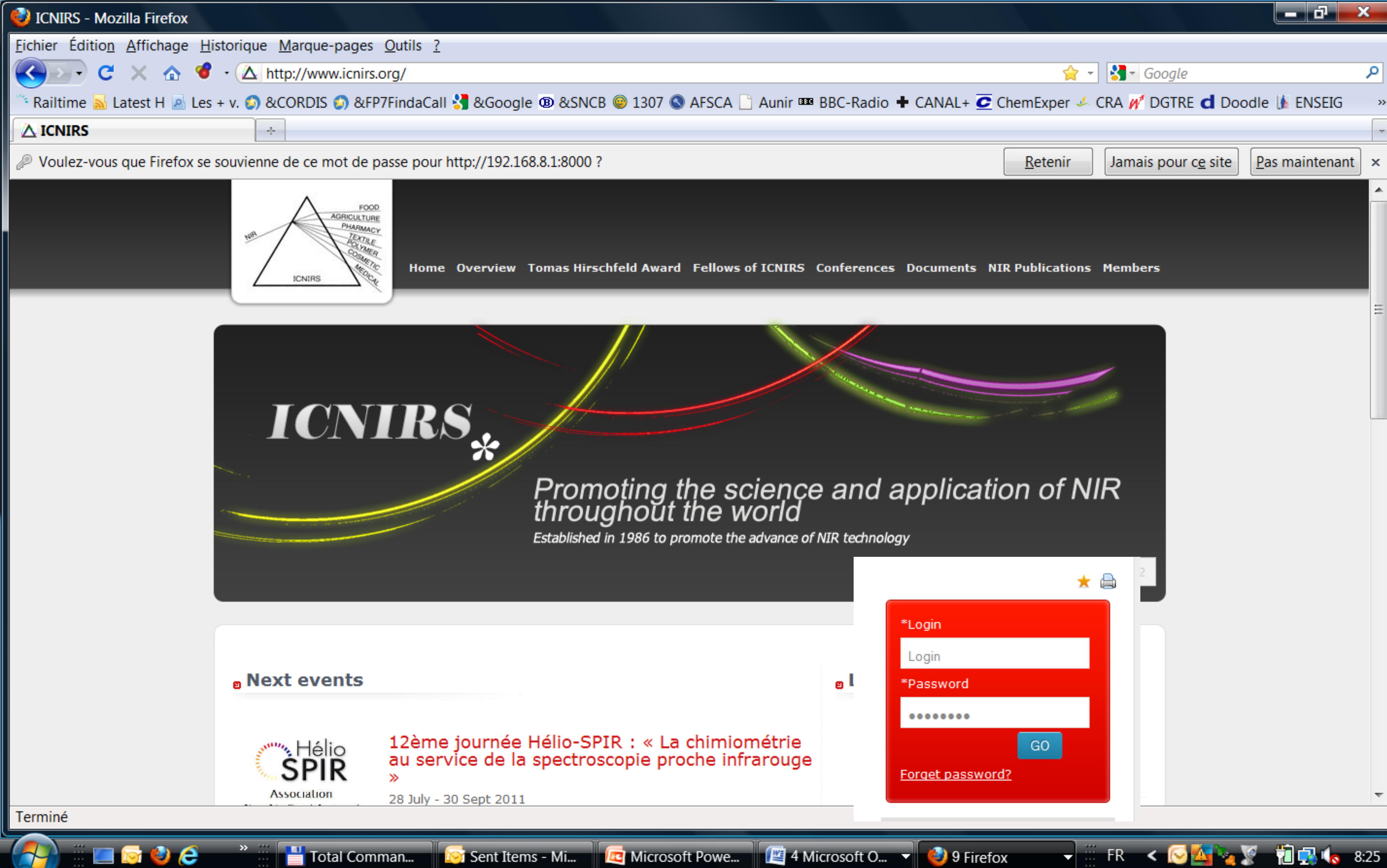

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