On-line Monitoring of Water during Reference Material Production by AOTF-NIR Spectrometry

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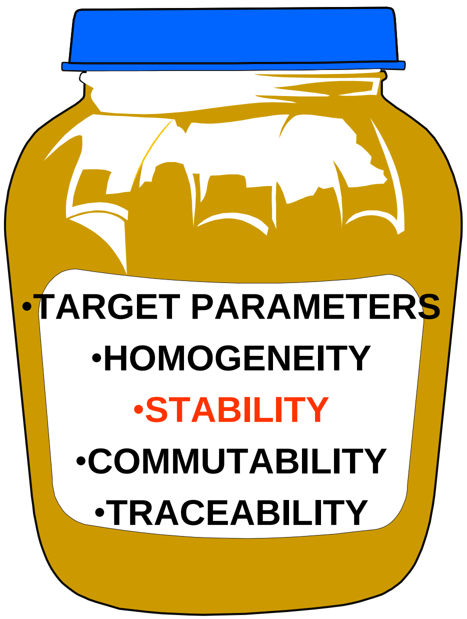
Institute for Reference Materials and Measurements, IRMM

- **IRMM is a part of the European Commissions' Joint Research Centre**
- **350 staff, four scientific units and four support units located just outside Geel in Belgium, 80 km from Brussels**
- **The scientific units are Reference Materials, Isotope Measurements, Neutron Physics and Food Safety and Quality**
- **The RM Unit is handling all aspects of CRM-production: Processing, Stability- and Homogeneity studies Certification, Keeping the sales and the CRM stock -All under ISO Guide 34 accreditation**

CRM / Stability / Water

- **Matrix reference materials are mainly dry powders because of their increased stability in comparison with fresh/wet materials**
- **There are some features common to all matrix reference materials as depicted below**



The stability of Reference Materials is intimately linked to the water content. One common way to improve stability is removal of water. Methods to control the water content are therefore very important for the process control during Reference Material production

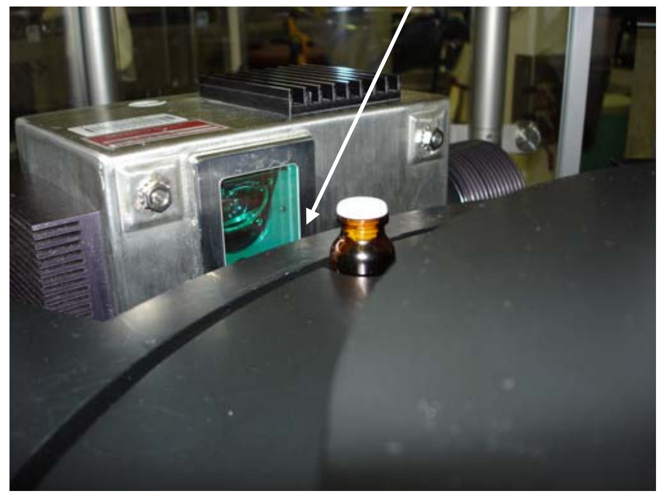
Methods for H_2O available at RM Unit

- **Volumetric Karl Fischer Titration V-KFT accredited under ISO 17025 (specific)**
- **Vaporisation Coulometric KFT (specific)**
- **Acousto Optical Tuneable Filter Near Infrared Spectrometry, AOTF-NIR (specific)**
- **Thermo Gravimetric Analysis, TGA (non specific)**
- **Mass loss on drying (non specific)**

Acousto Optical Tuneable Filter Near Infrared Spectrometry, AOTF-NIR

- The Brimrose Luminar 4030 Analyzer Measures diffuse reflectance in the NIR region
- High speed 16000 λ / s, one spectrum 1100 – 2300 nm takes 75 ms
- 65 mm Free Space™ (high S/N) with a 6 mm diameter spot size
- The capping machine was operated at 10 vials / minute so the vial is in the measurement position for < 6 s. All data based on 100 NIR spectra / vial, 1300 – 2100 nm which takes 5 s.

