



Limite de détection et incertitude en spectroscopie proche infrarouge

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LOD

detection limit : the smallest concentration difference that can be detected above the background noise level of a NIR instrument.



Rapid detection of melamine in milk powder by near infrared spectroscopy

than 1 ppm.²¹ In order to overcome the limitation of the methods which had already been evaluated, this study tried to establish a fast detection method for pure melamine in milk powder by near infrared (NIR) spectrometry together with LS-SVM and has shown some promise. The detection limit of this method was lower than 1 ppm. It conforms to the national standard for melamine in infant milk products. The

Melamine Detection in Infant Formula Powder Using Near- and Mid-Infrared Spectroscopy

models are not matrix independent. New calibration models are required for application to different brands or formulations of infant formula powders or other food products. It is expected that the analytical approach for quantifying or detecting melamine using NIR or FTIR spectroscopy would be applicable to other products. The NIR and FTIR methods meet the need for a rapid, simple, and available technique for detecting 1 ppm melamine in infant formula powder.

K. Norris, *J. Near Infrared Spectrosc.*
Received: 10 September 2007



the noise sources. Those responsible for developing calibrations for constituents at ppm levels must demonstrate the impact of the possible noise sources on their results before suggesting possible limits of detection. Of course, before putting the results into practice the technology must be tested with real food process samples.

All of this discussion has used only the detection of melamine, but the same noise sources are present with other possible contaminants.

Letter to the Editor

Hazards with near infrared spectroscopy in detecting contamination

Karl Norris

Consultant, Beltsville, MD 20705, USA. E-mail: knnirs@gmail.com

$$Abs. = A = -\log_{10}\left(\frac{I}{I_0}\right) = -\log_{10} R = \varepsilon.c.l$$

A : absorbance (OD)

I : energy of reflected light

I₀ : energy of initial light

R : reflectance

ε : absorptivity

c : concentration

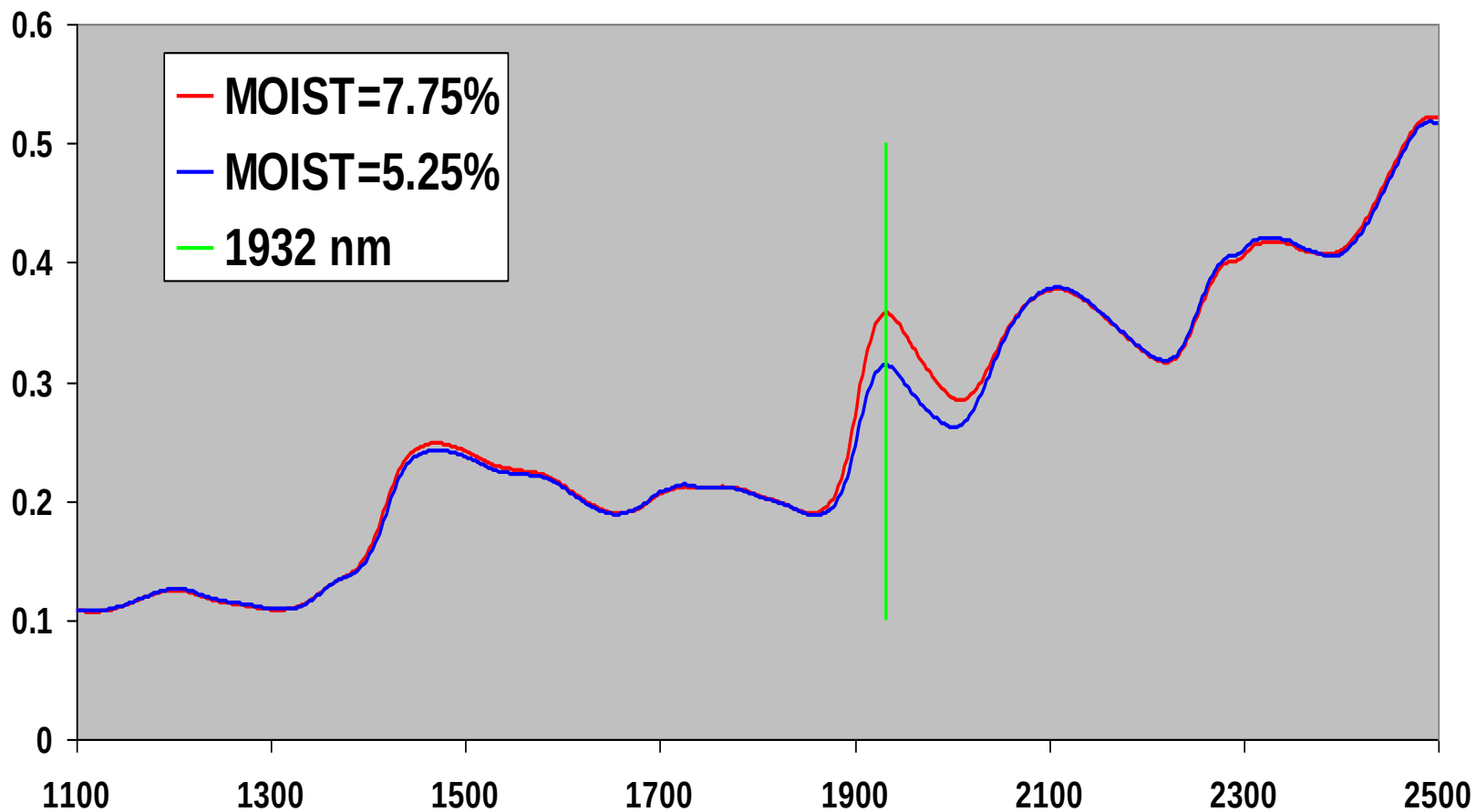
l : pathlength

$$A = \frac{L}{\text{moles} \cdot \text{cm}} \cdot \frac{\text{moles}}{L} \cdot \text{cm}$$

LOD of NIRS

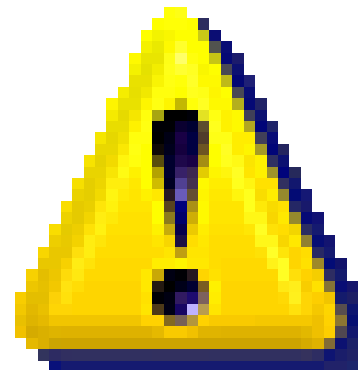
CORN SILAGE DATA SET 4816 spectra sorted/H2O %

CORN SILAGE - AVERAGE OF 2 x 2408 SPECTRA



LOD of NIRS

	1932
MOIST=7.75%	0.357243
MOIST=5.25%	0.313645
2.5	0.043598
1	0.017439



If <0.1%

A units	Water %	ppm	ppb
0.020 000	1	10 000	10 000 000
0.002 000	0.1	1 000	1 000 000
0.000 200	0.01	100	100 000
0.000 020	0.001	10	10 000



Villeneuve d'ascq, 5-6 Décembre 2012

Polytech'Lille, Université Lille1, FRANCE

Connexion

NAVIGATION

Accueil

Lieu de la conférence

Conférenciers invités

Liste de communications
acceptées

Programme
CHIMIOMETRIE 2012

Comités ▼

Résumé et inscription ▼

Publication dans
CHEMOLAB

Challenge 2012

Prix et récompenses

Hébergement

Exposants / Partenaires /
Sponsors

Devenir partenaire /
Sponsoriser cette
conférence

CHALLENGE 2012



Le Challenge est ouvert !

Le challenge organisé par le Groupe Français de Chimiométrie se présente sous la forme d'une énigme. Il s'agit de trouver les réponses d'un fichier "test" à partir d'un fichier dit d'étalonnage. Les données de ce dernier fichier peuvent être polluées (données manquantes, données aberrantes, etc.).

Le fichier d'étalonnage et le fichier "test" sont mis à votre disposition ci-dessous. L'analyse des solutions se fait au cours du congrès. Les congressistes ayant proposé les meilleurs solutions seront invités à présenter brièvement leur méthodologie lors d'une session spéciale CHALLENGE. Les meilleures solutions seront primées.

NOUVEAUTÉ : Afin de favoriser la participation des jeunes chimiométriciens (moins de 30 ans), le comité scientifique a décidé cette année de créer une catégorie spécifique dite "Junior". Ces contributions au Challenge seront ainsi étudiées séparément de celles des seniors.

Téléchargez le fichier de données : [ICI](#)

Description du CHALLENGE CHIMIOMETRIE 2012 :

270 spectra in a CAL set with known concentration of a contaminant.

276 spectra in a TEST set to be predicted.

CA SET (only soya meal (SM))

240 with 4 concentrations (0.10, 0.25, 0.50, 1.00%)

+30 randomly selected from the clean set

270 spectra

TEST SET

T1 = 40 SM randomly selected with high contamination (2, 3, 4, 5%)

T2 = 50 randomly selected from the **clean** set

T3 = 43 soyameal spl from another origin + another instrument

T4 = 78 wheat gluten (39 in duplicates)

T5 = 65 maize gluten

Total : 276

Foss XDS

Foss 6500
Clean & Conta.
Melamine
Cyanuric Acid

MLR : Multi Linear Regression – manual step up

WinISI Global

File Options Tables Graphs Help



Click on an option to continue

Percent C

Step-up Regression Statistics

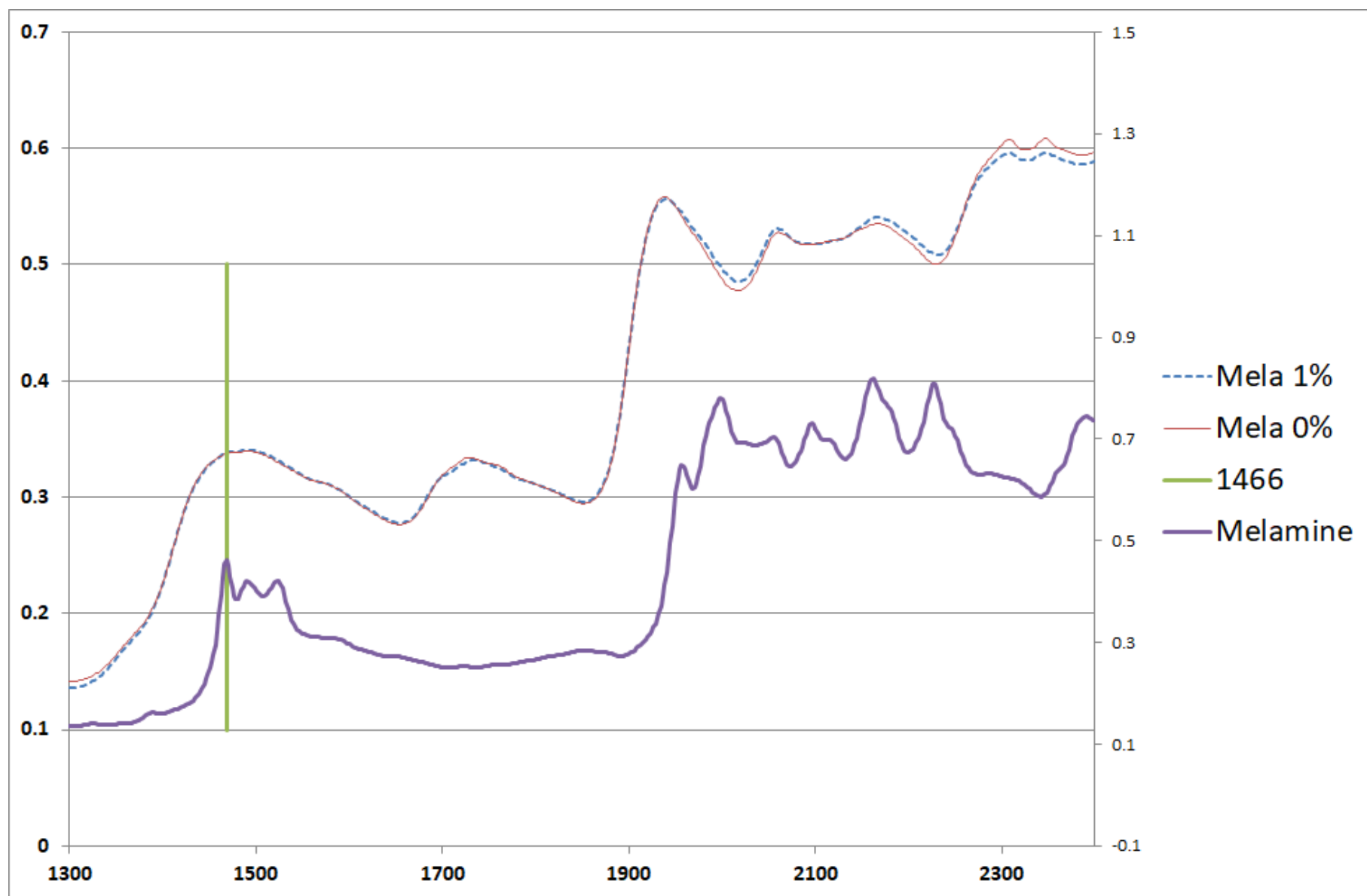
Input File	CALSET1S.CAL	REP File	None
Validation File	None	Equation File	None
Math Treatment	0, 0, 1, 1	Number of variables	550
Scatter Corrected	None	Downweight outliers	Yes
Constituent	mela	Number of samples	300
Cross validation	By groups, no pre-sort, form groups by blocks, group duplicates together		
Mean	0.370	Range	0.00 - 1.00
		Standard deviation	0.358
Number of terms	3	SEC	0.081
		AdjRSQ	0.949

