Détection de spectres anormaux \ atypiques test de conformité de produits

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Food and Feed Quality Unit

Wallonie recherche CRA-W

The context

Quality control and assurance

Ensuring an acceptable level of food/feed quality and safety is necessary to provide adequate protection for consumers and to facilitate trade.

This can be achieved by implementing and monitoring **quality assurance** measures along the entire food/feed chain - **from the receipt of the raw materials** (primary products and other ingredients) **to the shipping and marketing of the final products to the consumers** - when it is appropriate and when it is possible. Everyone involved with food/feed, **from the farmer to the consumer**, shares in the responsibilities to keep the food/feed supply safe by taking the necessary precautions to keep food/feed protected from hazards that can increase human/animal health risks.

Food and Agriculture Organization of the United Nations

The context

Industry

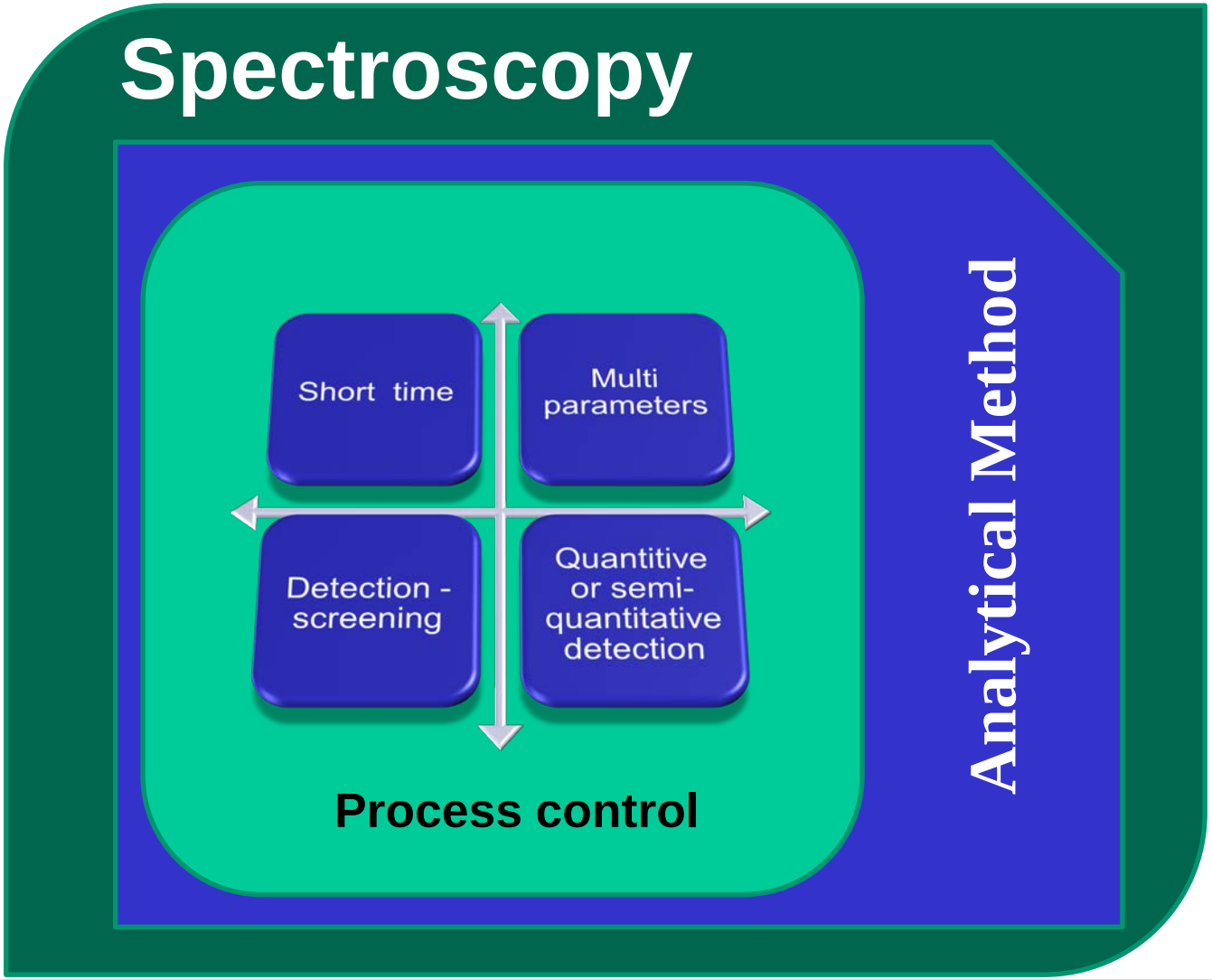
In developing countries, the Agrofood/feed industry is in the process of rapid integration.
Medium and large scale groups are expanding production capacities

More serious competition!

Food and feed industries need to distinguish themselves by suppling a final quality product. For this, quality control analysis should be performed, not only in the final product but, mainly at the entrance of the production chain when the raw material reaches the industry.