65 mm



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Principle of the AOTF Measurement

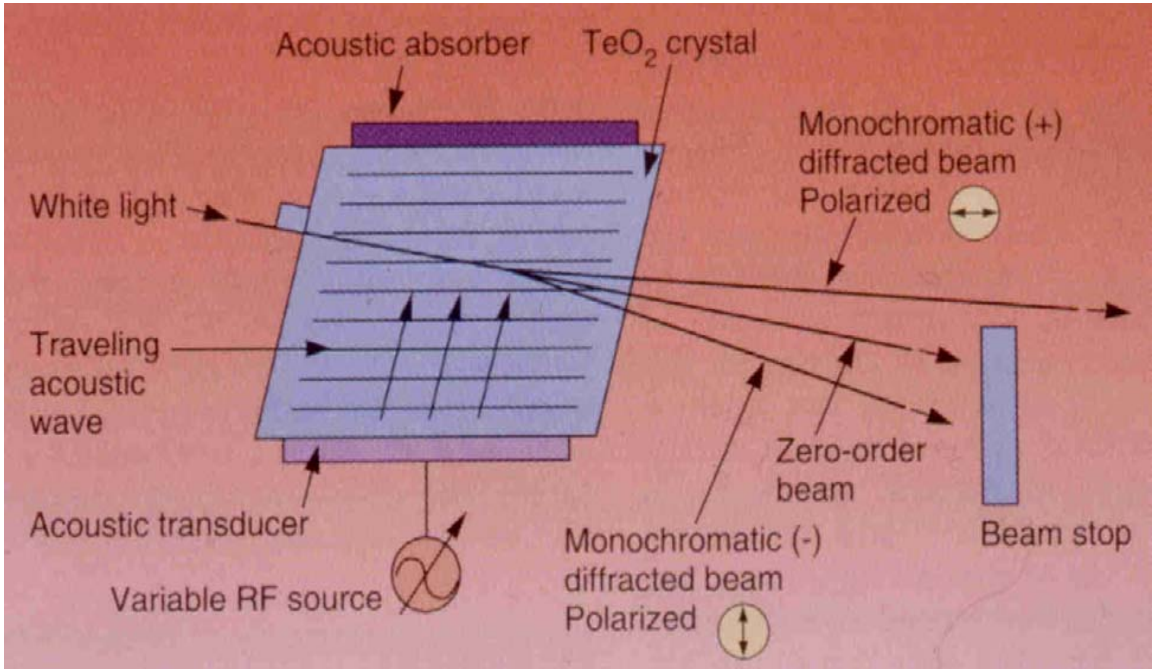
No moving parts

High S/N

Very fast

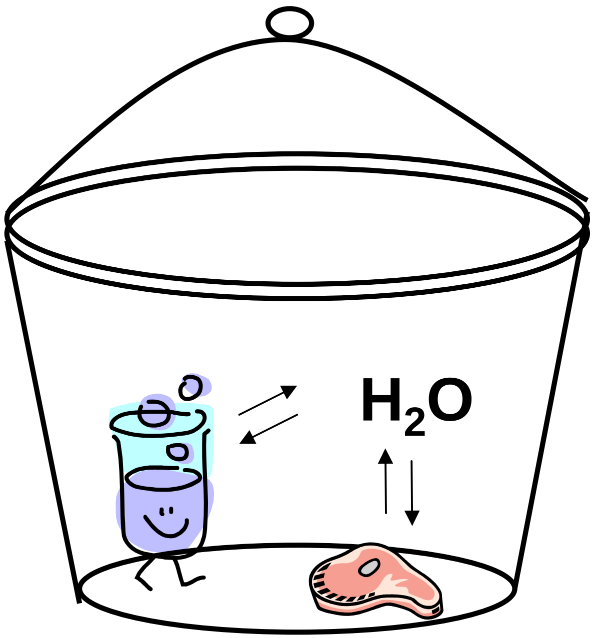
Excellent wavelength repeatability

Good resolution



Preparation of Calibrants with a known water content determined by V-KFT

NIR relies on external calibrants for quantification of water, in this case determined by Volumetric Karl Fischer Titration