	Coefficient	Data Point	Wavelength	F
B(0) =	-0.143			
B(1) =	-792.693	86	1470.0	1634.24
B(2) =	1714.127	84	1466.0	3500.19
B(3) =	-922.584	82	1462.0	5463.41

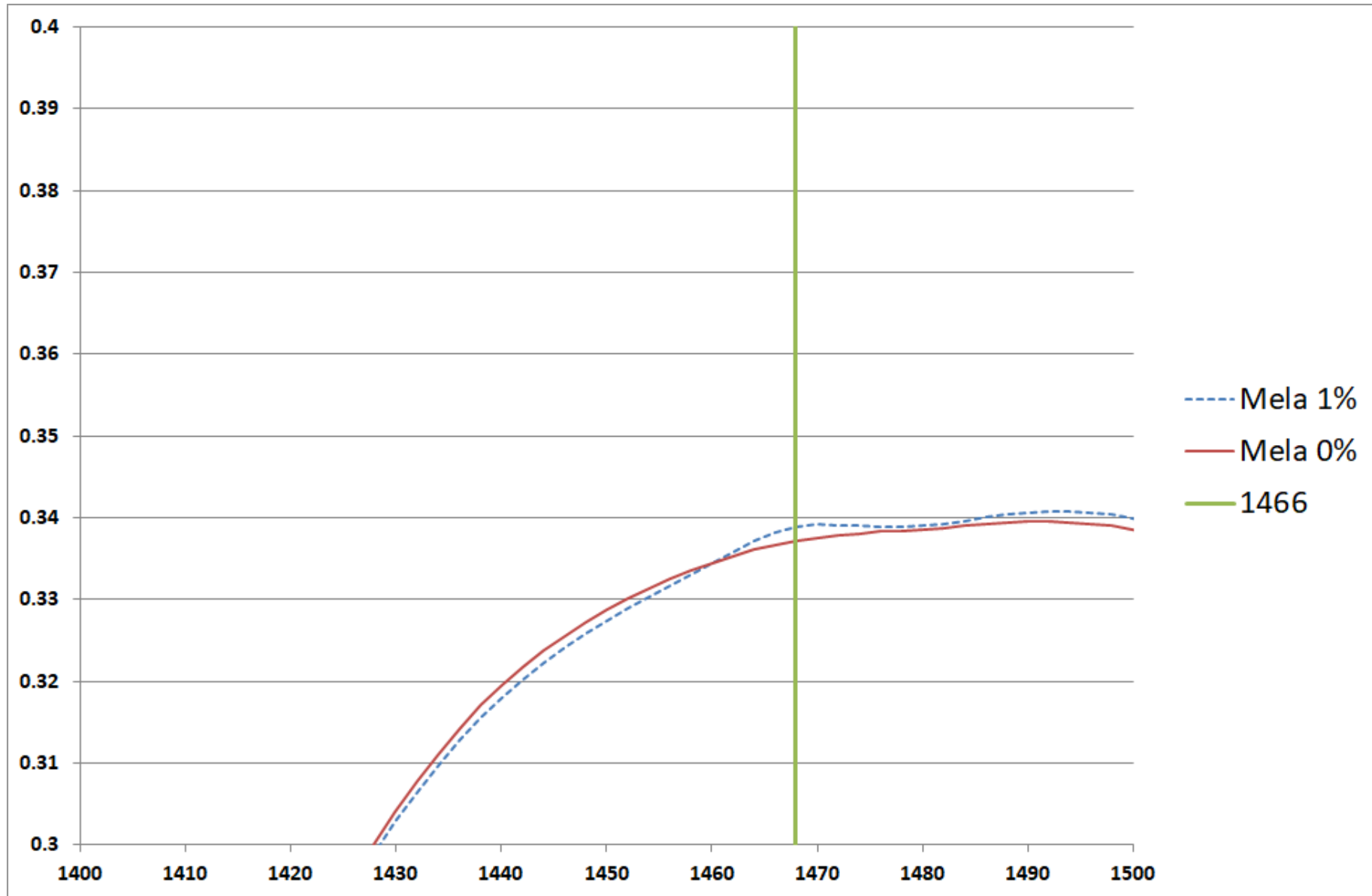
SEC= 0.08 → SECV = 0.1 (1 000 ppm)

Average 0 and 1 % (60 spectra)





Average 0 and 1 % (60 spectra)



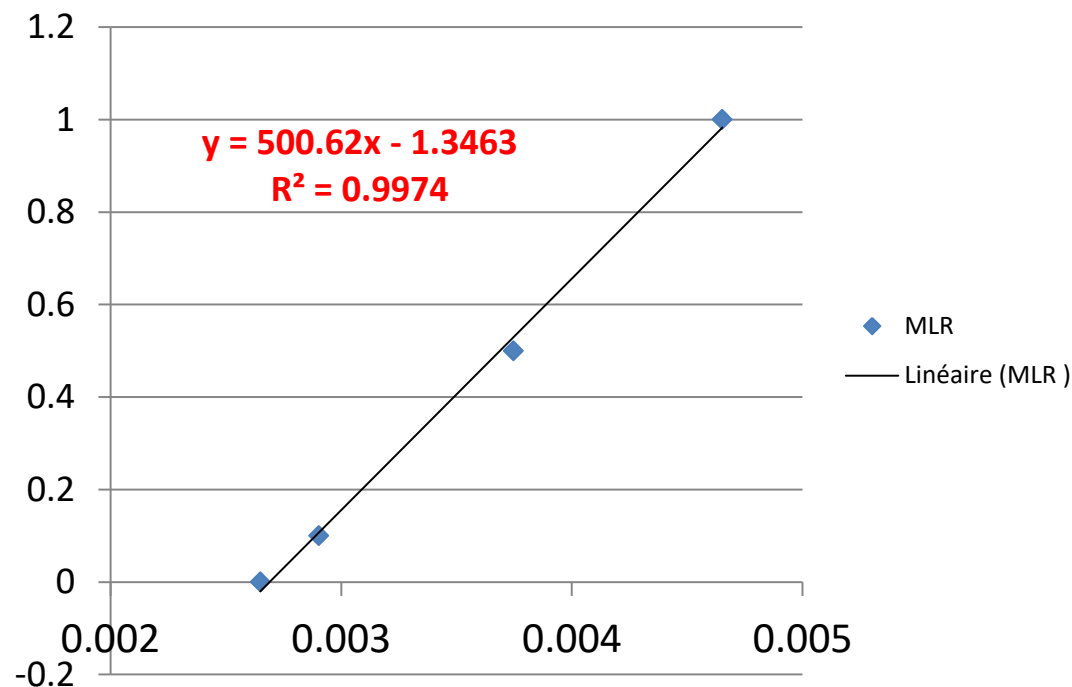
300 sp. → Average by group of 60 samples : 0.0, 0.10, 0.25, 0.50, 1%

Step-up Regression Statistics

Input File	totmeans6.cal	REP File	None
Validation File	None	Equation File	None
Math Treatment	0, 0, 1, 1	Number of variables	550
Scatter Corrected	None	Downweight outliers	Yes
Constituent	mela	Number of samples	5
Cross validation	By groups, no pre-sort, form groups by blocks, group duplicates together		
Mean	0.370	Range	0.00 - 1.00
		Standard deviation	0.399
Number of terms	2	SEC	0.032
		AdjRSQ	0.994

	Coefficient	Data Point	Wavelength	F
B[0] =	-0.209			
B[1] =	518.336	85	1468.0	613.22
B[2] =	-521.870	81	1460.0	614.07

MLR X=OD1468-OD1460



$$1/500 = 0.002$$

A OD difference of
0.002 = 1% melamine

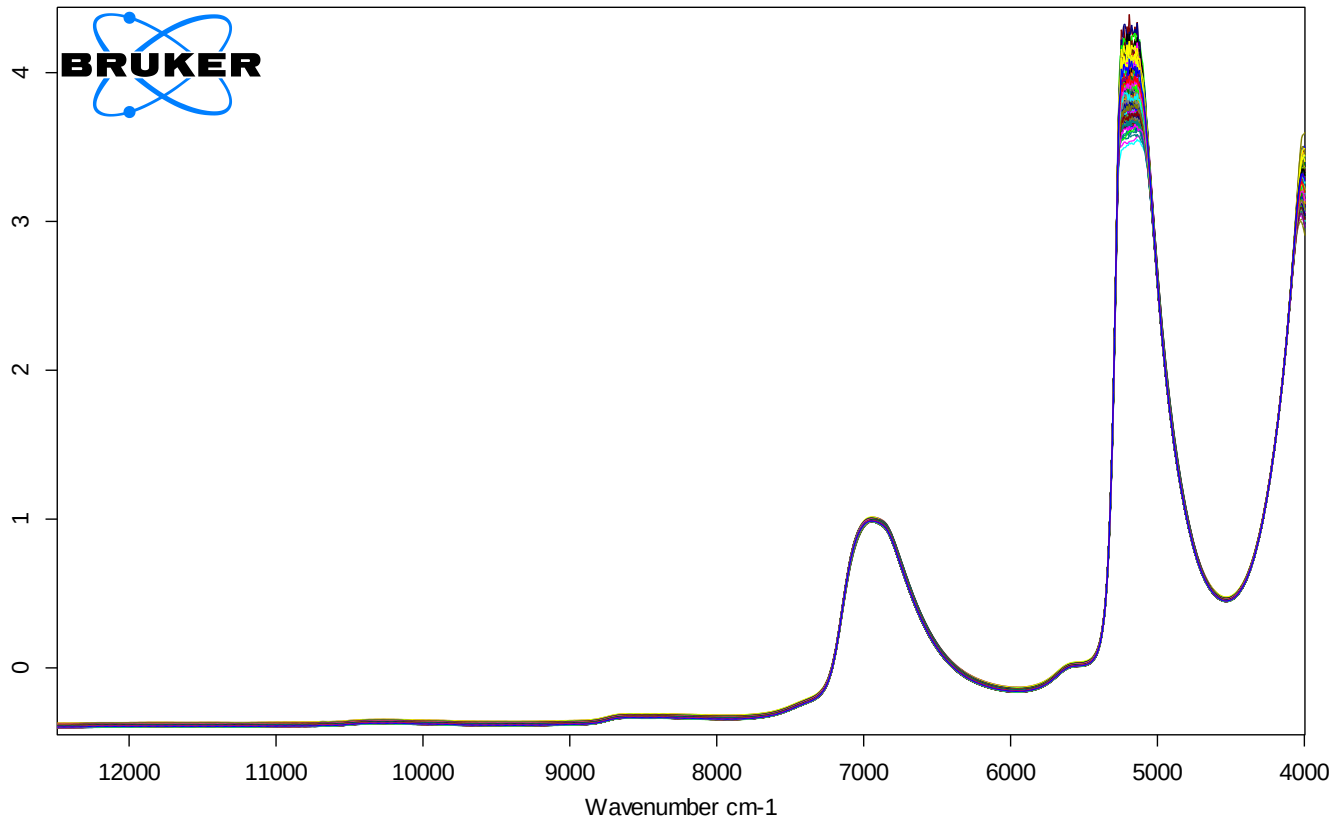
A Units	μLog	Melamine %	ppm	ppb
0.002	2000	1	10 000	10 000 000
0.000 2	200	0.1	1 000	1 000 000
0.000 02	20	0.01	100	100 000
0.000 002	2	0.001	10	10 000