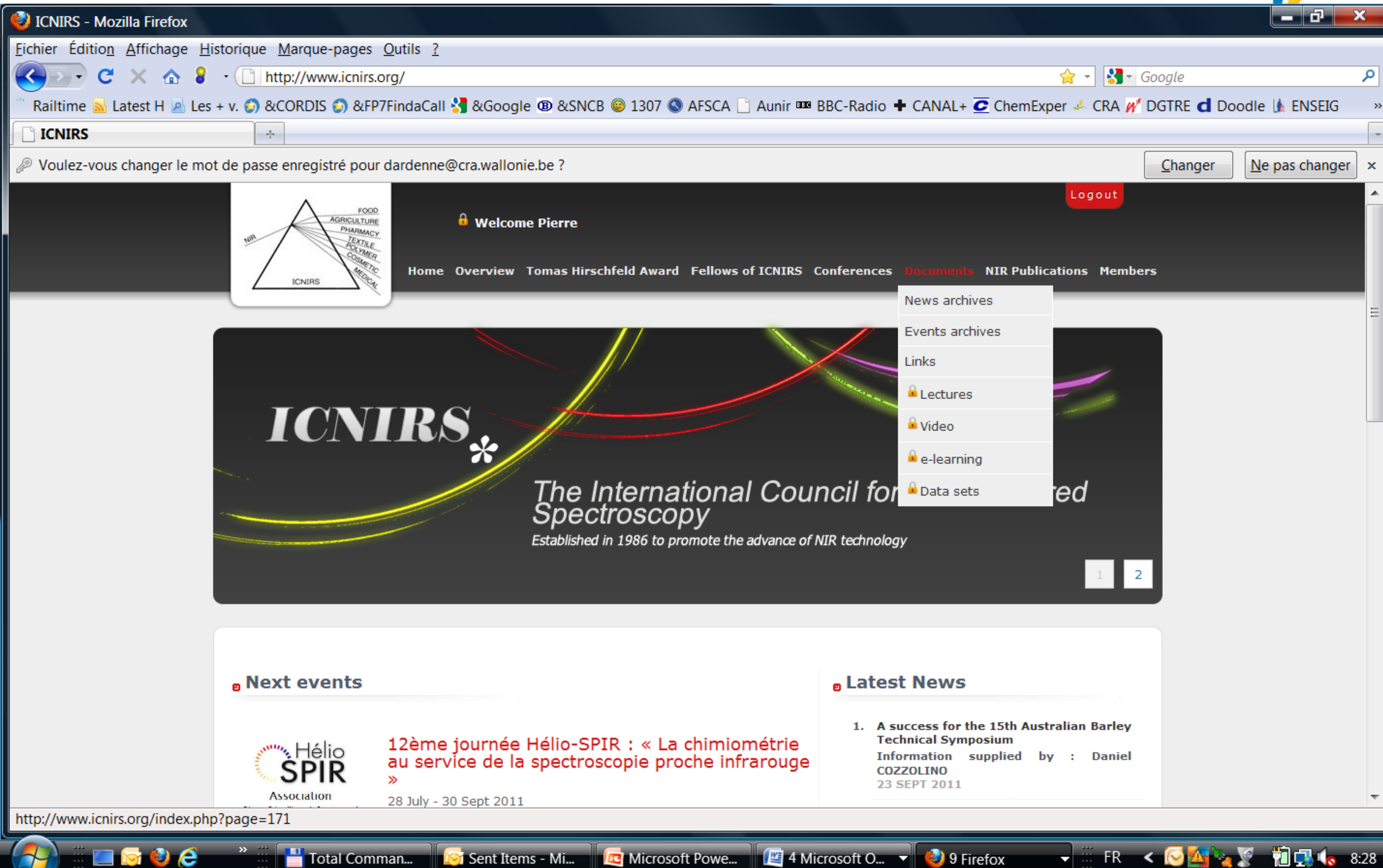

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