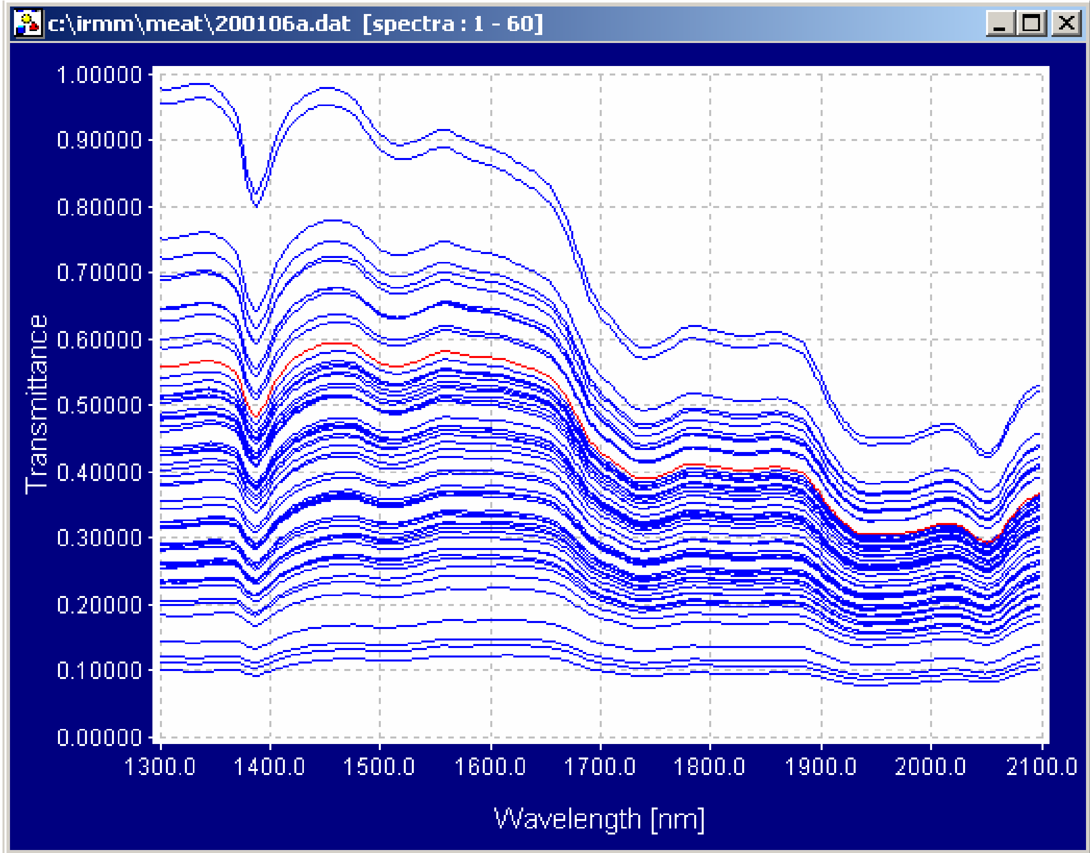


LiBr
LiCl
CH_3COOK
$MgCl_2$
K_2CO_3
NaBr

- Freeze dried meat powder was equilibrated with six different oversaturated hygrostatic solutions in a dessicator to give powders with different water content