MELAMINE ABSORBS 10 x LESS THEN WATER !!

Water analysis by NIRS



**702 spectra of water
(13 brands x 6 bottles/brand x 9 scans)**



DRY EXTRACT in mineral waters

: (values on the stickers : mg/L) (averages 54 spectra)

Step-up Regression Statistics

Input File	liste3m13.cal	REP File	None
Validation File	None	Equation File	None
Math Treatment	0, 0, 1, 1	Number of variables	1102
Scatter Corrected	None	Downweight outliers	No
Constituent	LAB1	Number of samples	11
Cross validation	By groups, no pre-sort, form groups by cycling, group duplicates together		
Mean	744.818	Range	33.00 - 2513.00
		Standard deviation	838.062
Number of terms	2	SEC	115.274
		AdjRSQ	0.981
	Coefficient	Data Point	Wavelength
B(0) =	1240184.220		
B(1) =	-1182091.610	727	727.0
B(2) =	1231799.860	806	806.0

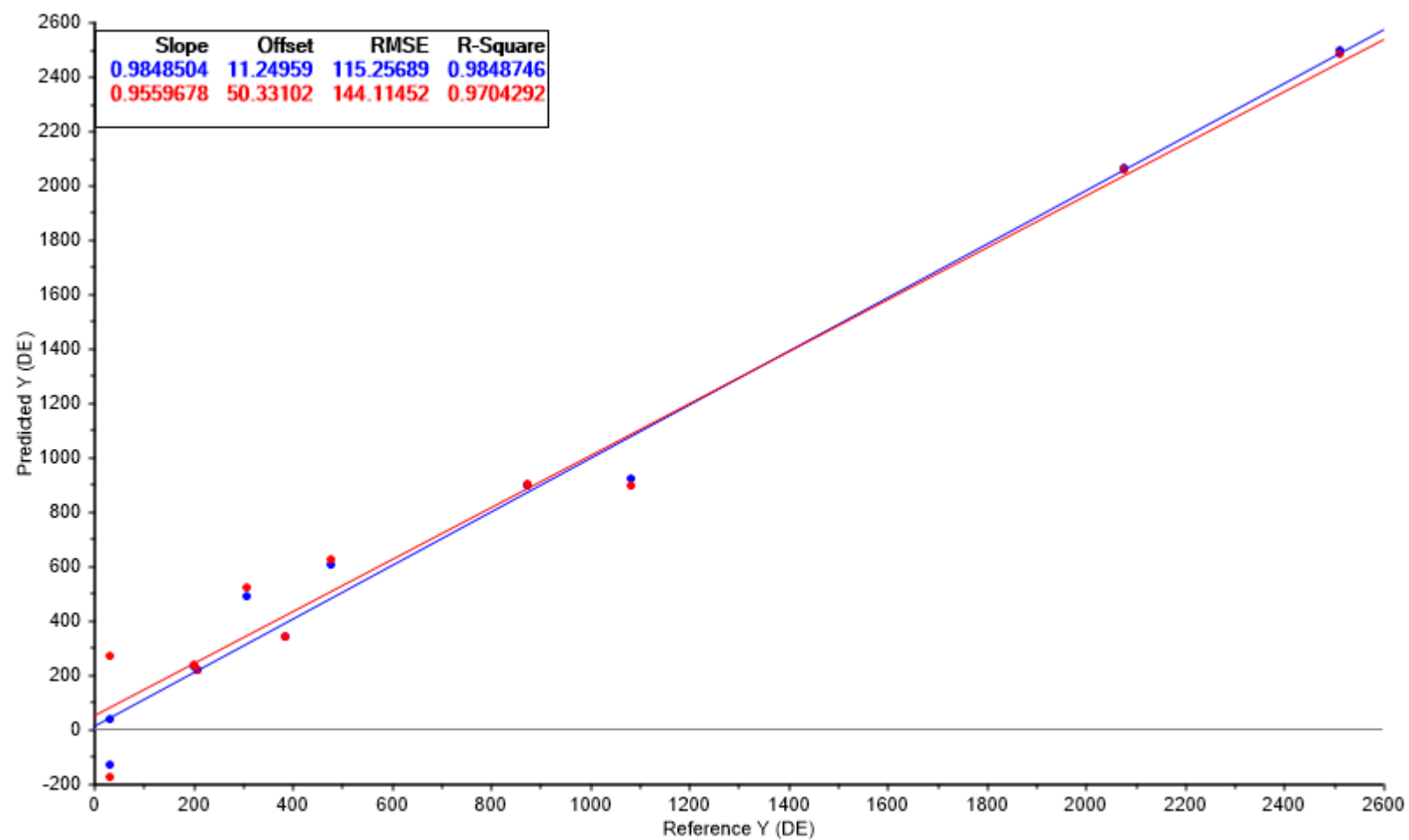
727
1452
6889

806
1593
6279

0.003 % - 0.25 % -> b: 1 200 000 → 120

99.75% - 99.997 % H2O

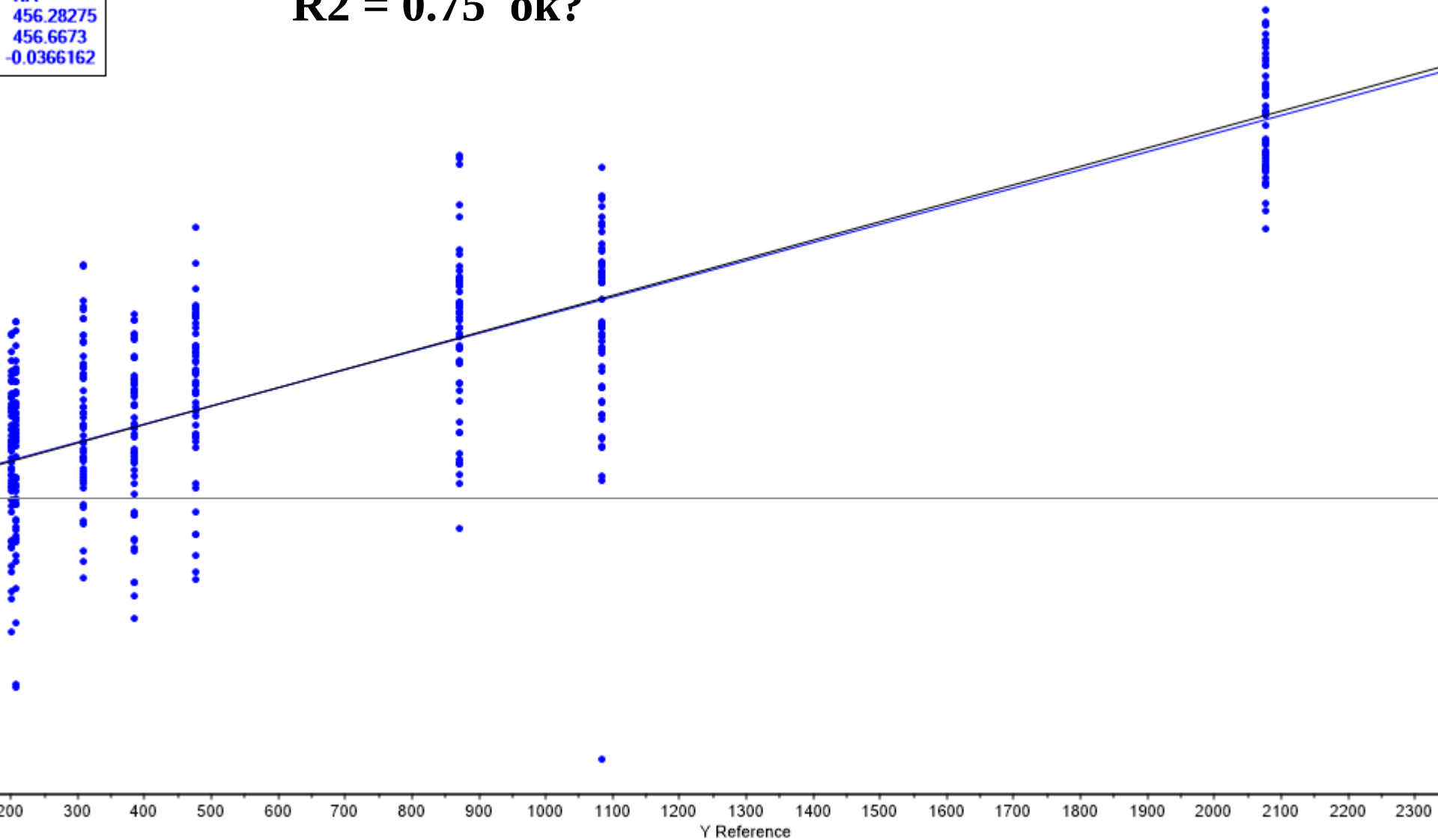
Predicted vs. Reference

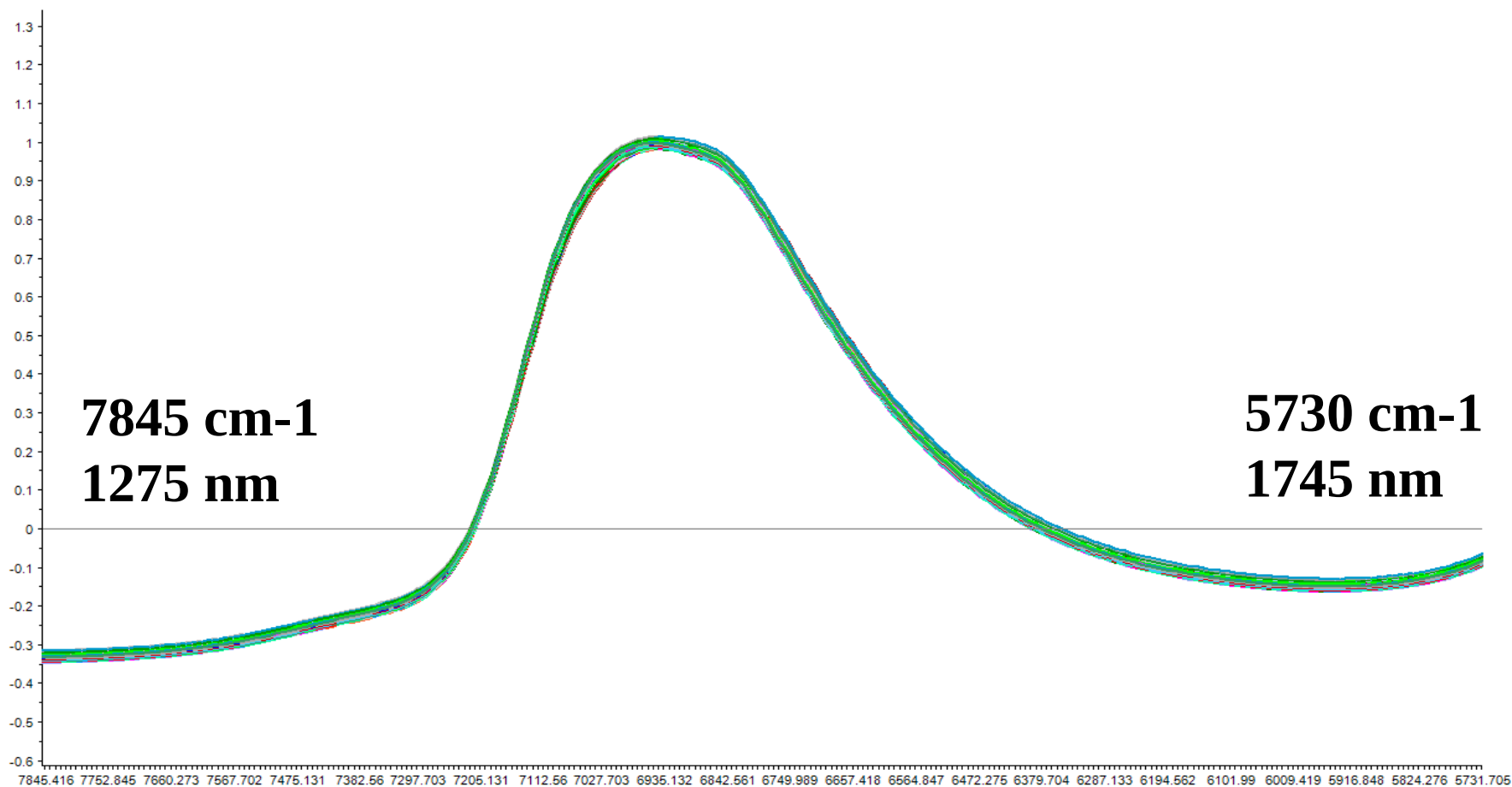


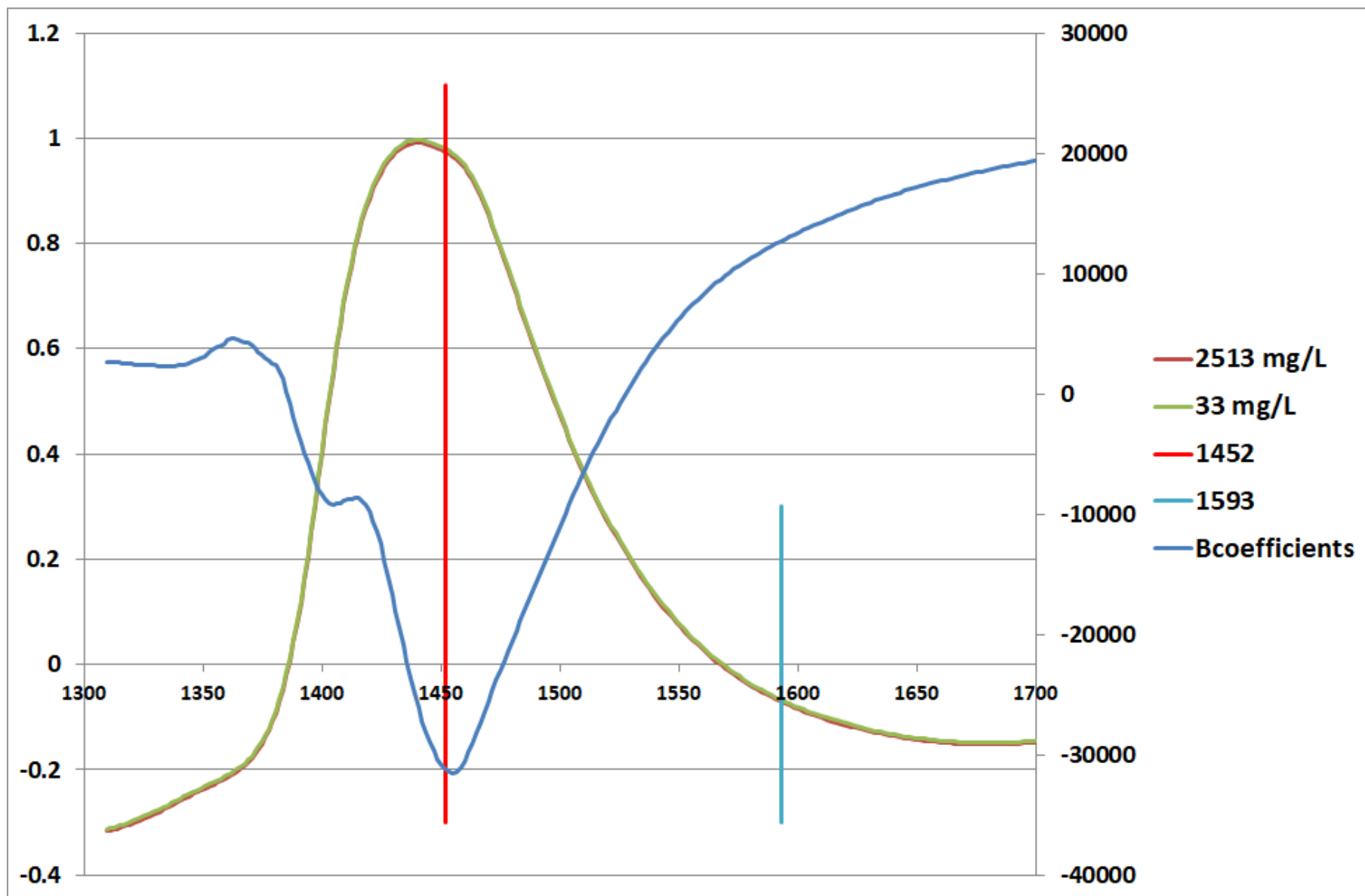
Predicted vs. Reference

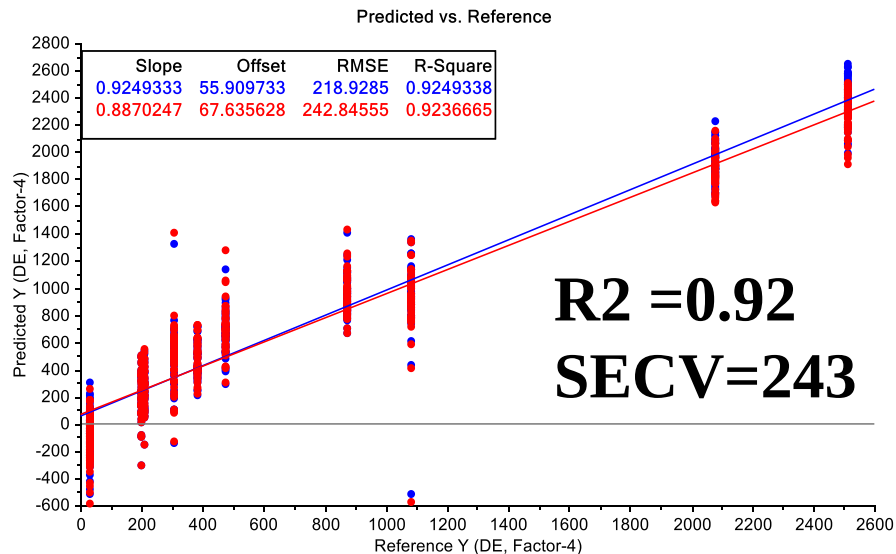
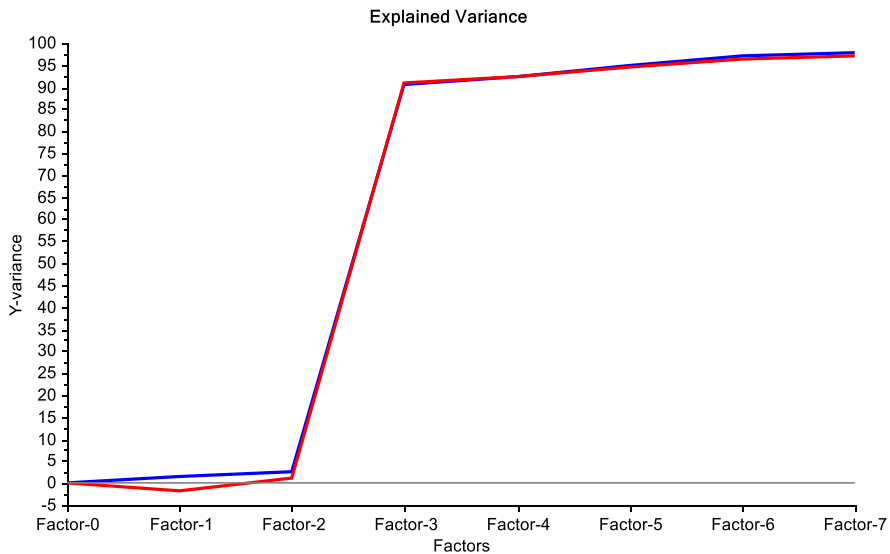
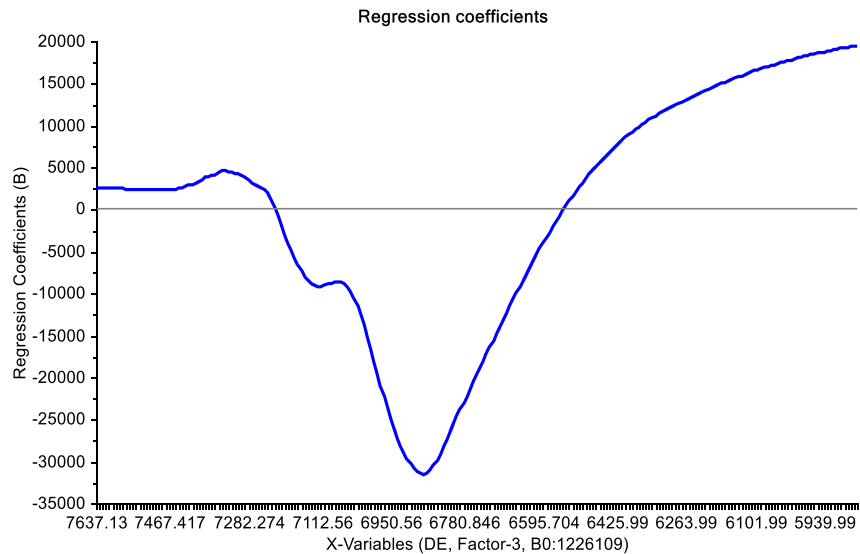
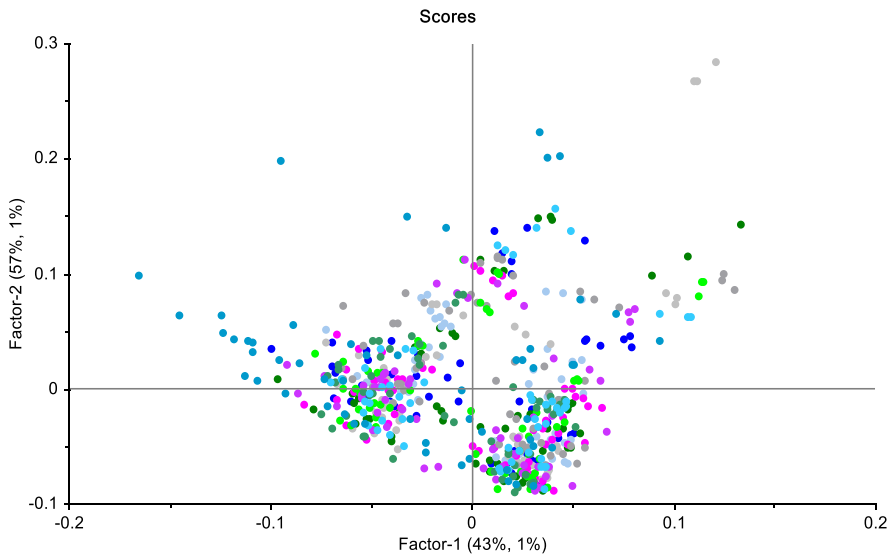
594
0.9848552
11.24349
0.865181
0.7485381
NA
456.28275
456.6673
-0.0366162

R2 = 0.75 ok?