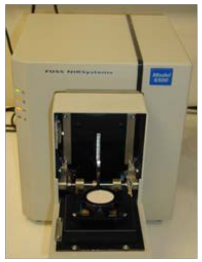
The context

Need of rapid methods

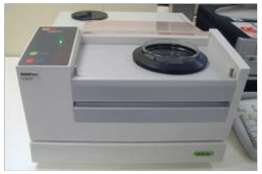


The context

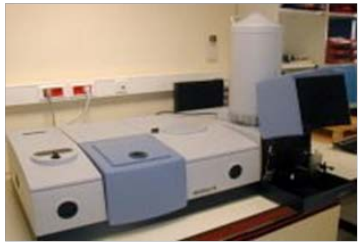
Vibrational Spectroscopy



Near infrared spectroscopy



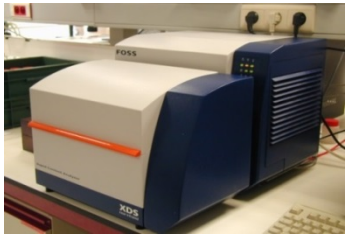
Raman and mid-infrared spectroscopy

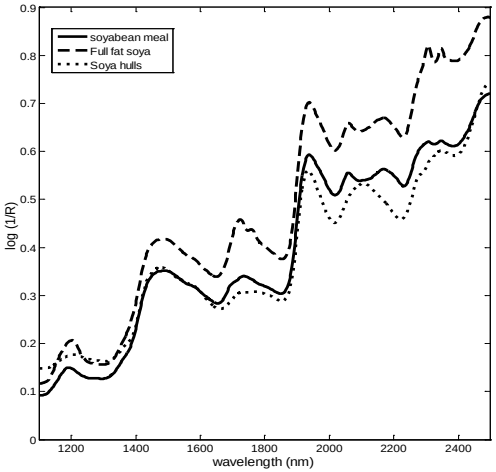


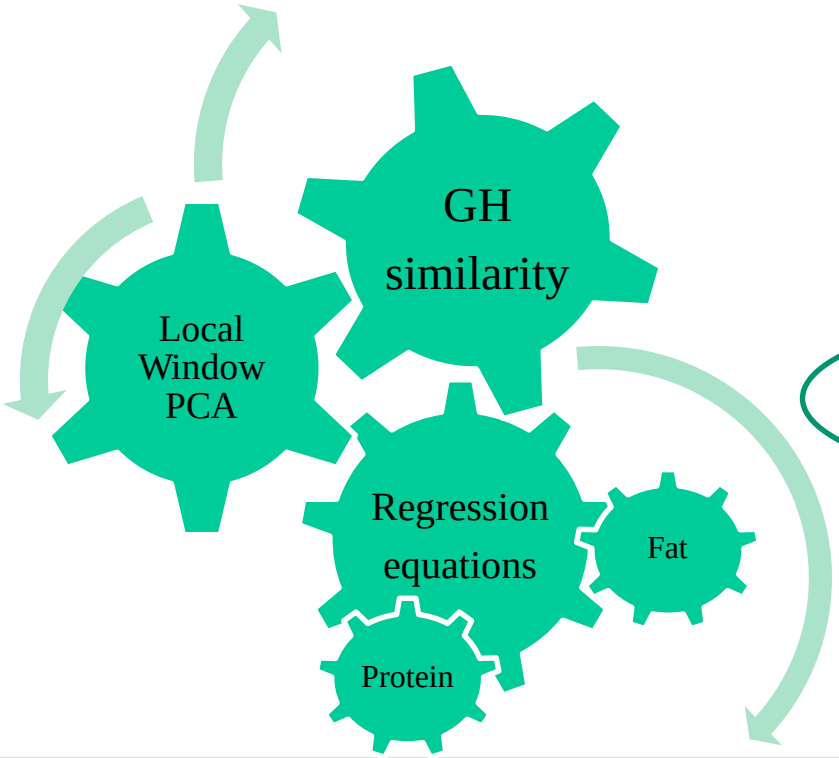
Hyperspectral Imaging

The aim

NIR analysis & chemometrics procedure



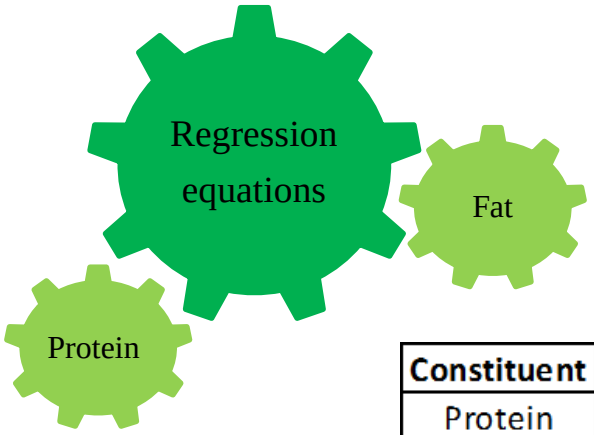




Several criteria

Procedure

NIR analysis & chemometrics



PLS models

Constituent	N	Mean	SD	SEC	RSQ	SECV
Protein	8610	46.62	1.93	0.68	0.88	0.68
Fat	5026	1.88	1.59	0.25	0.98	0.25

Soybean meal models from provimi
shaping tomorrow's nutrition

$$e = \sum_{k=1}^{m} (X_{\text{orig}_k} - X_{\text{pred}_k})^2$$

$$F_{\text{unk}} = n \frac{\left(\sum_{k=1}^{m} e_{\text{unk},k}^2\right)}{\left(\sum_{i=1}^{m}\sum_{k=1}^{m} e_{\text{cal},k}^2\right)}$$

where n is the number of calibration samples, m the number of wavelengths and e_{cal} and e_{unk} the spectral residuals for the calibration set and unknown sample respectively.

Haaland & Thomas, 1988

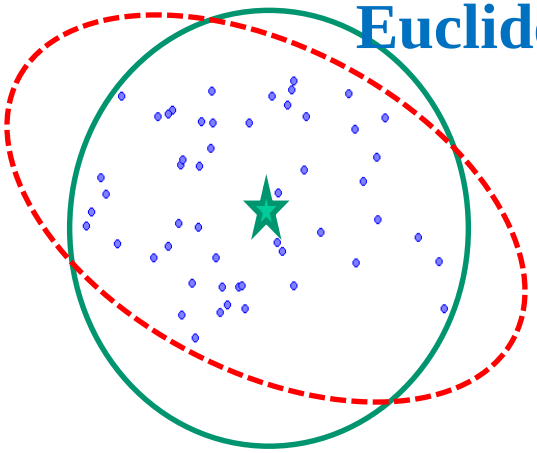
Procedure

NIR analysis & chemometrics

The Global H (GH) criteria is a modification of the Mahalanobis distance of each sample from the average spectrum. This distance takes into account the correlation of the data set.

$$GH = \frac{H^2}{f} = (S_i - \bar{S}) \left(\frac{(S_i - \bar{S})'(S_i - \bar{S})}{n-1} \right) (S_i - \bar{S})'$$

where S is the $n \times f$ matrix of training samples scores with n the number of samples and f the number of terms.



Euclidean

Mahalanobis

GH value < 3 will guarantee homogeneous spectra

GH value > 3 will guarantee that the spectra are a result of random chance and hence are most likely to have outliers

Procedure

NIR analysis & chemometrics

Local Window Principal Component Analysis (LWPCA)

ELSEVIER

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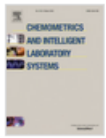


Use of a multivariate moving window PCA for the untargeted detection of contaminants in agro-food products, as exemplified by the detection of melamine levels in milk using vibrational spectroscopy ☆