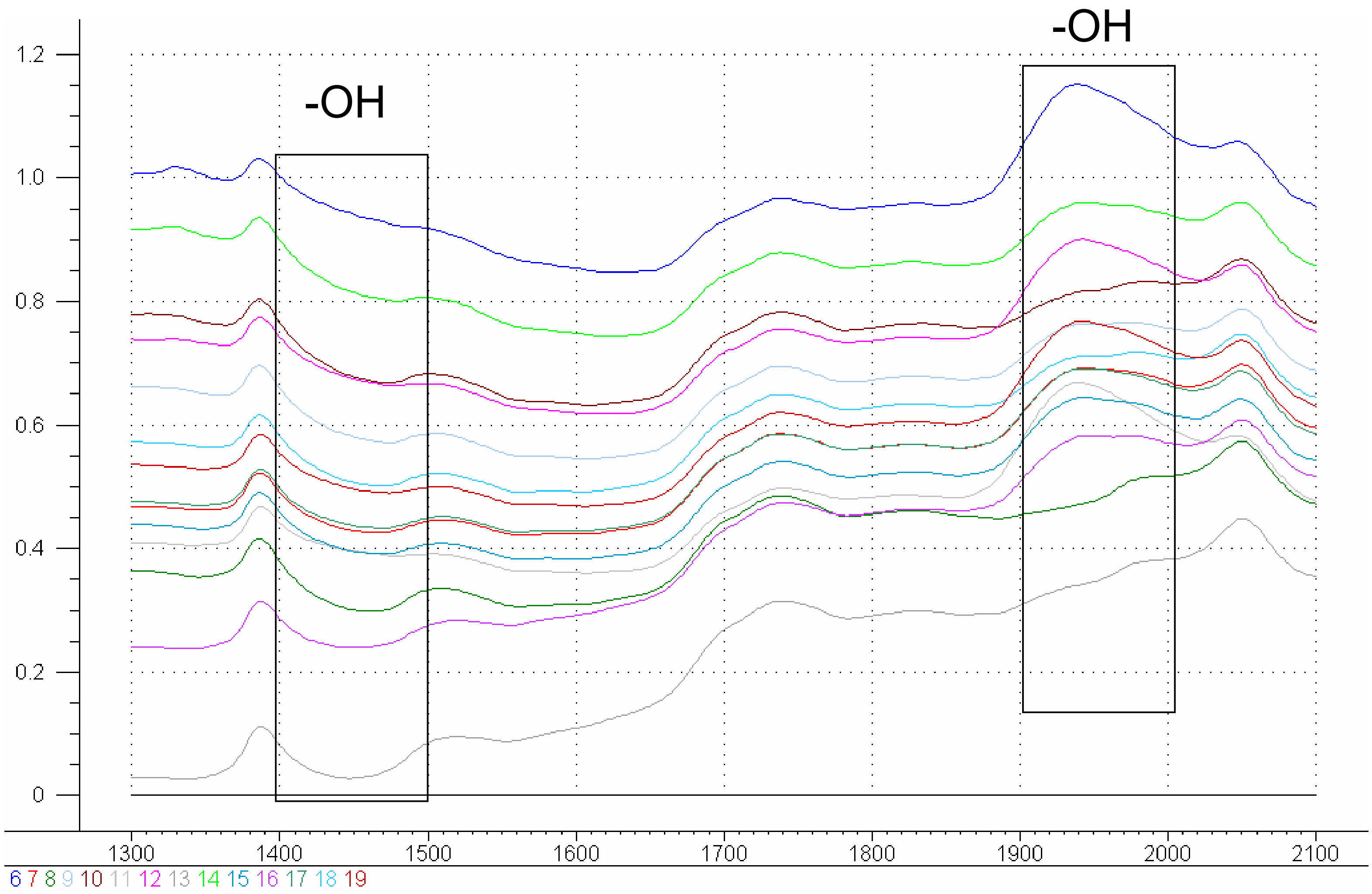
- Equilibrated powders were also mixed carefully with each other to give intermediate levels. Finally 19 calibrants from 0.5 to 8.3 % H_2O (m/m) were obtained