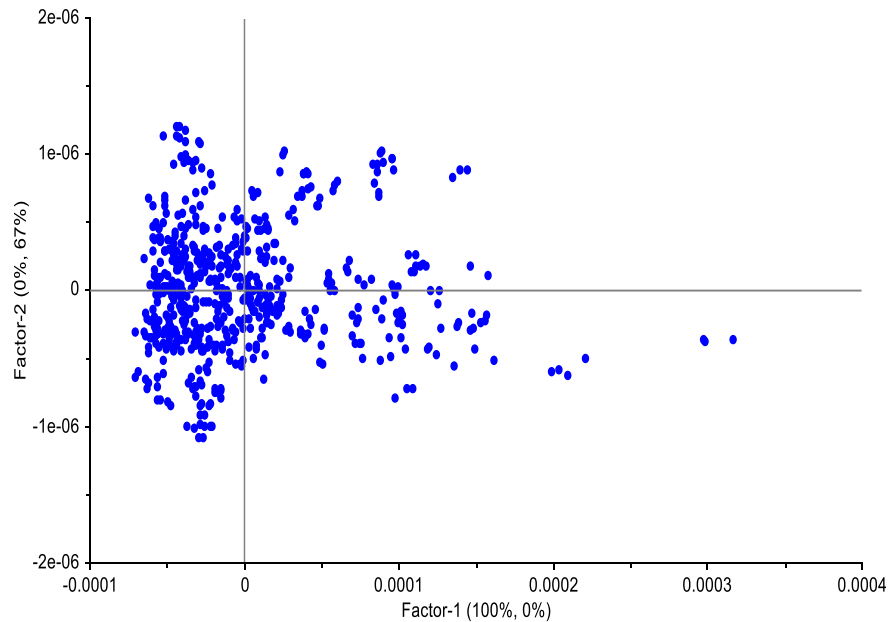




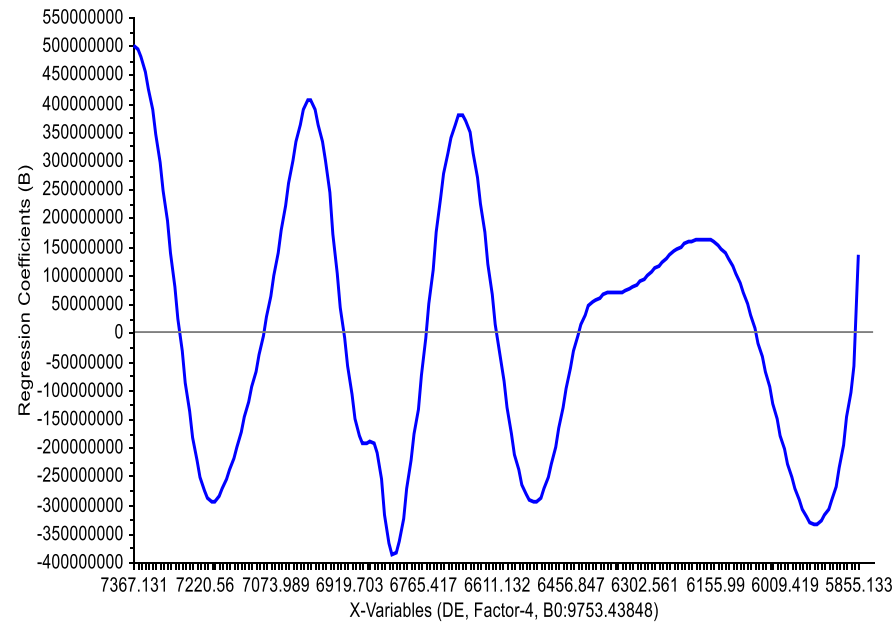




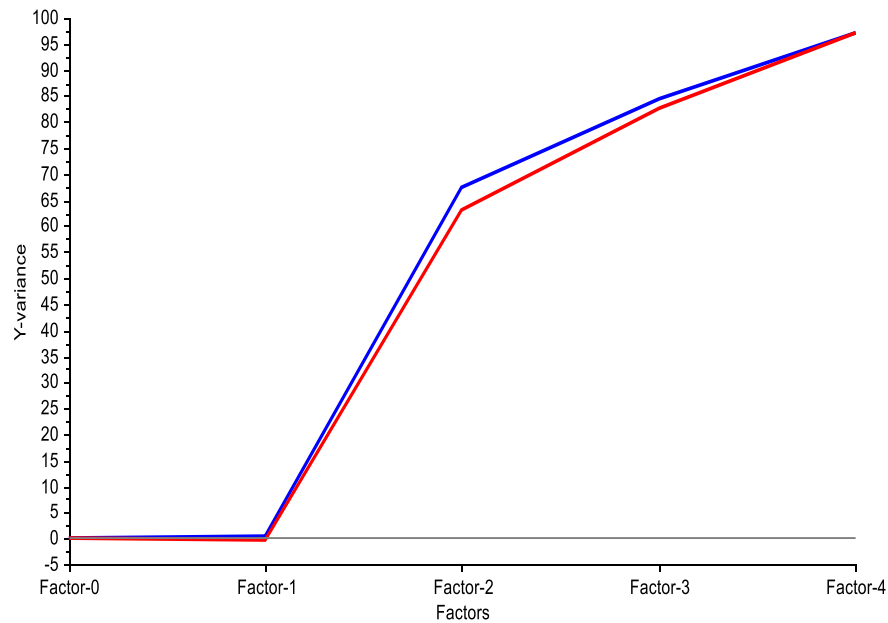
Scores



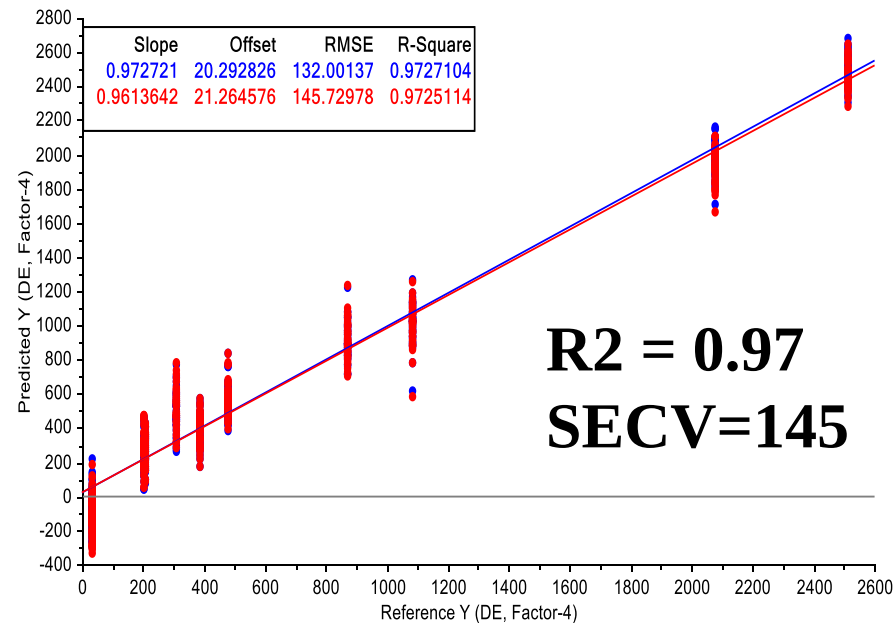
Regression coefficients



Explained Variance



Predicted vs. Reference



Full Fat Soya (2000 spl, sorted/oil, average/100)

Step-up Regression Statistics

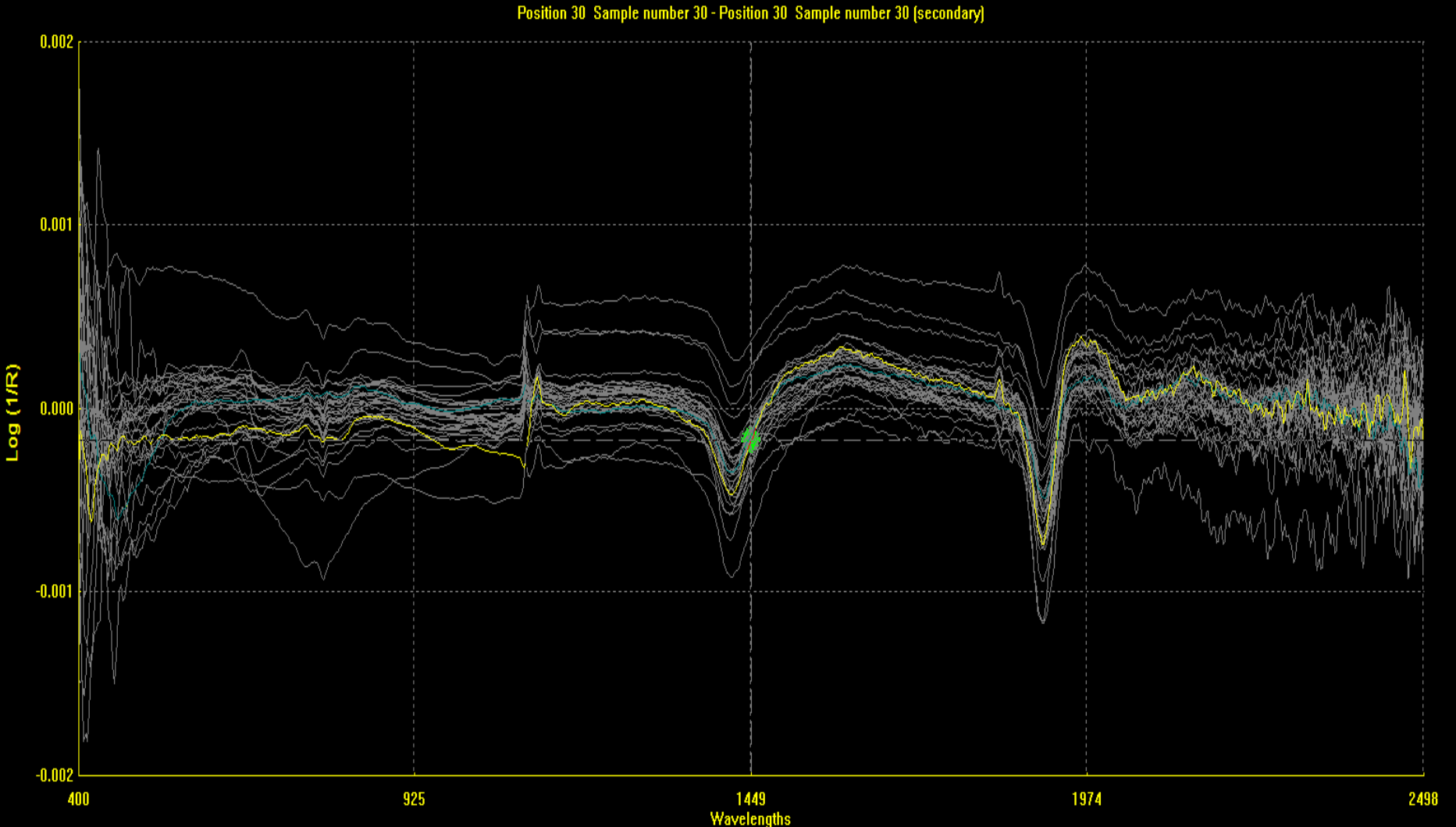
Input File	oila100.cal	REP File	None
Validation File	None	Equation File	None
Math Treatment	0, 0, 1, 1	Number of variables	693
Scatter Corrected	None	Downweight outliers	No
Constituent	Oila_as	Number of samples	20
Cross validation	By groups, no pre-sort, form groups by cycling, group duplicates together		
Mean	19.434	Range	15.89 - 22.49
		Standard deviation	1.582
Number of terms	2	SEC	0.324
		AdjRSQ	0.958
	Coefficient	Data Point	Wavelength
B(0) =	25.541		
B(1) =	236.127	313	1724.0
B(2) =	-178.299	505	2108.0
			437.15
			423.30