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

Procedure

Local discrimination modelling

Workflow of LWPCA

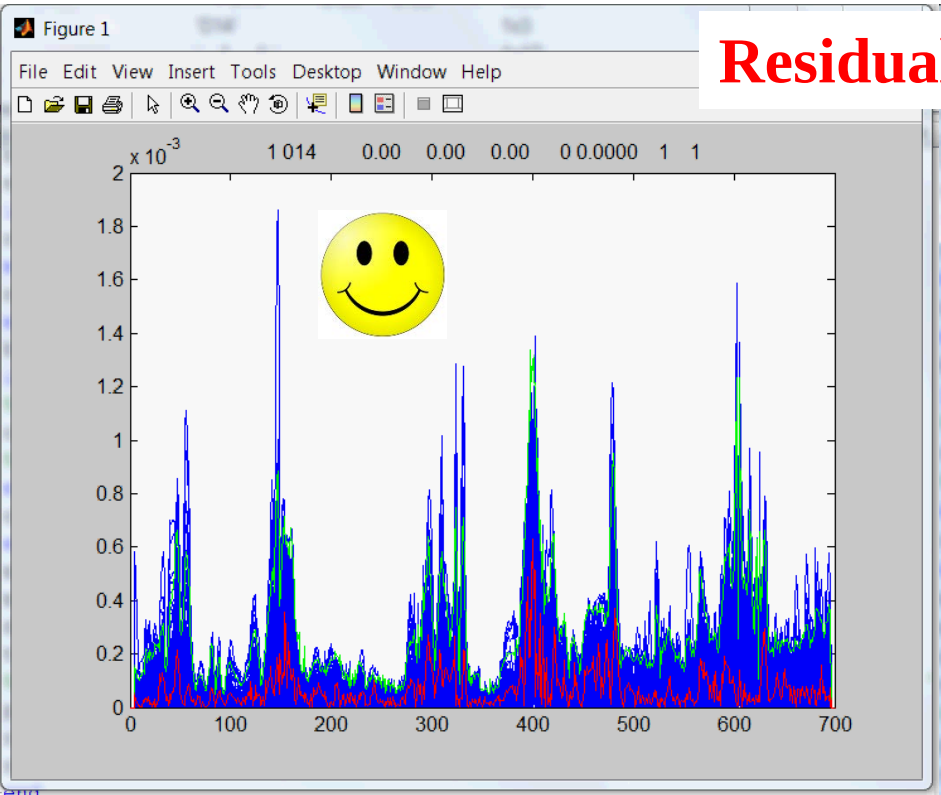
1. Set up a "clean" set = **reference** set
2. For each unknown new spectrum, **Select k** closest spectra from the clean set based on correlation
3. Build a **PCA** model from the selected spectra for each window along the wavelength range
4. Compute the **residuals limits** of the PCA models
5. Apply the PCA models to **project** the unknown new spectrum
6. Compute the **residuals** of the projected spectrum
7. **Check if these residuals** are within the PCA residual limits

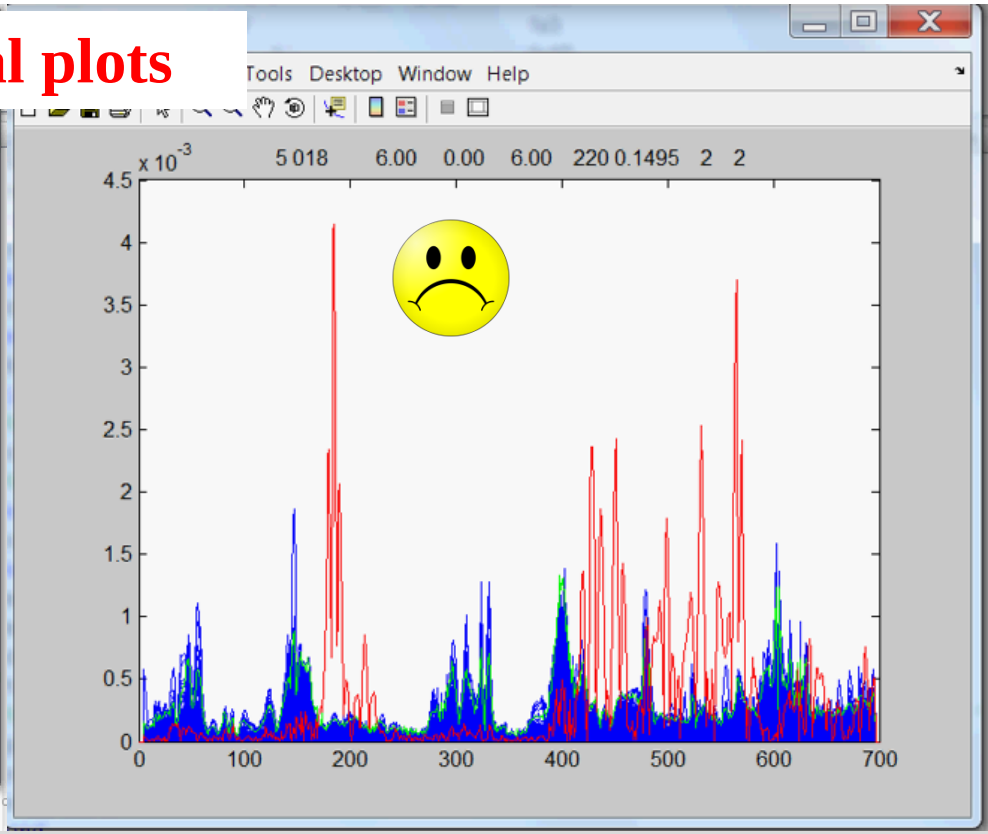
Procedure

NIR analysis & chemometrics

Residuals are used to build thresholds to be applied to the residuals of the samples to be predicted.

Residual plots





[ConfMatrix,crat,mat2]=confumatr(cm(:,1),cm(:,2))

Study case 1

Feed contamination

Study case 1

Feed contamination

- Contamination by **microorganism** and **animal by-products** (salmonella, animal proteins…)
- Contamination by persistent **organic pollutants** and **toxic metals** (melamine, dioxins, brominated flame retardants…)
- Natural **toxins** in animal feed (mycotoxins, plant toxins…)
- **Veterinary medicinal products** in feeds (antibiotics, …)
- Risks from **emerging technologies** (GM crops, biofuel and food industry by-products…)

Study case 1
Feed contamination

Targeted and Untargeted early detection of contaminants

Near Infrared Spectroscopy
+
Chemometrics

Vincent Baeten, Philippe Vermeulen, Juan Antonio Fernández Pierna and Pierre Dardenne
Walloon Agricultural Research Centre (CRA-W), Belgium

From targeted to untargeted detection of contaminants and foreign bodies in food and feed using NIR spectroscopy

For decades, Near InfraRed Spectroscopy (NIRS) has been widely used in the food and feed industry in order to implement rapid, relat
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function of frequency r
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780-2500 nm (12820 –

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NIR fingerprint screening for early control of non-conformity at feed mills

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Study case 1
Feed contamination

The aim of this work is to propose a procedure based on Near Infrared (NIR) spectroscopy and Chemometrics in order to characterize a typical feed product (soybean meal) as well as to detect the presence of any possible contaminant.