Typical NIR spectra of meat



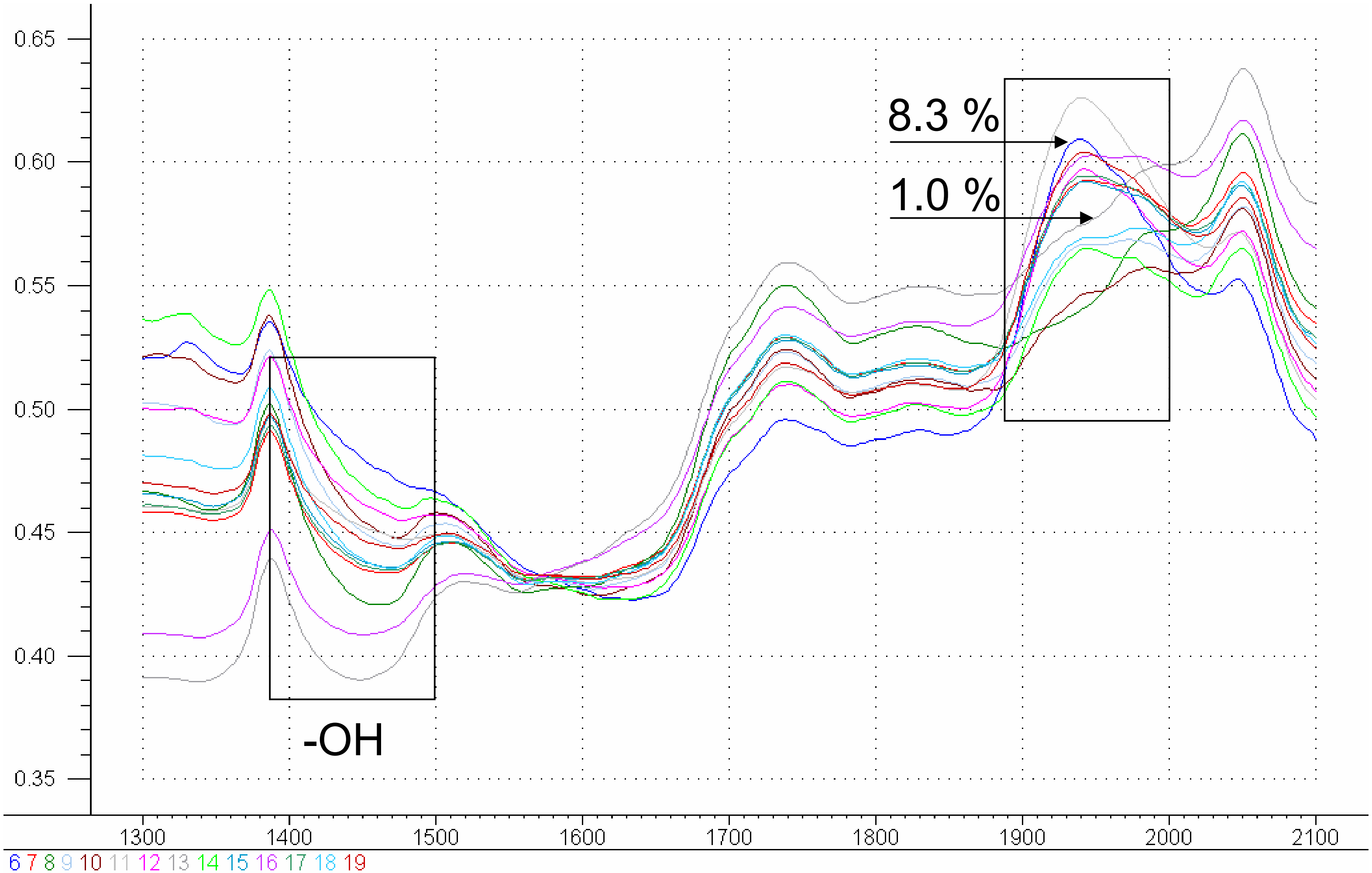
AOTF-NIR spectra collected from 100 mL amber glass vials, transmittance in ratio mode

Transformation of data in Unscrambler®



Transformation to absorbance

