Early detection of contaminants by Near Infrared Spectroscopy and Chemometrics
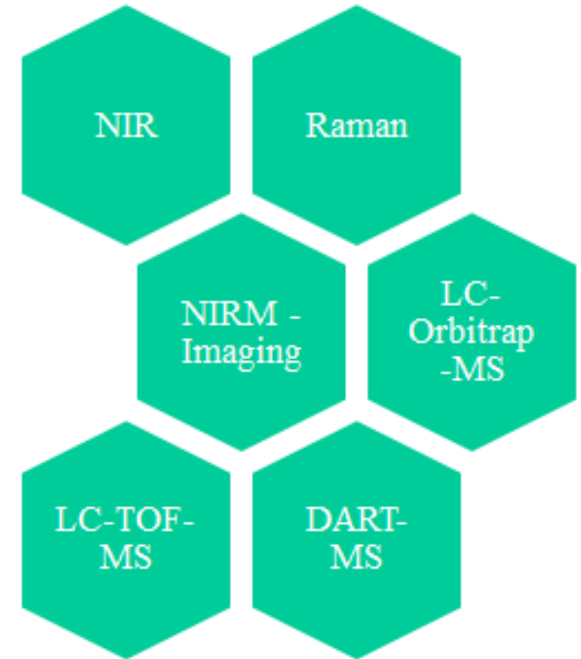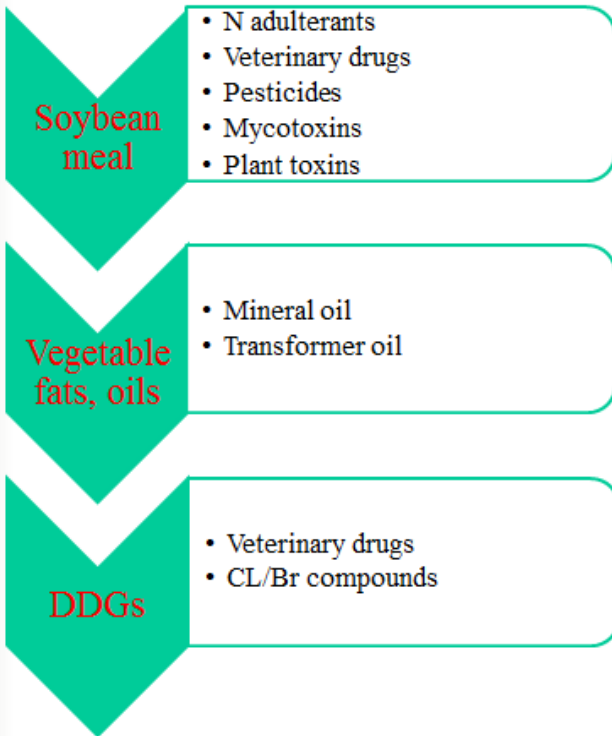
The case of melamine in Feed

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WP1
STRATEGIES FOR THE EARLY QUALITY AND SAFETY ASSURANCE IN THE FEED CHAIN

Aim of this work

Targeted and **Untargeted** early detection of contaminants

**Near Infrared Spectroscopy
+
Chemometrics**

■ Vincent Baeten, Philippe Vermeulen, Juan Antonio Femández Piema 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

Contents lists available at ScienceDirect

Food Chemistry

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FOOD CHEMISTRY

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

CrossMark

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Aim of this work

Preventing
Pet Food
Outbreaks

Aim

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

Feed plant level

Melamine

State of the art

Outcomes from melamine contamination:

- cat and dog illnesses/deaths
- front-page national/international news
- massive economic fallout
- industry changes
- new regulations & enhanced programs