	Au	%	Bcoeff
Water	0.02	1	50
DE	0.01	1	100
OIL	0.005	1	200
Melamine	0.002	1	500
	microLog	100 ppm	
Water	200	0.01	50
DE	100	0.01	100
OIL	50	0.01	200
Melamine	20	0.01	500

?

STD BOX : 30 sealed cups





X = 1450	Y = -0.00016090	Position 28 Sample number 28 - Position 28 Sample number 28 (secondary)
NIR region		Position 29 Sample number 29 - Position 29 Sample number 29 (secondary)
Absorption by stretching - bending		Position 30 Sample number 30 - Position 30 Sample number 30 (secondary)

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



Contrast Output

sg6120216 a.nir vs. sg6120216 b.nir:

Pos	Sample No.	Seg	R ²	RMS	Standard Bias	RMSC
		2	1.0000	247	-206	136
28	28	1	1.0000	75	12	74
		2	1.0000	132	79	105
29	29	1	1.0000	169	28	167
		2	1.0000	135	68	116
30	30	1	1.0000	178	-156	84
		2	1.0000	207	67	196
Segment Averages:						
	Segment No.	1	1.0000	273	-30	194
		2	1.0000	258	70	174
Overall Aves:			1.0000	263	20	181

 Contrast Output

sg6120216 a.nir vs. sg6120216 b.nir:

Pos	Sample No.	Seg	R^2	RMS	Standard Bias	RMSC
		2	1.0000	247	-206	136
28	28	1	1.0000	75	12	74
		2	1.0000	132	79	105
29	29	1	1.0000	169	28	167
		2	1.0000	135	68	116
30	30	1	1.0000	178	-156	84
		2	1.0000	207	67	196
Segment Averages:						
	Segment No.	1	1.0000	273	-30	194
		2	1.0000	258	70	174
Overall Aves:			1.0000	263	20	181

Pos	Sample No.	R^2	RMS	Bias	RMSC
14	15	1.0000	1594	1171	1081
15	17	1.0000	9193	-8789	2695
16	19	0.9997	9086	7067	5716
17	20	0.9998	16823	15188	7242
18	21	0.9998	4002	-883	3907
19	22	0.9999	8049	-7814	1930
20	23	0.9993	14352	-12081	7755
21	24	1.0000	8414	8161	2047
22	25	1.0000	3572	1547	3223
23	26	1.0000	5137	-4963	1330
24	27	1.0000	5701	-5625	930
25	28	1.0000	10316	-10120	2001
26	29	0.9997	8607	-4368	7423
27	30	0.9997	6955	6084	3373
Overall Aves:		0.9999	9729	-963	3988

Pos	Sample No.	Seg	R ²	RMS	Bias	RMSC
28	#28	2	1.0000	89	0	89
		1	1.0000	46	-19	42
		2	1.0000	90	0	91
29	#29	1	1.0000	197	-24	196
		2	1.0000	106	3	106
30	#30	1	1.0000	78	-14	76
		2	1.0000	123	3	123
Segment Averages:						
	Segment No.	1	1.0000	110	2	108
		2	0.9999	153	-2	153
	Overall Aves:		1.0000	140	0	139

Pos	Sample No.	R ²	RMS	Bias	RMSC
14	15	0.9998	313	-45	310
15	17	0.9996	437	-122	420
16	19	0.9982	1606	288	1581
17	20	0.9991	1324	-372	1272
18	21	0.9993	1063	-152	1053
19	22	0.9990	669	82	665
20	23	0.9981	1378	301	1346
21	24	0.9999	530	19	530
22	25	0.9996	518	-124	503
23	26	0.9999	228	-34	225
24	27	0.9998	329	34	327
25	28	0.9998	298	132	267
26	29	0.9982	1250	400	1185
27	30	0.9988	1077	87	1075
Overall Aves:		0.9994	826	34	803

1st DERIVATIVE

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



Detection of melamine and cyanuric acid in feed ingredients by near infrared spectroscopy and chemometrics

O. Abbas,* B. Lecler, P. Dardenne and V. Baeten

Food and Feed Quality Unit, Valorisation of Agricultural Products Department, Walloon Agricultural Research Centre (CRA-W),
Chaussée de Namur 24, B-5030 Gembloux, Belgium. E-mail: o.abbas@cra.wallonie.be



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journal homepage: www.elsevier.com/locate/chemolab

Use of a multivariate moving window PCA for the untargeted detection of contaminants in agro-food products, as exemplified by the detection of melamine levels in milk using vibrational spectroscopy☆

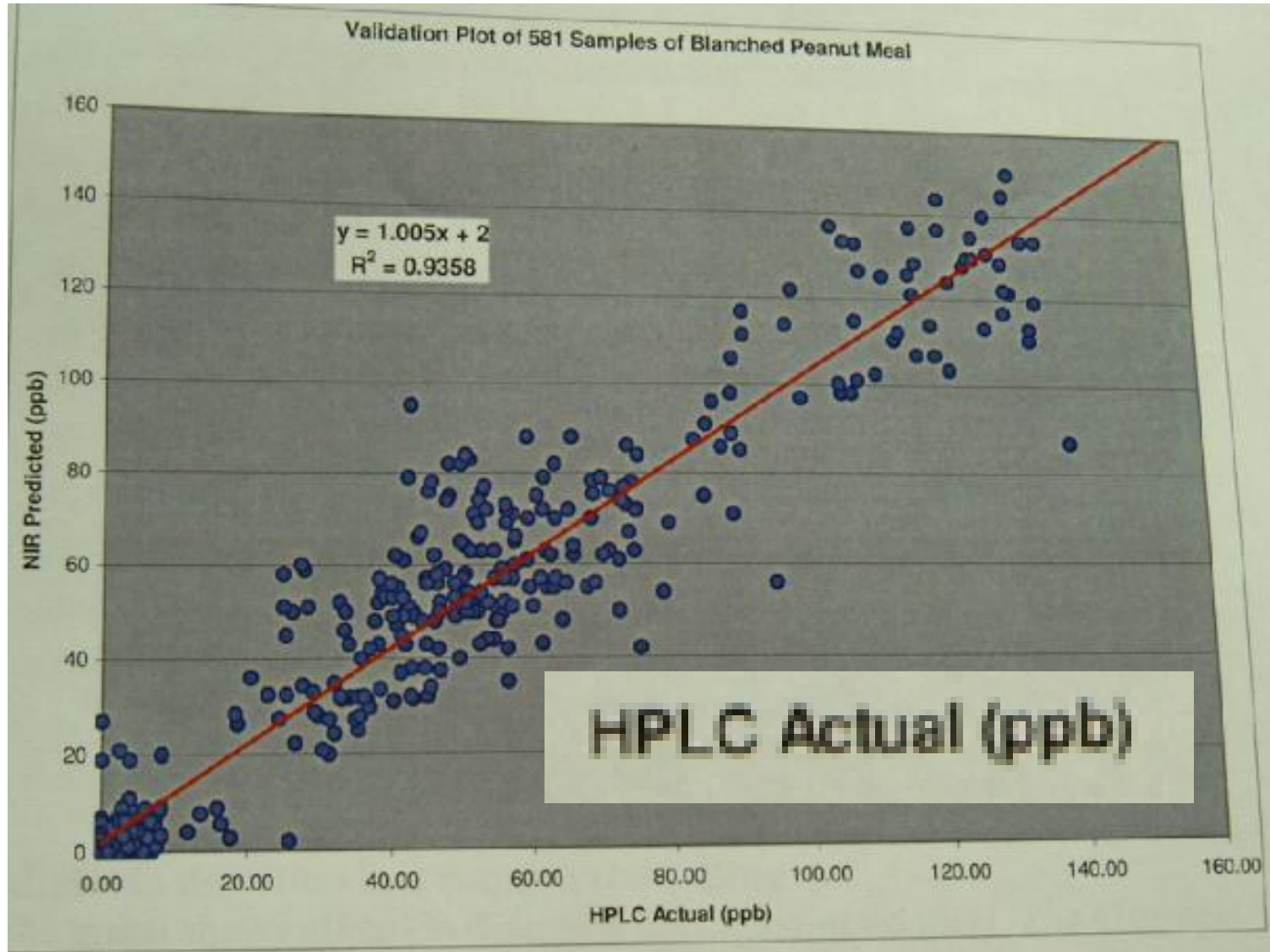
J.A. Fernández Pierna, D. Vincke, V. Baeten, C. Grelet, F. Dehareng, P. Dardenne *

Walloon Agricultural Research Centre (CRA-W), Valorisation of Agricultural Products Department, Chaussée de Namur n°24, 5030 Gembloux, Belgium

MID-IR MILK & Melamine → 250 ppm

**NIR SOYAMEAL & Melamine → 1000 ppm
(60 samples at 0.1 = 4 misses)**

Rapid and Non-destructive Mycotoxin Assay with NIRS, *Russel Wilkie* (ICNIR2005, Auckland)





Virtual Issue: [Papers Presented at NIR-2015, October 2015, Foz do Iguassu, Brazil](#)

LOCAL regression algorithm improves near infrared spectroscopy predictions when the target constituent evolves in breeding populations

F. Davrieux,^{a,*} D. Dufour,^{b,e} P. Dardenne,^c J. Belalcazar,^d M. Pizarro,^d J. Luna,^d L. Londoño,^e A. Jaramillo,^e T. Sanchez,^d N. Morante,^d F. Calle,^d L.A. Becerra Lopez-Lavalle^d and H. Ceballos^d

carotenoids content of cassava roots

TCC values ranged from 0.11 $\mu\text{g g}^{-1}$ to 29.0 $\mu\text{g g}^{-1}$ (ppm)