Transformation of data in Unscrambler®



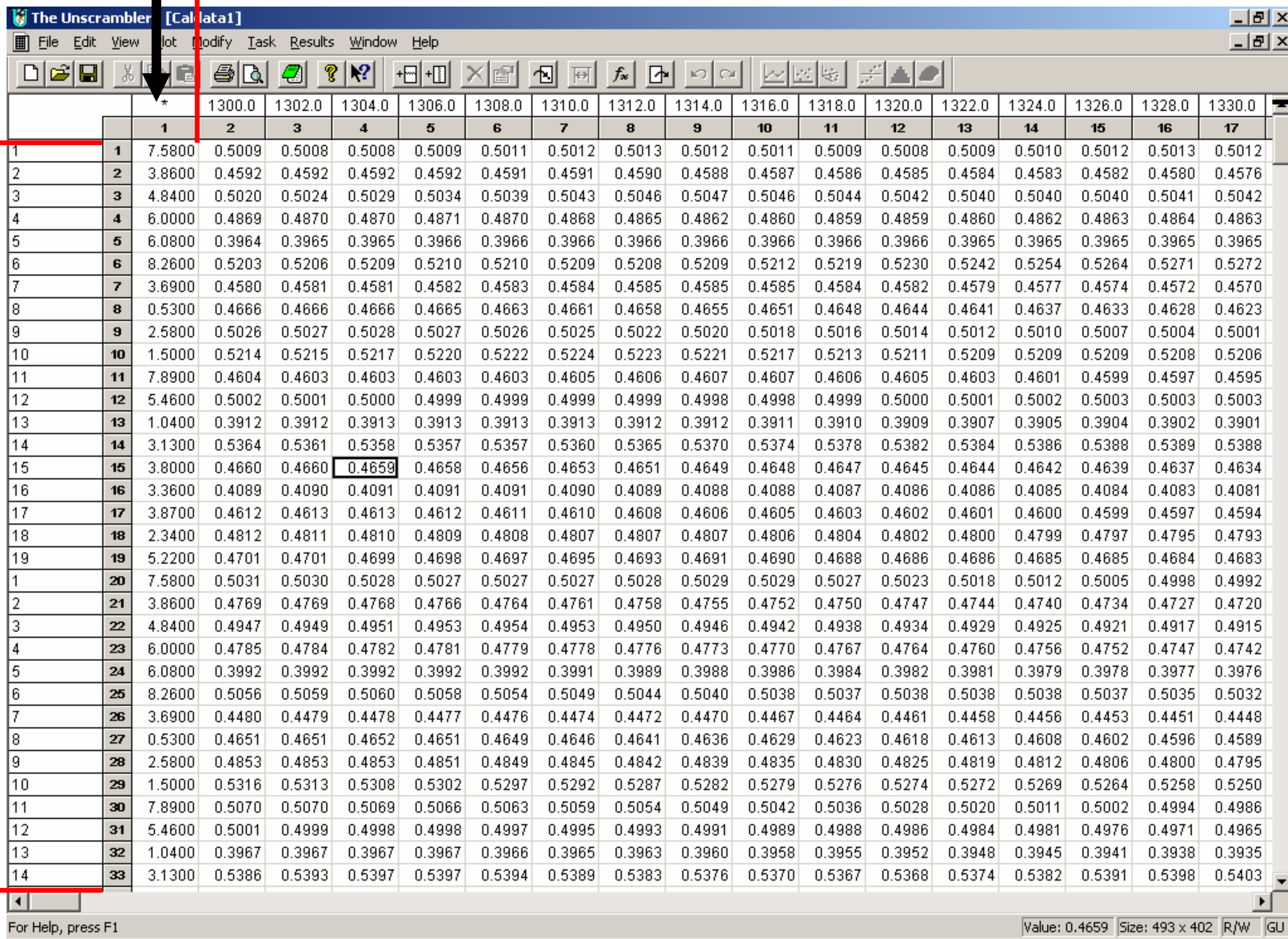
Corrections for offset and slope of NIR-spectra by applying Multiplicative Scatter Correction, MSC on graphs from previous slide