Definitions

melamine   cyanuric acid

melamine + cyanuric acid = melamine cyanurate
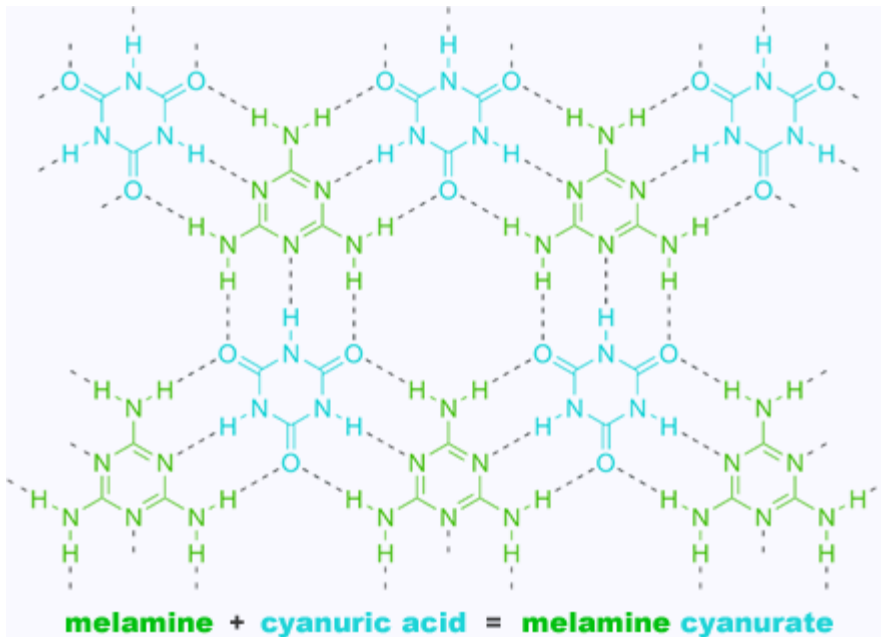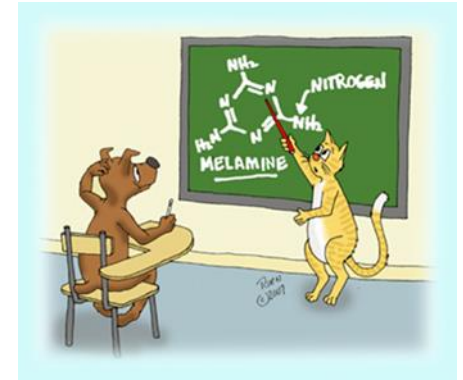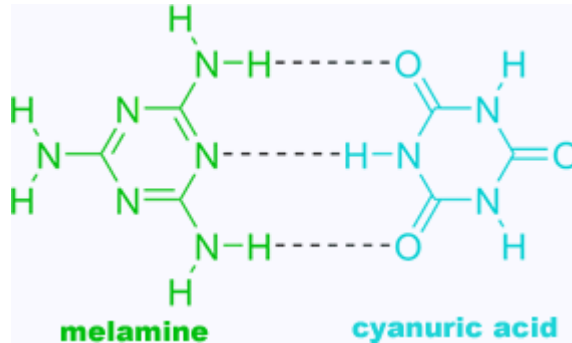
Melamine is illegally added to food/feed to artificially elevate the protein content values of products.