>6000 samples and cross year validation

MIXTURE DESIGN

- ~~a. 1 pure sample~~
- ~~b. 1 contaminant -> 20 samples by mixing at # %~~

Collect real samples >>

Collect contaminant from different origins if possible

Only use **one** # at a given %

	Contaminant		
SPL	a	b	c
1	1a5		
2		2b10	
3			1c15
4			4c5
5	5a10		
6		6b15	
.			
.			
n			
1		1b5	
2			2c10
3	3a15		
4		4b10	
5			5c5
6	6a5		
.			
.			
n			

CONCLUSION LOD

**When $Y < 0.1$ %, be sure what you analyze is
(significantly) present in the spectra;
Look at the ratio absorptivity/noise**

**Analytes < 0.1 % can be well predicted and provide
useful results
But these analytes are likely correlated with something
else into the matrix.**

**For powders with separated particles,
Hyperspectral Imaging can improve the LOD significantly
→ ppm ?**

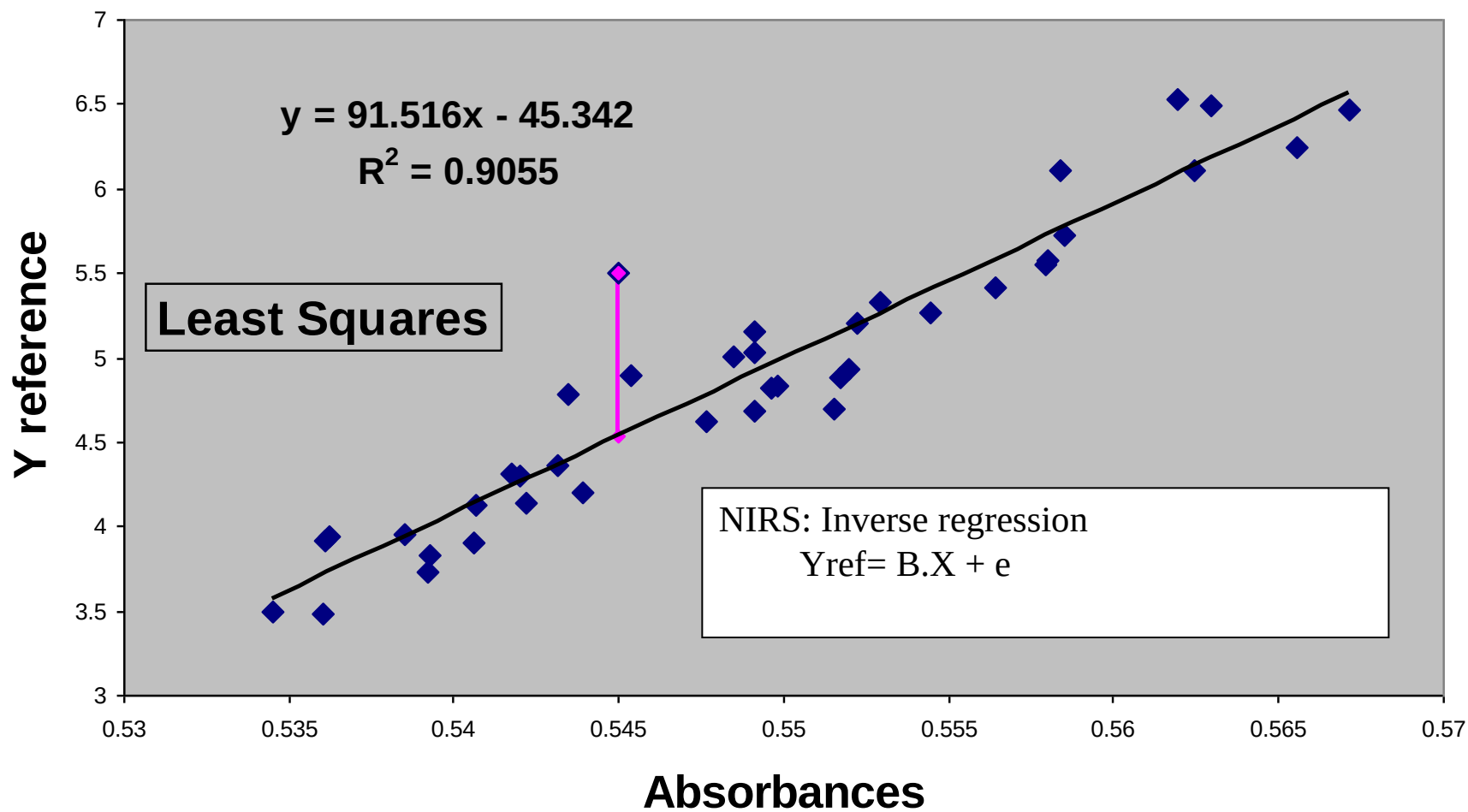
2

UNCERTAINTY

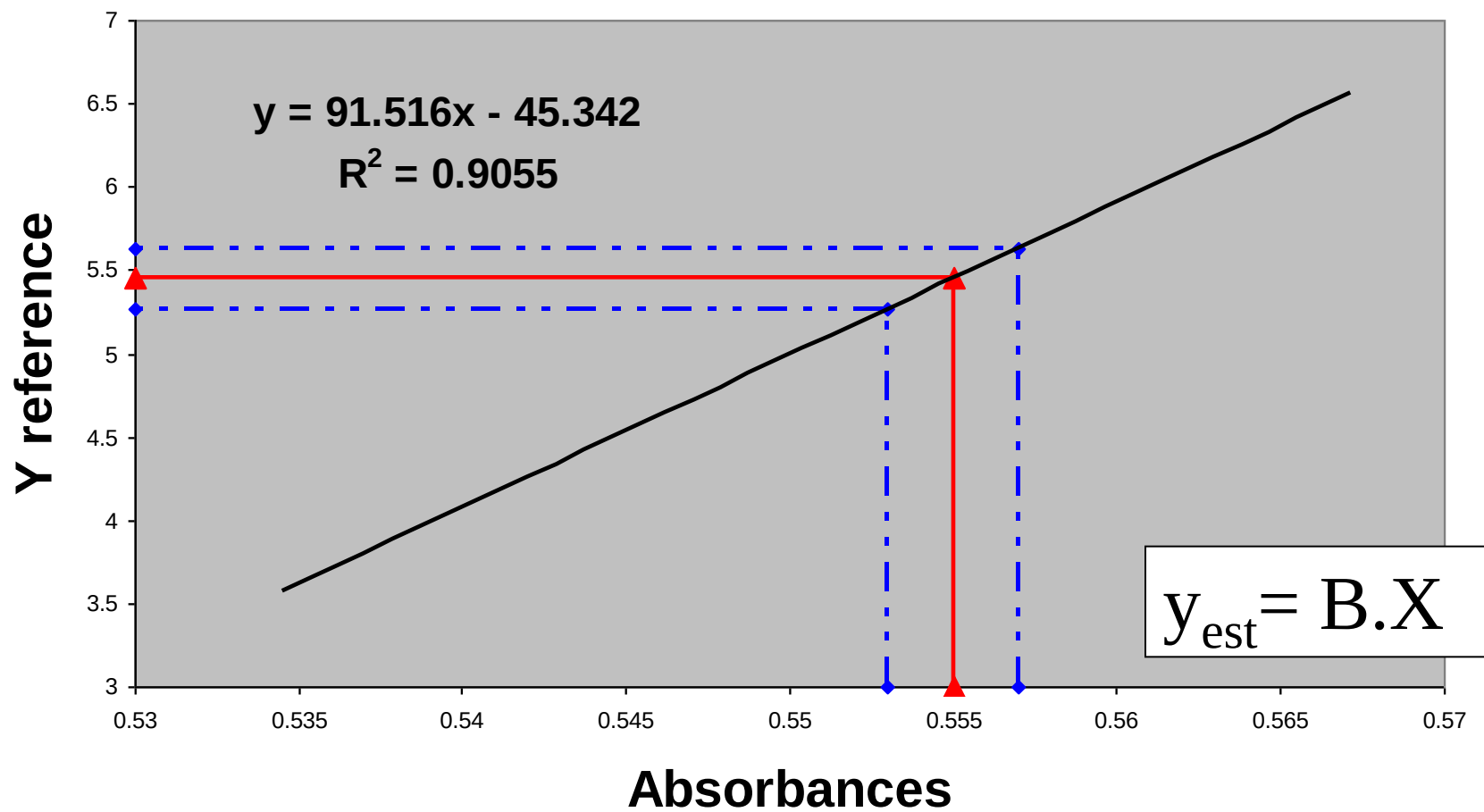
$$s(\hat{y}_i - y_i)?$$

uncertainty

CALIBRATION



PREDICTION

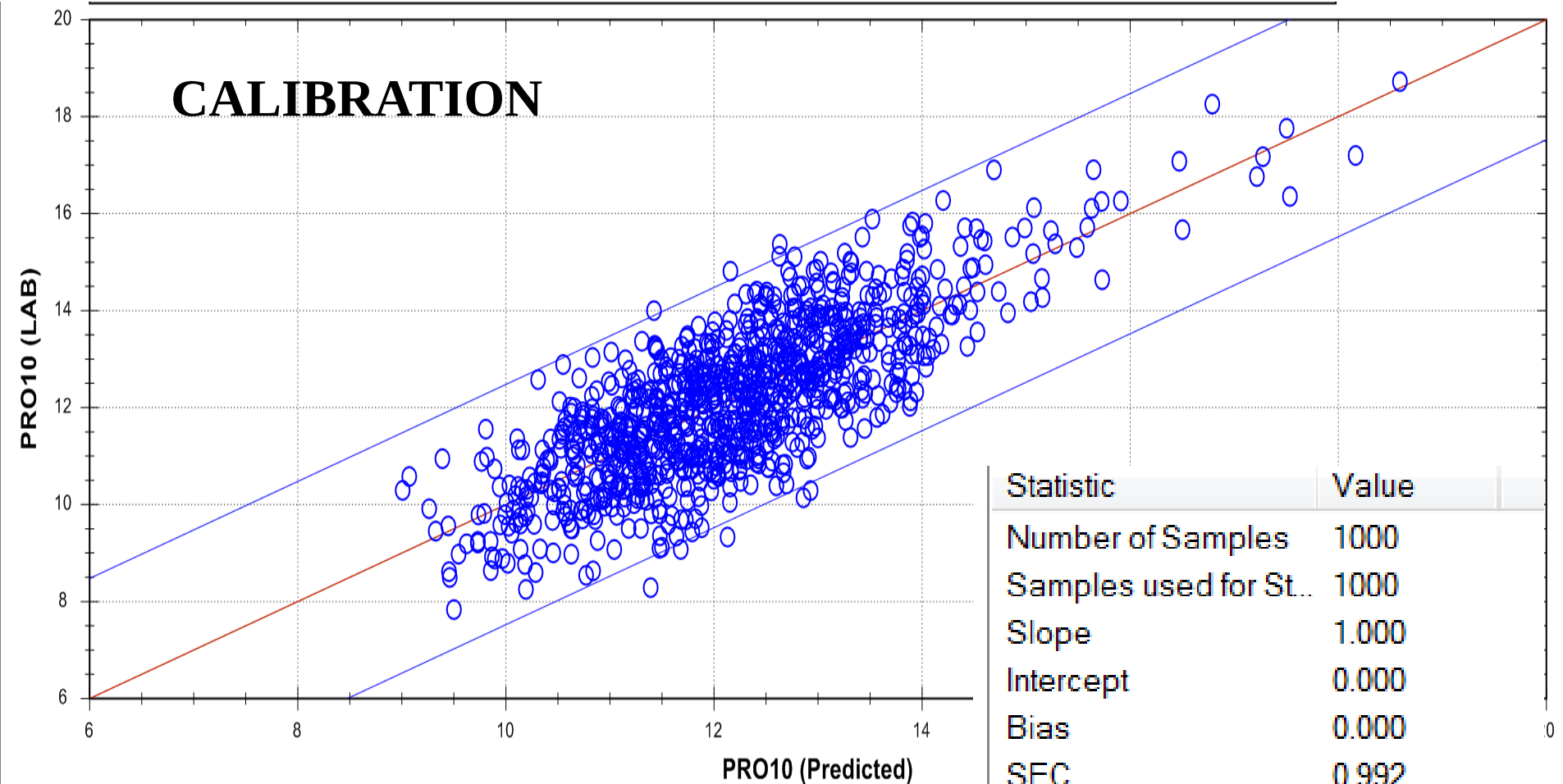


2000 spectra of ground wheat

Spilt $\frac{1}{2}$ -> CAL and VAL

CAL y values are modified by a vector of Gaussian noise of mean =0 and sd of 0.1, 0.2, ...1.0, ..1.5