Laboratory level

- Melamine
- Whey

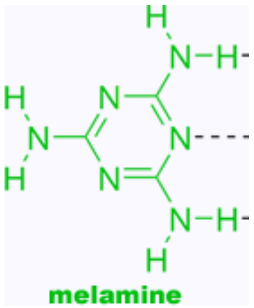
Feed plant level

- Whey

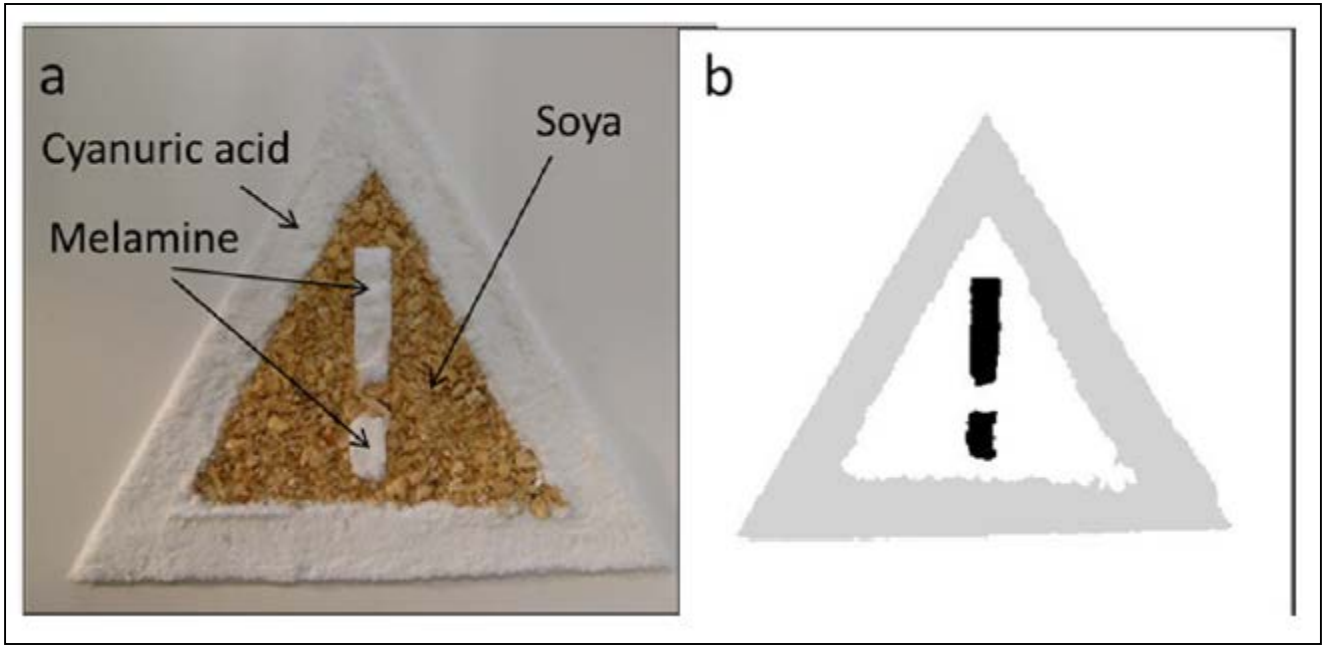
Study case 1

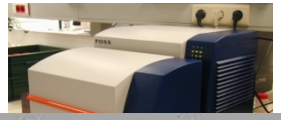
Melamine in soybean meal

Rapid
detection of any modification
by non-authorized additives like
Melamine



❑ **NIR/NIR Hyperspectral imaging and chemometrics make it possible to compare efficiently suspected spectra of new samples and detect melamine in feed.**