Melamine in Soybean meal – NIR spectroscopy
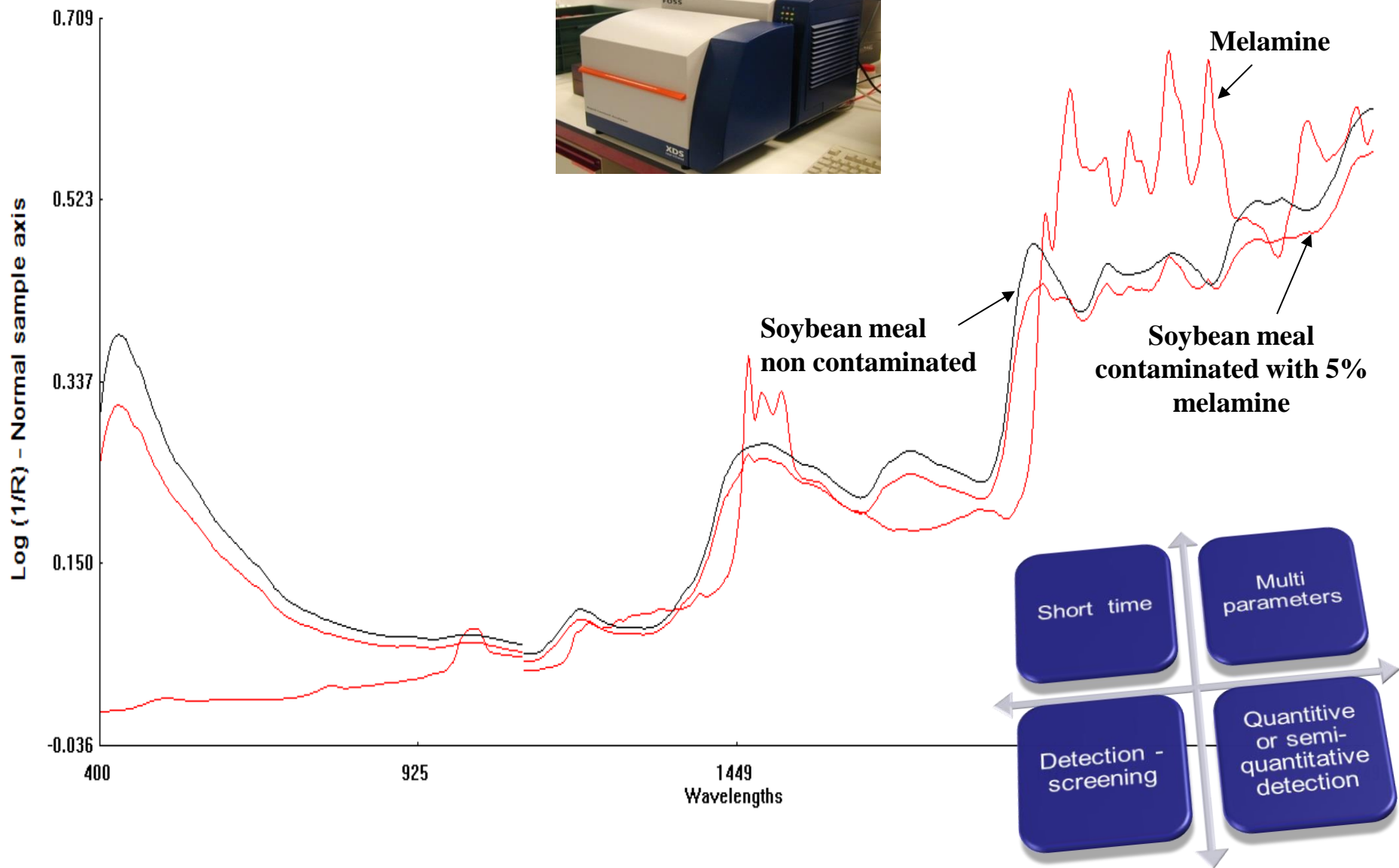
Chemometrics - procedure