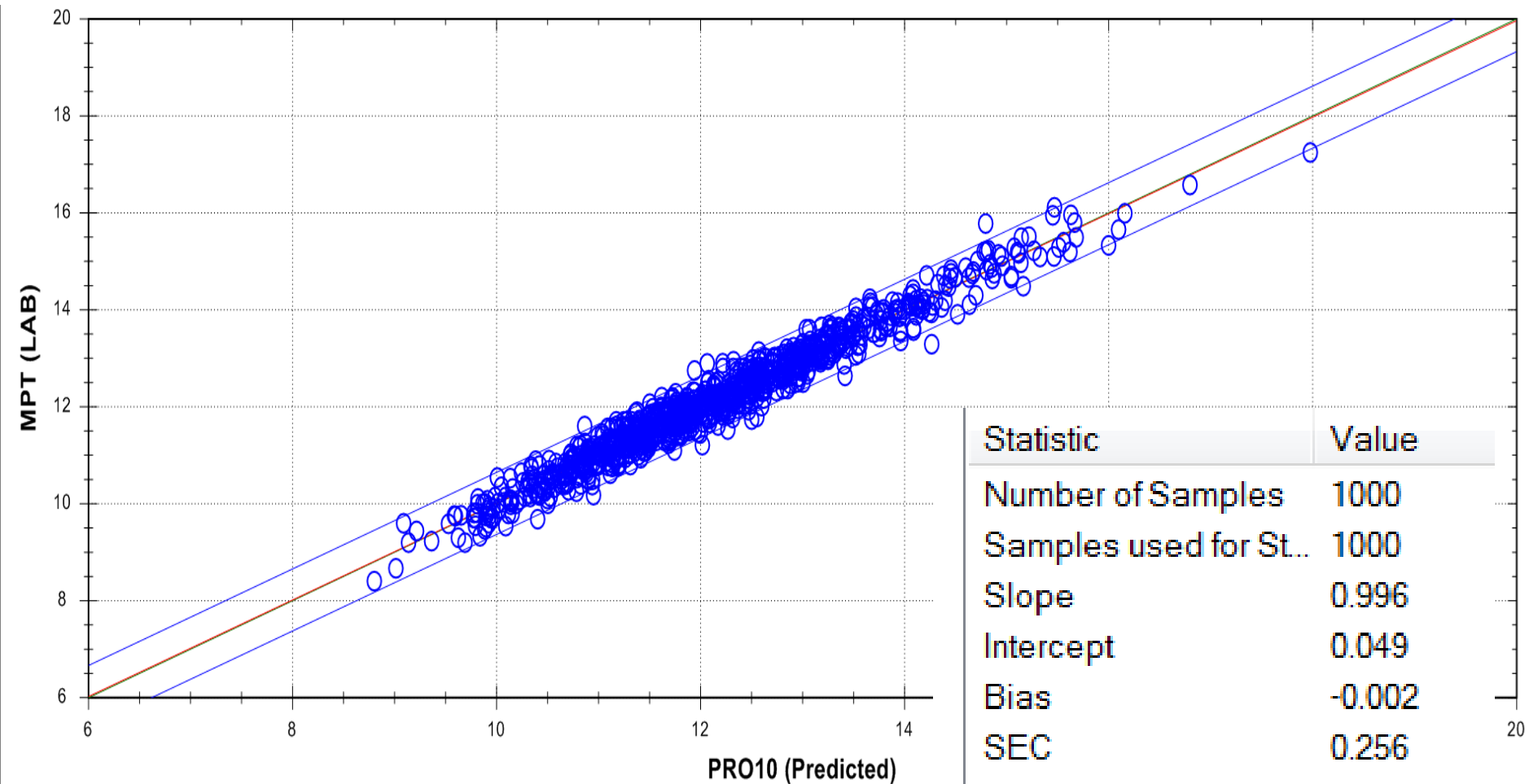
CALIBRATION



Y modified with noise $N(0,1)$

mean = 0

sd = 1

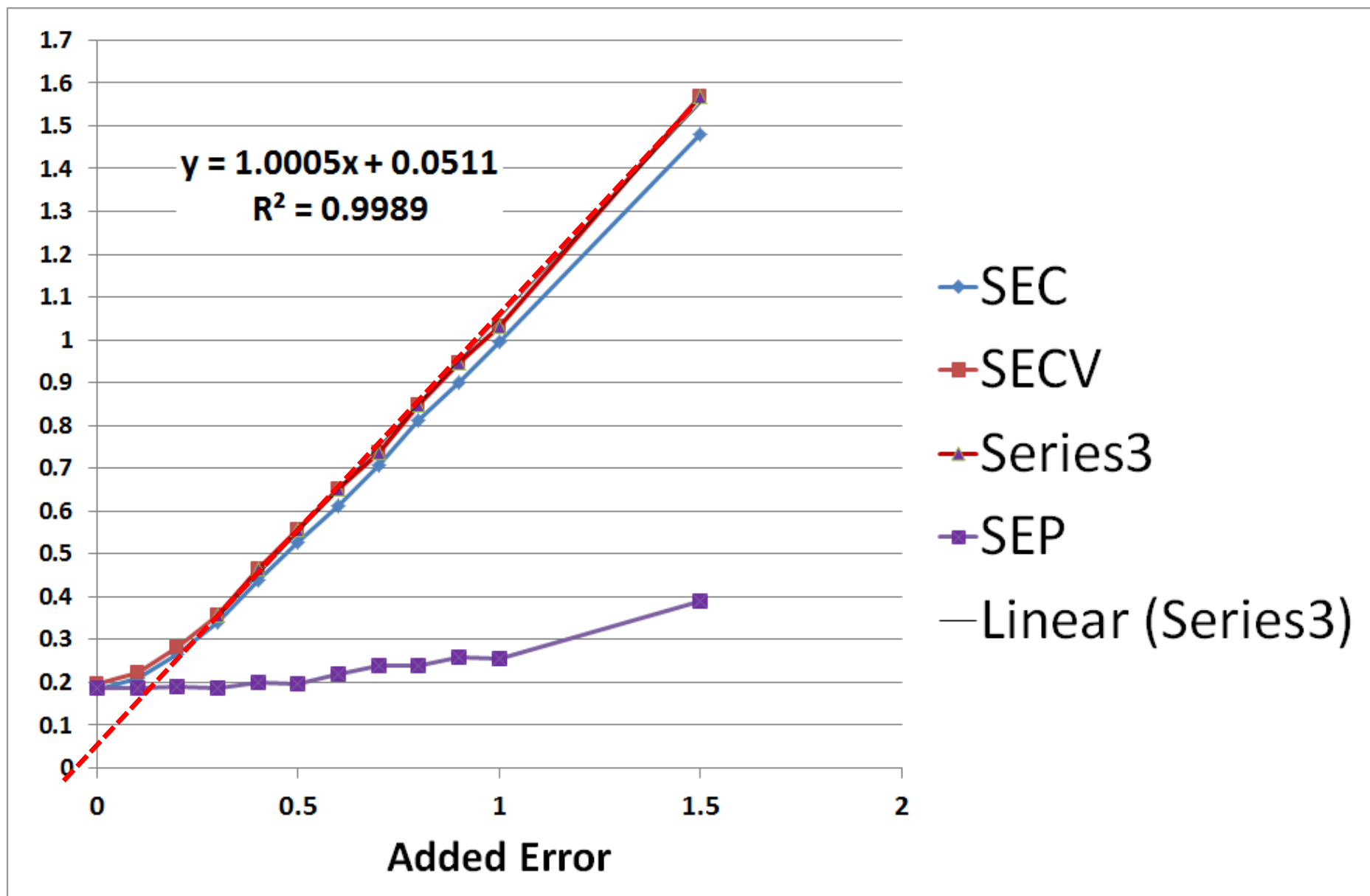


TEST SET N= 1000

Statistic	Value
Number of Samples	1000
Samples used for St...	1000
Slope	0.996
Intercept	0.049
Bias	-0.002
SEC	0.256
SEP	0.256
SEP(C)	0.256
RSQ	0.960
Predicted Average	12.150
Actual Average	12.148
Predicted SD	1.268
Actual SD	1.268

Added

Error	SECV	SEP
0.0	0.20	0.19
0.1	0.22	0.19
0.2	0.28	0.19
0.3	0.36	0.19
0.4	0.47	0.20
0.5	0.56	0.20
0.6	0.65	0.22
0.7	0.74	0.24
0.8	0.85	0.24
0.9	0.95	0.26
1.0	1.03	0.26
1.5	1.57	0.39



Uncertainty of the NIR analyses

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

Faber and Bro, *Chemom., Intell. Lab. Syst.* 61, 133 (2002)

Fernandez Pierna & al., *Chemom., Intell. Lab. Syst.* 65, 281 (2003)

[https://doi.org/10.1016/S0169-7439\(02\)00139-9](https://doi.org/10.1016/S0169-7439(02)00139-9)

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

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

BIPEA 02/2017
Blé tendre

Critère / Criterion	Unités / Unit	X	u _x	s* _x	p _x
HECT01	kg.hl ⁻¹	80,7	0,0	0,1	10
EAUB01	%	12,76	0,01	0,03	14
EAUA01	%	12,76	0,01	0,03	14
PROT01	%	12,32	0,03	0,17	68

An example:

Protein in wheat: SEL = 0,17

SEP_{observed} = 0,23

SEP_{actual} = SQRT(0,23² – 0,17²) = 0,15



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2 FIGURES OF MERIT: RMSEP SEL

Original Article

Tutorial: Items to be included in a report on a near infrared spectroscopy project

Phil Williams¹, Pierre Dardenne² and Peter Flinn³

What is the **MOST** important in a model ?

Not the stats : sec, sep, R2,... = gauges

B coefficients = engine

$$\hat{Y} = X.b$$

$$n.1 = (n.m) * (m.1)$$

CONCLUSION UNCERTAINTY

**In NIR applications, NIR values are more accurate than it appears
and sometimes better than the reference method ones.**

But it is not easy to prove it!

Do not try to obtain the smallest SEC (outliers)

**Just try to compute stable Bcoefficients from spectra
containing the expected future variation.**

Chimiométrie 2018
30 – 31 Janvier 2018



<https://chemom2018.sciencesconf.org/resource/page/id/5>

CHALLENGE

dardennepaj@gmail.com

Fichiers à télécharger :

- **Description du Challenge :** [Challenge 2018](#)
- **Fichiers CSV :** [CAL / VAL \(2018\)](#)

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Association

Réseau Scientifique de Spectroscopie
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S'identifier o Inscription

■ 18ÈMES RENCONTRES

What is HelioSPIR ?

Merci bramin p'o m'awès choutè