a
Cyanuric acid
Melamine
Soya
b



Sample	Melamine (%)	Cyan acid (%)	Total (%)	F ratio Protein	Conclusion prot (C if >8.42)		F ratio Fat	Conclusion fat (C if>8.54)		GH	Conclusion GH (C if>3)	
1	0	0	0	1.00	NC	✓	0.87	NC	✓	0.97	NC	✓
2	1.94	0	1.94	60.46	C	✓	48.30	C	✓	13.42	C	✓
3	2.95	0	2.95	42.48	C	✓	34.15	C	✓	9.73	C	✓
4	5.05	0	5.05	313.00	C	✓	248.59	C	✓	63.85	C	✓
5	6	0	6	503.22	C	✓	399.55	C	✓	101.12	C	✓
6	0	0.53	0.53	1.67	NC	X	1.37	NC	X	1.52	NC	X
7	0	1.95	1.95	13.15	C	✓	10.14	C	✓	11.19	C	✓
8	0	4.54	4.54	57.48	C	✓	44.02	C	✓	47.36	C	✓
27	0	0	0	1.60	NC	✓	1.47	NC	✓	1.96	NC	✓
28	0.53	0	0.53	68.65	C	✓	55.45	C	✓	18.06	C	✓
29	1.97	0	1.97	2251.73	C	✓	1773.88	C	✓	497.58	C	✓
30	4.48	0	4.48	3618.86	C	✓	2853.95	C	✓	805.04	C	✓
31	6.03	0	6.03	7068.65	C	✓	5555.57	C	✓	1575.18	C	✓
32	0	1.96	1.96	583.72	C	✓	457.02	C	✓	512.59	C	✓
33	0	2.98	2.98	466.13	C	✓	368.11	C	✓	400.75	C	✓
34	0	4.96	4.96	742.44	C	✓	583.42	C	✓	648.05	C	✓
35	0	6.04	6.04	1793.01	C	✓	1404.16	C	✓	1624.22	C	✓
25	2	2.01	4.01	322.73	C	✓	257.55	C	✓	115.67	C	✓
26	1.48	4.46	5.94	339.15	C	✓	270.13	C	✓	216.16	C	✓
27	0	0	0	1.60	NC	✓	1.47	NC	✓	1.96	NC	✓
28	0.53	0	0.53	68.65	C	✓	55.45	C	✓	18.06	C	✓
29	1.97	0	1.97	2251.73	C	✓	1773.88	C	✓	497.58	C	✓
30	4.48	0	4.48	3618.86	C	✓	2853.95	C	✓	805.04	C	✓
31	6.03	0	6.03	7068.65	C	✓	5555.57	C	✓	1575.18	C	✓
32	0	1.96	1.96	583.72	C	✓	457.02	C	✓	512.59	C	✓
33	0	2.98	2.98	466.13	C	✓	368.11	C	✓	400.75	C	✓
34	0	4.96	4.96	742.44	C	✓	583.42	C	✓	648.05	C	✓
35	0	6.04	6.04	1793.01	C	✓	1404.16	C	✓	1624.22	C	✓
36	0.4	0.14	0.54	18.80	C	✓	15.88	C	✓	9.41	C	✓
37	0.55	0.53	1.08	37.27	C	✓	31.26	C	✓	19.59	C	✓
38	2.61	0.93	3.54	1481.06	C	✓	1180.04	C	✓	432.00	C	✓
39	3.73	1.2	4.93	2226.34	C	✓	1769.05	C	✓	575.96	C	✓
40	0	0	0	2.24	NC	✓	2.29	NC	✓	3.16	C	X
41	0.55	0	0.55	81.51	C	✓	64.57	C	✓	21.16	C	✓
42	0.94	0	0.94	300.01	C	✓	237.63	C	✓	69.82	C	✓
43	3.56	0	3.56	1112.48	C	✓	881.08	C	✓	244.33	C	✓
44	5.53	0	5.53	2207.28	C	✓	1745.78	C	✓	488.96	C	✓
45	0	2.54	2.54	120.56	C	✓	96.57	C	✓	105.95	C	✓
46	0	3.04	3.04	863.00	C	✓	677.97	C	✓	745.38	C	✓
47	0	4.93	4.93	1592.99	C	✓	1246.44	C	✓	1394.09	C	✓
48	0	5.55	5.55	1337.01	C	✓	1051.49	C	✓	1169.07	C	✓
49	0.41	1.09	1.5	62.33	C	✓	50.69	C	✓	39.90	C	✓
50	0.82	2.26	3.08	136.28	C	✓	110.88	C	✓	91.71	C	✓
51	2	2.01	4.01	707.29	C	✓	570.81	C	✓	375.27	C	✓
52	1.08	3.42	4.5	2415.73	C	✓	1921.24	C	✓	1784.39	C	✓
53	0	0	0	0.99	NC	✓	0.75	NC	✓	1.04	NC	✓
54	1	0	1	56.06	C	✓	44.62	C	✓	12.45	C	✓
55	1.55	0	1.55	175.90	C	✓	139.70	C	✓	37.66	C	✓
56	3.51	0	3.51	852.98	C	✓	674.66	C	✓	180.83	C	✓
57	3.98	0	3.98	917.80	C	✓	727.20	C	✓	191.04	C	✓
58	0	0.5	0.5	11.07	C	✓	8.49	NC	X	9.44	C	✓
59	0	0.98	0.98	29.42	C	✓	22.76	C	✓	24.83	C	✓
60	0	3.56	3.56	262.68	C	✓	203.71	C	✓	222.45	C	✓
61	0	5.55	5.55	543.70	C	✓	421.85	C	✓	460.37	C	✓
62	0.37	0.13	0.5	13.76	C	✓	11.15	C	✓	4.20	C	✓
63	0.37	1.11	1.48	30.22	C	✓	24.18	C	✓	19.35	C	✓
64	3.72	1.27	4.99	772.89	C	✓	616.19	C	✓	194.17	C	✓
65	1.53	4.53	6.06	426.35	C	✓	339.97	C	✓	271.17	C	✓

C: Contaminated
NC: Not contaminated

No false positives

Study case 1
Feed contamination

Lab level - whey

Sample	Whey powder (%)	F ratio Protein	Conclusion prot (C if >8.42)		F ratio Fat	Condusion fat (C if>8.54)		GH	Conclusion GH (C if>3)	
1	0	8.61	C	X	7.57	NC	✓	1.29	NC	✓
2	0.5	19.91	C	✓	16.21	C	✓	3.50	C	✓
3	1	34.41	C	✓	27.15	C	✓	5.83	C	✓
4	2	144.41	C	✓	109.25	C	✓	21.20	C	✓
5	4	233.96	C	✓	177.74	C	✓	33.01	C	✓
6	5	299.43	C	✓	226.59	C	✓	41.08	C	✓
7	100	2007.49	C	✓	1481.39	C	✓	224.81	C	✓