GH similarity

Local Window PCA

Regression equations

Fat

Protein
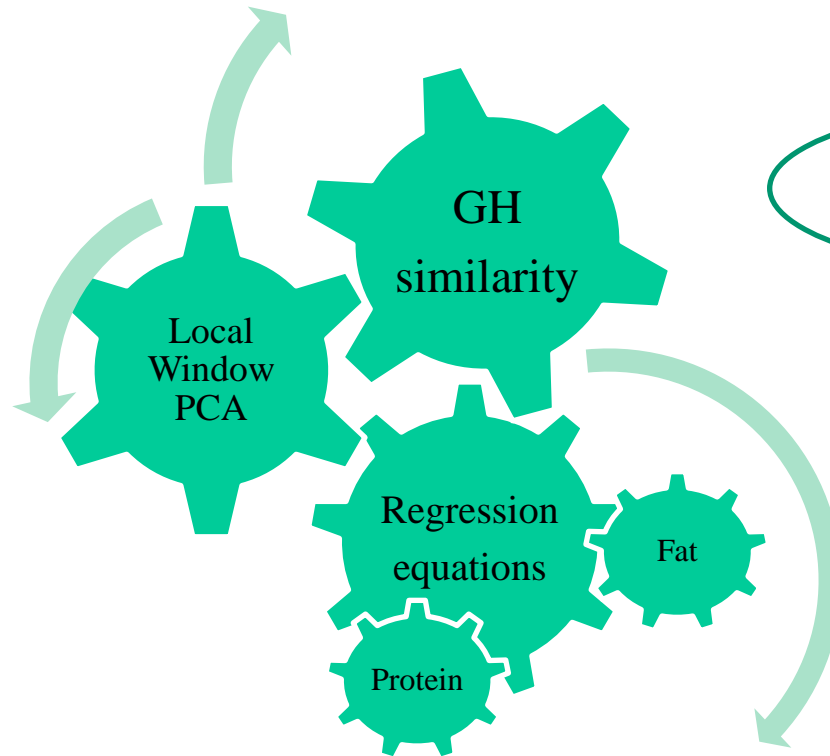
Several criteria

Local Window PCA

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

Poster 4

Local Window PCA

Melamine in milk

0.025% = 250ppm

Original spectrum
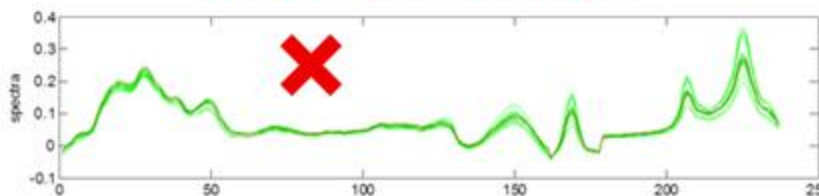
GH (Mahalanobis dist.)

LWPCA

Results – lab level – melamine in soybean

No false positives

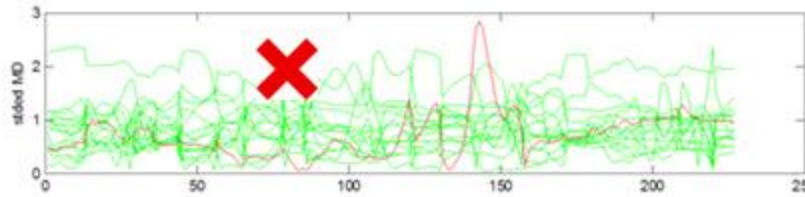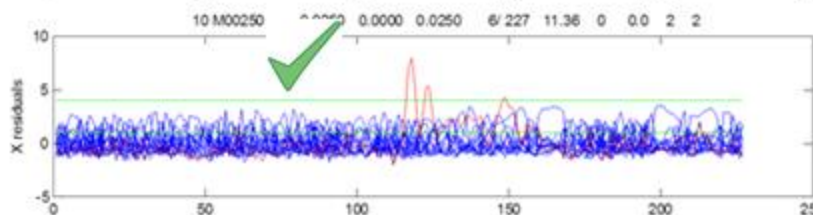| Sample	Melamine (%)	Cyan acid (%)	Total (%)	F ratio Protein	Conclusion prot (C if >8.42)		F ratio Fat	Conclusion fat (C if>8.54)		GH	Conclusion GH (C if>3)	
1	0	0	0	1.00	NC	✓	0.87	NC	✓	0.97	NC	✓
2	1.94	0	1.94	60.46	C	✓	48.30	C	✓	13.42	C	✓
3	2.95	0	2.95	42.48	C	✓	34.15	C	✓	9.73	C	✓
4	5.05	0	5.05	313.00	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	✓
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

Results

Lab level - whey

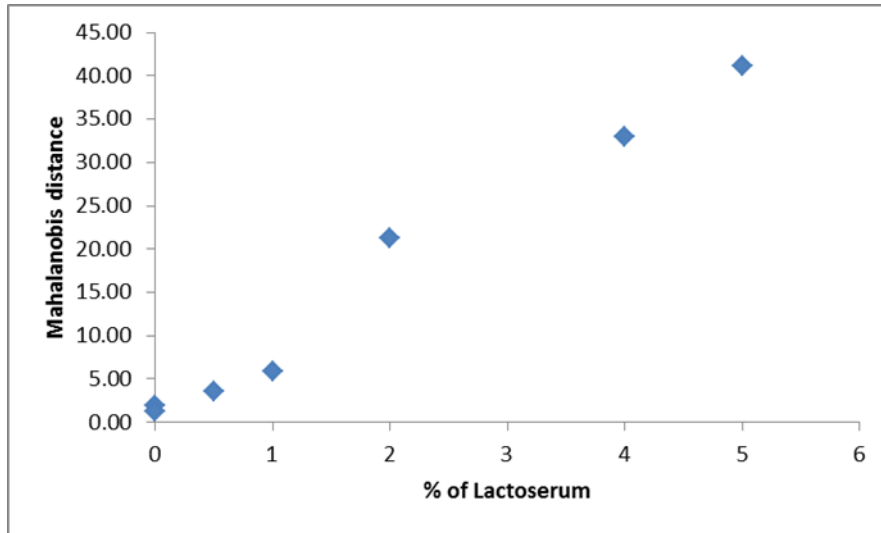| Sample	Whey powder (%)	F ratio Protein	Conclusion prot (C if >8.42)		F ratio Fat	Conclusion fat (C if>8.54)		GH	Conclusion GH (C if>3)	
1	0	8.61	C	X	7.57	NC	✓	1.29	NC	✓
2	0.5	19.91	C	✓	16.21	C	✓	3.50	C	✓
3	1	34.41	C	✓	27.15	C	✓	5.83	C	✓
4	2	144.41	C	✓	109.25	C	✓	21.20	C	✓
5	4	233.96	C	✓	177.74	C	✓	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

# Results

Lab level - whey
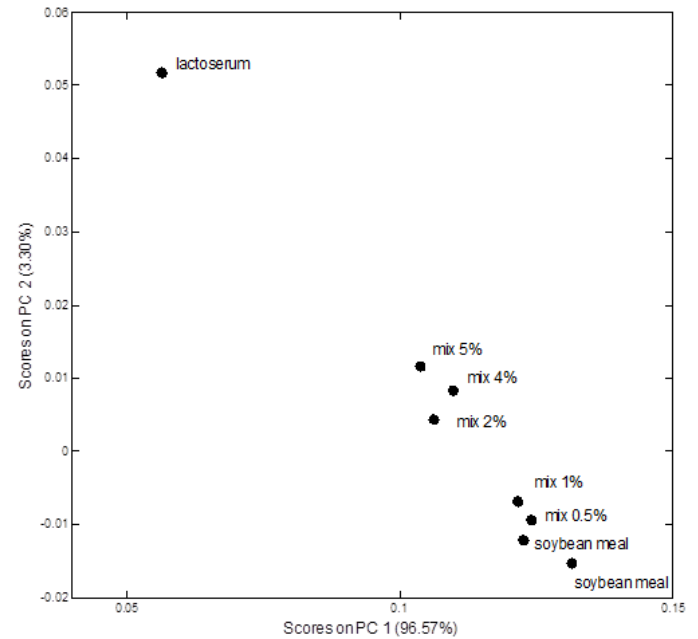
Extension to feed mills

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.