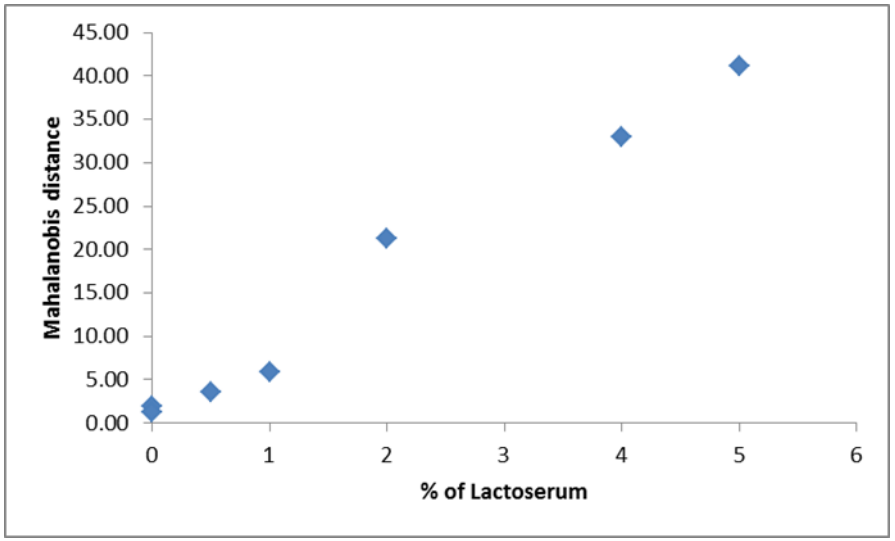
C: Contaminated
NC: Not contaminated

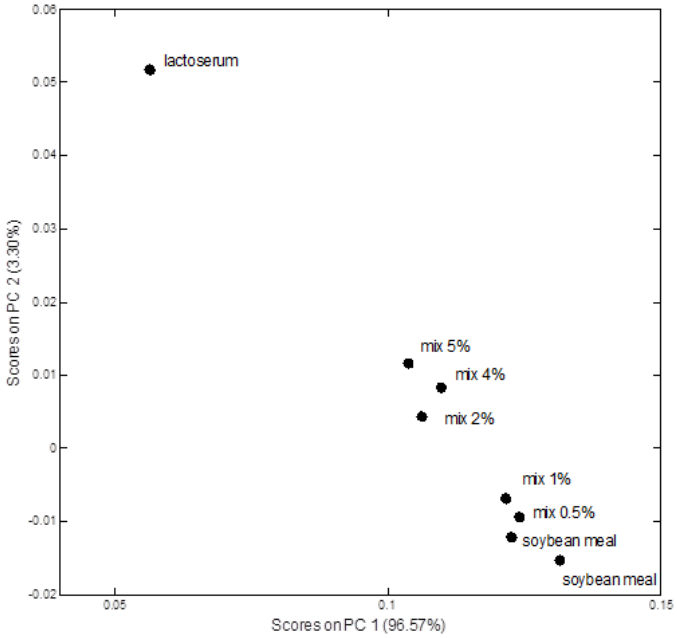
No false positives

Study case 1

Feed contamination

Lab level - whey

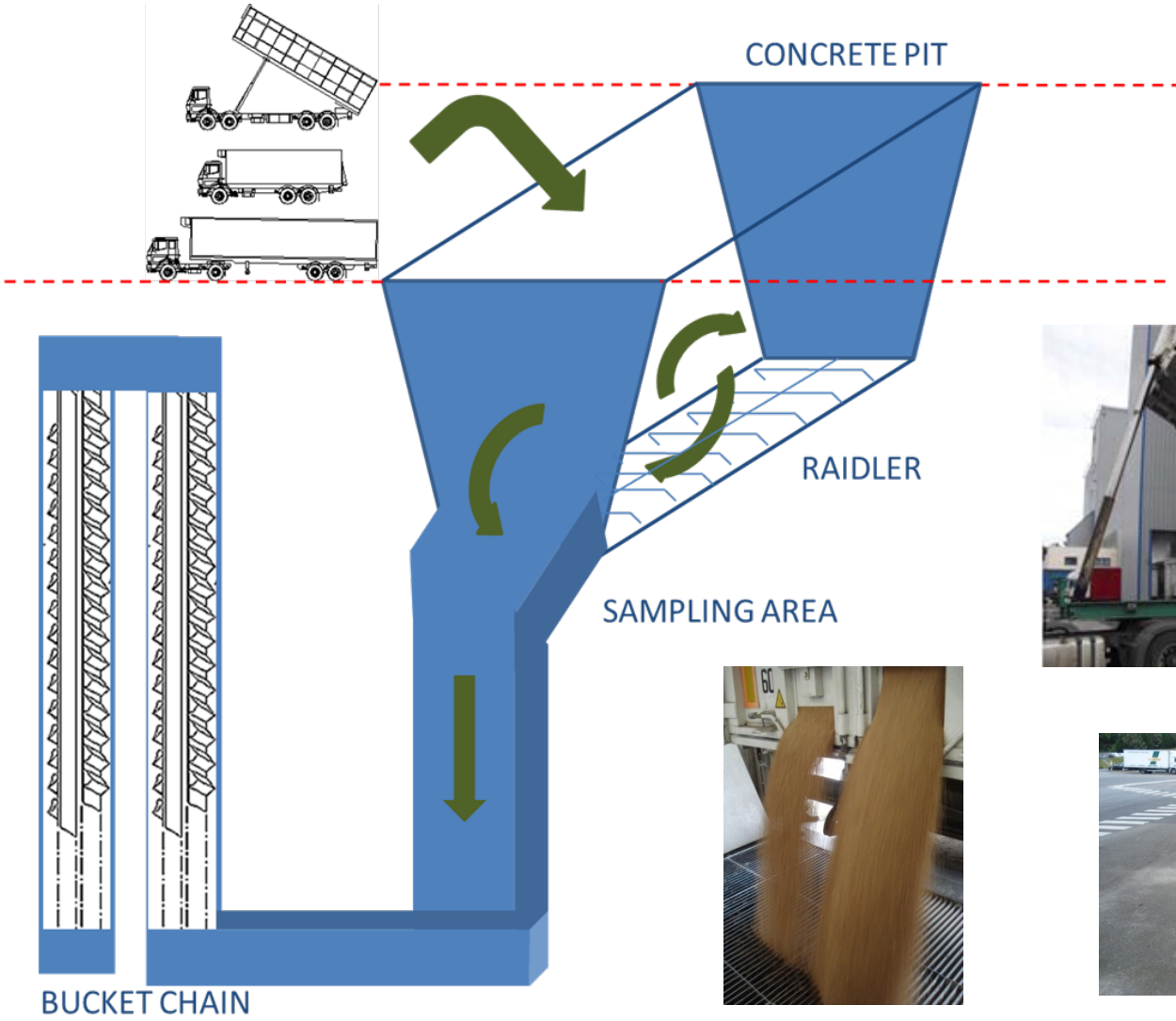




Study case 1

Feed contamination

Extension to feed mills



provimi
shaping tomorrow's nutrition

Study case 1
Feed contamination

Feed mill contamination

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SAFFE

STEP 1
Loading of 5 Tons of Soya bean directly from the truck

STEP 2
Loading of 5 Tons of Soya bean from the truck contaminated by simulating a local contamination

STEP 3
Loading of 5 Tons of Soya bean directly from the truck

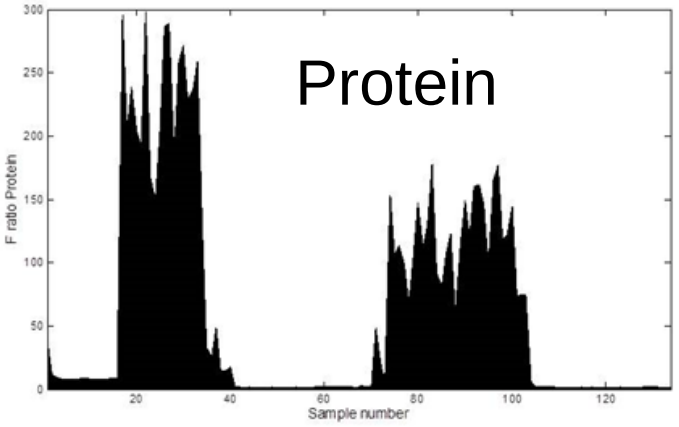
STEP 4
Loading of 5 Tons of Soya bean from the truck contaminated by mixing

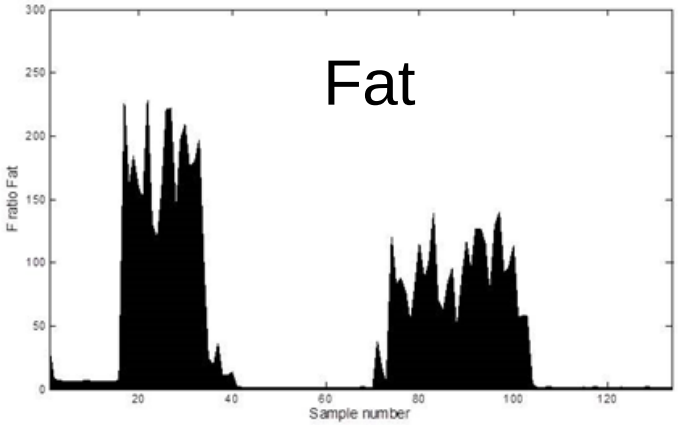
STEP 5
Emptying of the truck. No deliberate pollution done

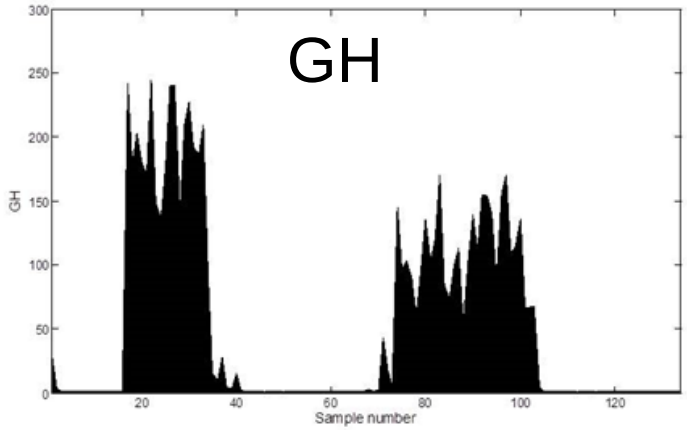
Study case 1

Feed contamination

Feed mill contamination







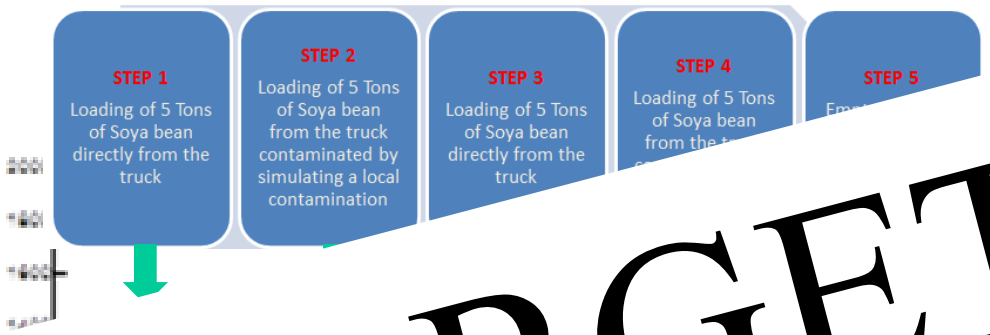
Whey – set 1

Study case 1

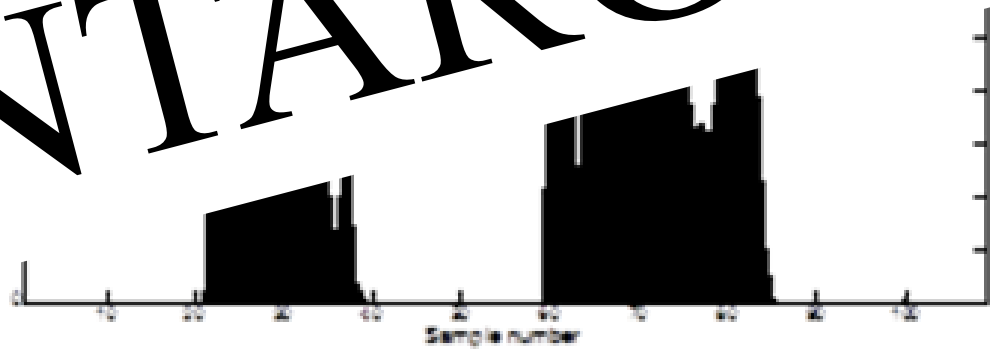
Feed contamination

Feed mill contamination

LWPCA



UNTARGETED



provimi
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SAFFO

Study case 2

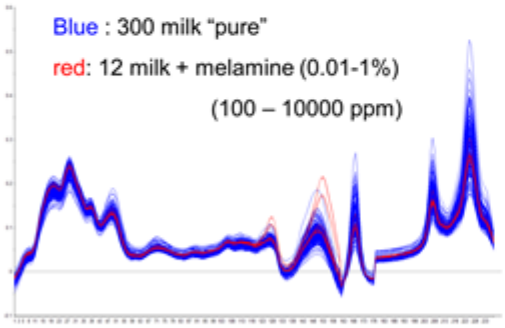
Milk contamination

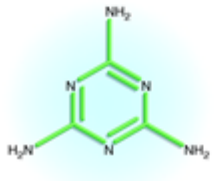
Study case 2

Milk contamination

A case study

The study selected is based on milk contaminated with melamine. Melamine (2,4,6-triamino-1,3,5-triazine) is a chemical compound rich in nitrogen, which is illegally added to food/feed to artificially elevate the protein content values of products.