Extension to feed mills

CONCRETE PIT

RAIDLER

SAMPLING AREA
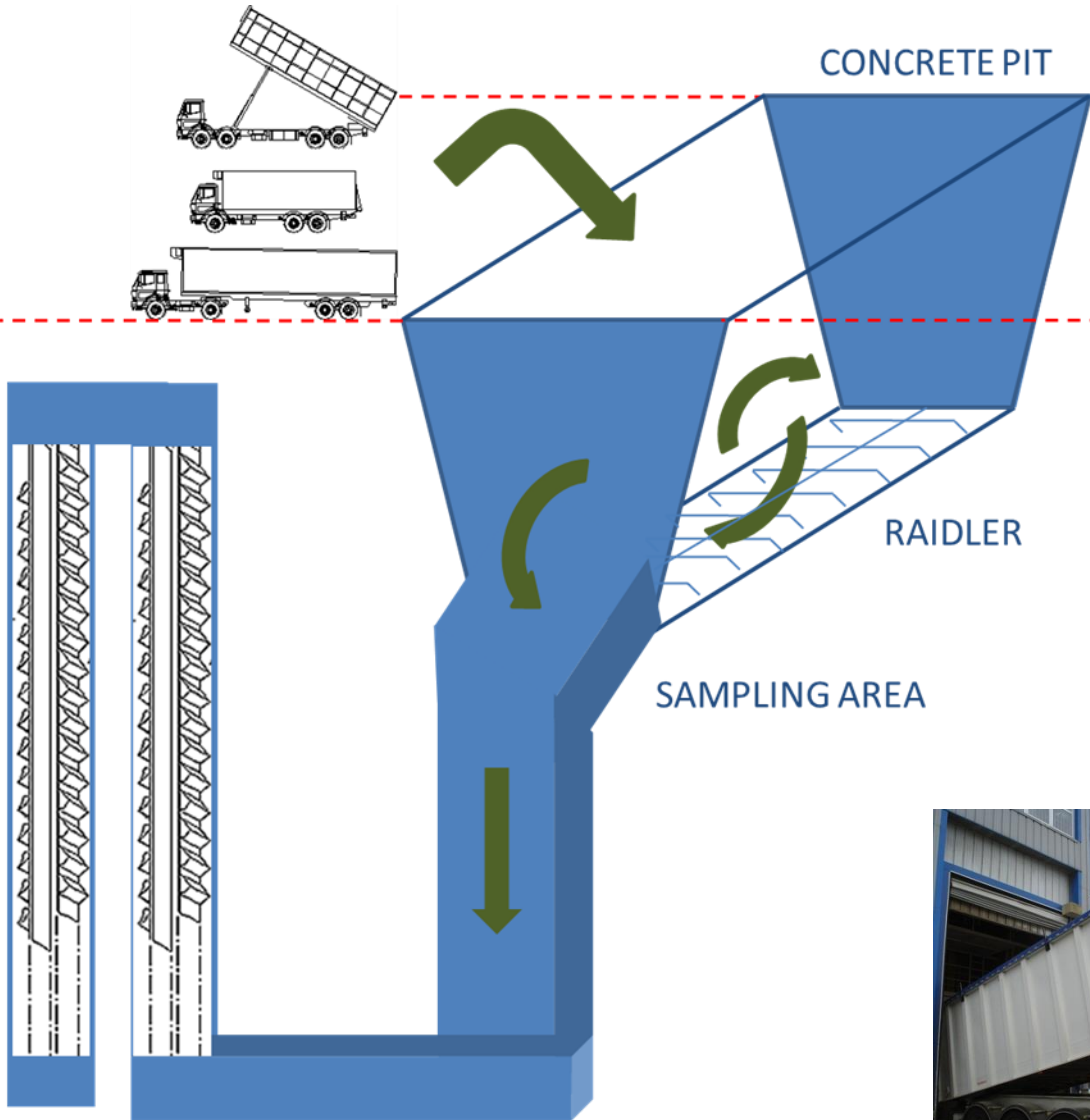
BUCKET CHAIN

Extension to feed mills

Extension to feed mills

Real case studies at

- Two trucks of soybean meal – simulating a contamination with whey.

Extension to feed mills

| STEP 1	STEP 2	STEP 3	STEP 4	STEP 5
Loading of 5 Tons of Soya bean directly from the truck	Loading of 5 Tons of Soya bean from the truck contaminated by simulating a local contamination	Loading of 5 Tons of Soya bean directly from the truck	Loading of 5 Tons of Soya bean from the truck contaminated by mixing	Emptying of the truck. No deliberate pollution done

Extension to feed mills

Whey contamination   DDGS contamination

15/1/2013	number of samples	7/2/2013	number of samples	25/2/2013	number of samples
Group 1/A	15	Group 2/A	20	Group 3/A	20
Group 1/B	24	Group 2/B	18	Group 3/B	25
Group 1/C	29	Group 2/C	20	Group 3/C	23
Group 1/D	35	Group 2/D	25	Group 3/D	23
Group 1/E	31	Group 2/E	26	Group 3/E	14
	134		109		105
		Total	348	samples	