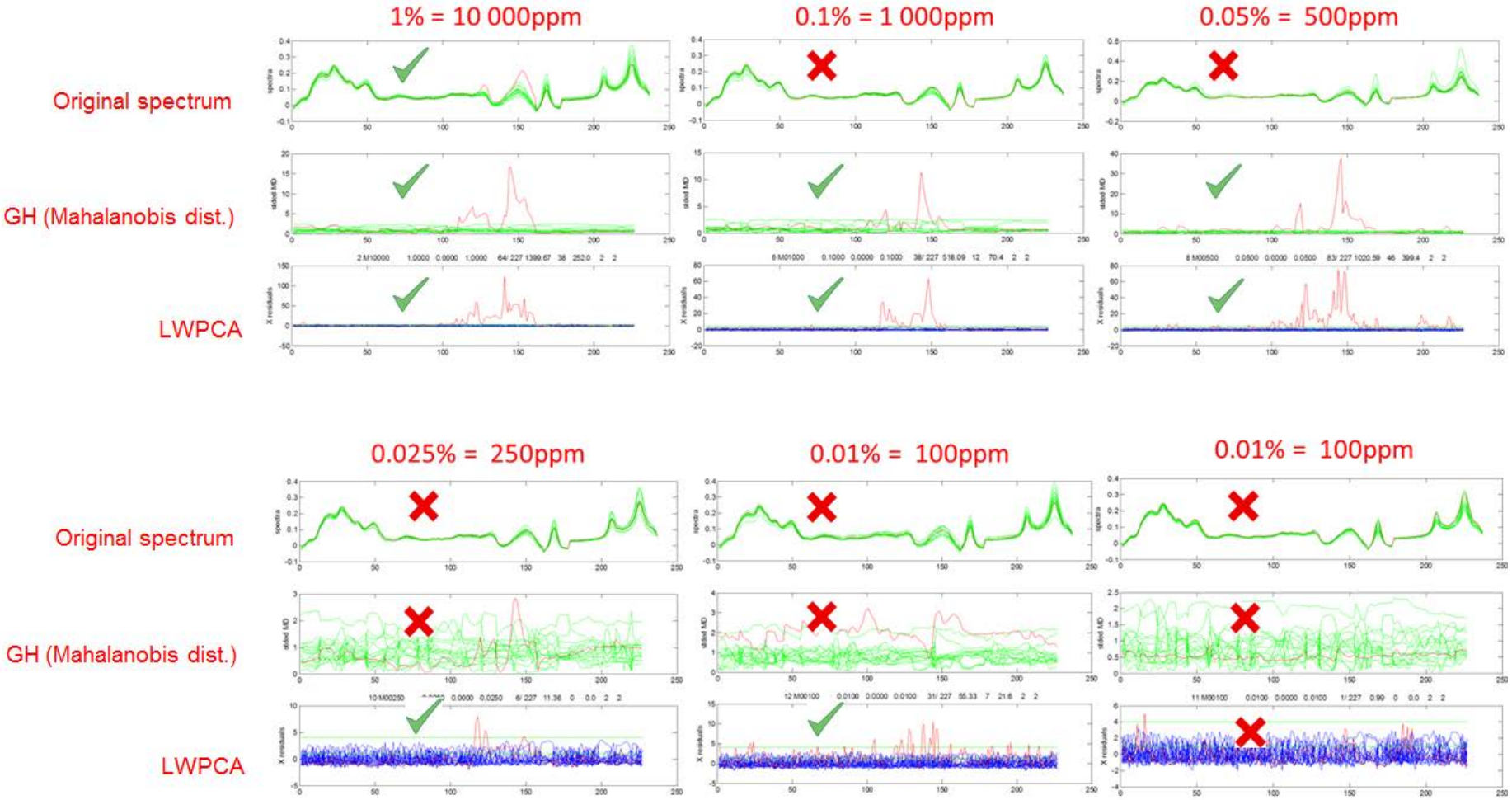




A data set consisting on 300 samples of UHT liquid milk was used as 'clean' data set. Moreover other 12 UHT liquid milk samples have been contaminated with melamine at different levels ranging from 0.01% to 1% (100 – 10000 ppm). All these samples have been measured using a Fourier transform mid-infrared (FT-MIR) spectrometer type FT 6000 (Foss, Hillerød, Denmark).

Study case 2

Milk contamination



Study case 2

Milk contamination

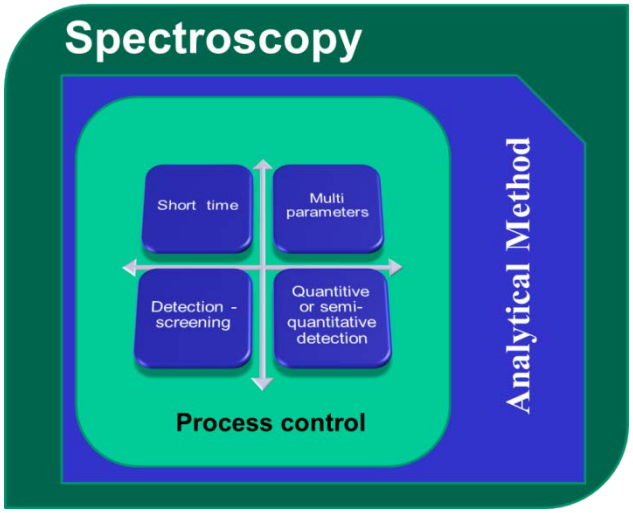
- These results show that no clear conclusion can be obtained when looking directly at the spectra.
- GH values detect abnormalities at levels higher than 500 ppm.
- LWPCA allows detecting contamination at levels up to 100 ppm; however at those levels the detection of melamine in milk becomes unstable, which is an indication that the technique has probably reached its limit of detection.

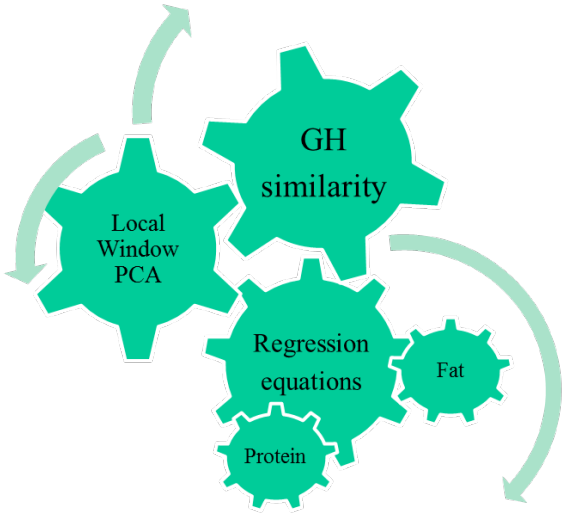
Conclusion

Local discrimination modelling

- Local moving window PCA method is proposed for the characterization of agronomical products and the detection of possible contaminants using vibrational spectroscopy.
- In the examples presented here, soybean meal and liquid UHT samples have been contaminated with melamine/whey, making them thus semi-targeted studies.
- However the method should be used as a method for the untargeted detection of abnormalities (real contamination or fraud) in the data and a previous step for further analyses.

Conclusion





NIR spectroscopy in combination with a chemometrics based protocol is a perfect tool, at laboratory and at industry levels, for:

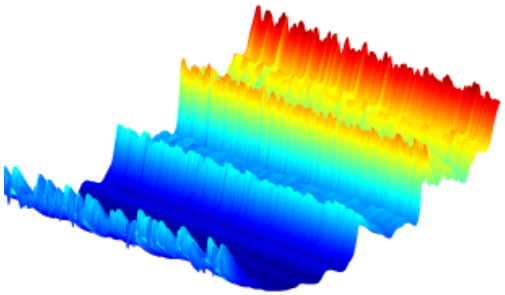
- the **characterization of food/feed materials**
- **Detection of targeted and untargeted adulteration / contamination**

More info?

Vibrational Spectroscopy and Chemometrics

Training Session

12 March–16 March 2018



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Thanks!

http://www.cra.wallonie.be/en/events/