Extension to feed mills


Whey – set 1
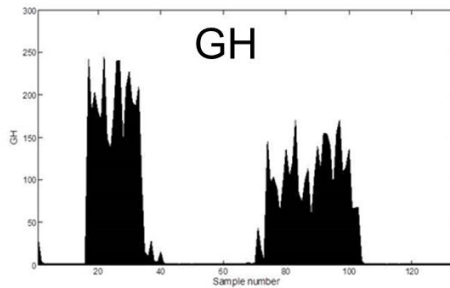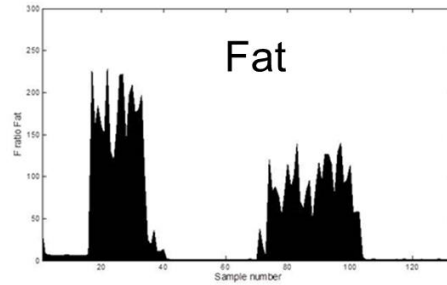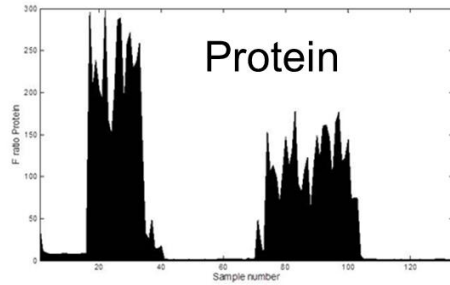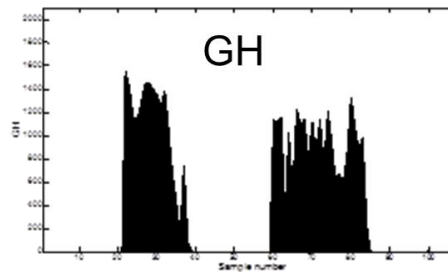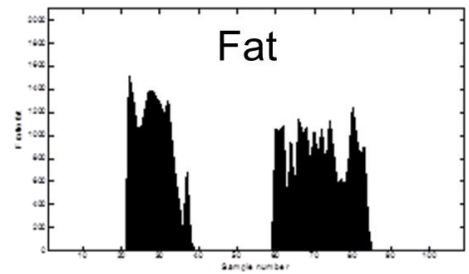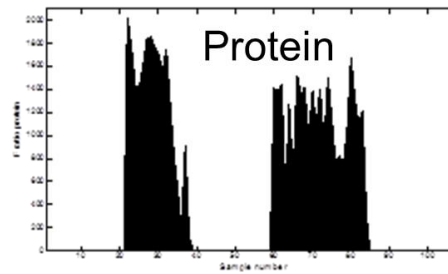
Whey – set 2

Feed plant level - output

- A NIR emission head, connected to a spectrometer via optical fiber, has been installed on the slope in between the horizontal conveyer and the elevator to collect spectra 'on the process'... at the entrance of the raw materials in the factory.

- Today, each raw material delivered in bulk is NIR scanned. LWPCA allows detecting abnormalities in the spectra.

- NIR spectra per truck are collected.

Conclusions
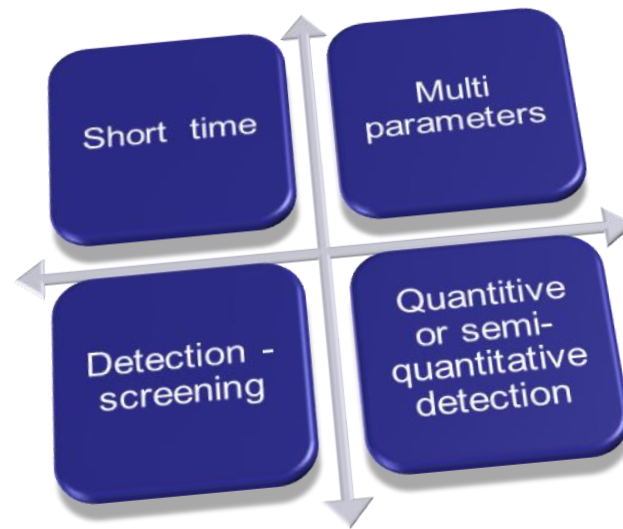
NIR spectroscopy in combination with chemometrics is a perfect tool, at laboratory, at feed mill and at port of entry levels, for:

- the **characterization of feed materials**, as soybean meal
- **Detection of targeted and untargeted adulteration / contamination**

Thank you