Master data table in Unscrambler®

Y-data, water content from KFT

Wavelengths 1300-2100 nm, spectral X-data

Samples for calibration



		*	1300.0	1302.0	1304.0	1306.0	1308.0	1310.0	1312.0	1314.0	1316.0	1318.0	1320.0	1322.0	1324.0	1326.0	1328.0	1330.0
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	1	7.5800	0.5009	0.5008	0.5008	0.5009	0.5011	0.5012	0.5013	0.5012	0.5011	0.5009	0.5008	0.5009	0.5010	0.5012	0.5013	0.5012
2	2	3.8600	0.4592	0.4592	0.4592	0.4592	0.4591	0.4591	0.4590	0.4588	0.4587	0.4586	0.4585	0.4584	0.4583	0.4582	0.4580	0.4576
3	3	4.8400	0.5020	0.5024	0.5029	0.5034	0.5039	0.5043	0.5046	0.5047	0.5046	0.5044	0.5042	0.5040	0.5040	0.5040	0.5041	0.5042
4	4	6.0000	0.4869	0.4870	0.4870	0.4871	0.4870	0.4868	0.4865	0.4862	0.4860	0.4859	0.4859	0.4860	0.4862	0.4863	0.4864	0.4863
5	5	6.0800	0.3964	0.3965	0.3965	0.3966	0.3966	0.3966	0.3966	0.3966	0.3966	0.3966	0.3966	0.3965	0.3965	0.3965	0.3965	0.3965
6	6	8.2600	0.5203	0.5206	0.5209	0.5210	0.5210	0.5209	0.5208	0.5209	0.5212	0.5219	0.5230	0.5242	0.5254	0.5264	0.5271	0.5272
7	7	3.6900	0.4580	0.4581	0.4581	0.4582	0.4583	0.4584	0.4585	0.4585	0.4585	0.4584	0.4582	0.4579	0.4577	0.4574	0.4572	0.4570
8	8	0.5300	0.4666	0.4666	0.4666	0.4665	0.4663	0.4661	0.4658	0.4655	0.4651	0.4648	0.4644	0.4641	0.4637	0.4633	0.4628	0.4623
9	9	2.5800	0.5026	0.5027	0.5028	0.5027	0.5026	0.5025	0.5022	0.5020	0.5018	0.5016	0.5014	0.5012	0.5010	0.5007	0.5004	0.5001
10	10	1.5000	0.5214	0.5215	0.5217	0.5220	0.5222	0.5224	0.5223	0.5221	0.5217	0.5213	0.5211	0.5209	0.5209	0.5209	0.5208	0.5206
11	11	7.8900	0.4604	0.4603	0.4603	0.4603	0.4603	0.4605	0.4606	0.4607	0.4607	0.4606	0.4605	0.4603	0.4601	0.4599	0.4597	0.4595
12	12	5.4600	0.5002	0.5001	0.5000	0.4999	0.4999	0.4999	0.4999	0.4998	0.4998	0.4999	0.5000	0.5001	0.5002	0.5003	0.5003	0.5003
13	13	1.0400	0.3912	0.3912	0.3913	0.3913	0.3913	0.3913	0.3912	0.3912	0.3911	0.3910	0.3909	0.3907	0.3905	0.3904	0.3902	0.3901
14	14	3.1300	0.5364	0.5361	0.5358	0.5357	0.5357	0.5360	0.5365	0.5370	0.5374	0.5378	0.5382	0.5384	0.5386	0.5388	0.5389	0.5388
15	15	3.8000	0.4660	0.4660	0.4659	0.4658	0.4656	0.4653	0.4651	0.4649	0.4648	0.4647	0.4645	0.4644	0.4642	0.4639	0.4637	0.4634
16	16	3.3600	0.4089	0.4090	0.4091	0.4091	0.4091	0.4090	0.4089	0.4088	0.4088	0.4087	0.4086	0.4086	0.4085	0.4084	0.4083	0.4081
17	17	3.8700	0.4612	0.4613	0.4613	0.4612	0.4611	0.4610	0.4608	0.4606	0.4605	0.4603	0.4602	0.4601	0.4600	0.4599	0.4597	0.4594
18	18	2.3400	0.4812	0.4811	0.4810	0.4809	0.4808	0.4807	0.4807	0.4807	0.4806	0.4804	0.4802	0.4800	0.4799	0.4797	0.4795	0.4793
19	19	5.2200	0.4701	0.4701	0.4699	0.4698	0.4697	0.4695	0.4693	0.4691	0.4690	0.4688	0.4686	0.4686	0.4685	0.4685	0.4684	0.4683
1	20	7.5800	0.5031	0.5030	0.5028	0.5027	0.5027	0.5027	0.5028	0.5029	0.5029	0.5027	0.5023	0.5018	0.5012	0.5005	0.4998	0.4992
2	21	3.8600	0.4769	0.4769	0.4768	0.4766	0.4764	0.4761	0.4758	0.4755	0.4752	0.4750	0.4747	0.4744	0.4740	0.4734	0.4727	0.4720
3	22	4.8400	0.4947	0.4949	0.4951	0.4953	0.4954	0.4953	0.4950	0.4946	0.4942	0.4938	0.4934	0.4929	0.4925	0.4921	0.4917	0.4915
4	23	6.0000	0.4785	0.4784	0.4782	0.4781	0.4779	0.4778	0.4776	0.4773	0.4770	0.4767	0.4764	0.4760	0.4756	0.4752	0.4747	0.4742
5	24	6.0800	0.3992	0.3992	0.3992	0.3992	0.3992	0.3991	0.3989	0.3988	0.3986	0.3984	0.3982	0.3981	0.3979	0.3978	0.3977	0.3976
6	25	8.2600	0.5056	0.5059	0.5060	0.5058	0.5054	0.5049	0.5044	0.5040	0.5038	0.5037	0.5038	0.5038	0.5038	0.5037	0.5035	0.5032
7	26	3.6900	0.4480	0.4479	0.4478	0.4477	0.4476	0.4474	0.4472	0.4470	0.4467	0.4464	0.4461	0.4458	0.4456	0.4453	0.4451	0.4448
8	27	0.5300	0.4651	0.4651	0.4652	0.4651	0.4649	0.4646	0.4641	0.4636	0.4629	0.4623	0.4618	0.4613	0.4608	0.4602	0.4596	0.4589
9	28	2.5800	0.4853	0.4853	0.4853	0.4851	0.4849	0.4845	0.4842	0.4839	0.4835	0.4830	0.4825	0.4819	0.4812	0.4806	0.4800	0.4795
10	29	1.5000	0.5316	0.5313	0.5308	0.5302	0.5297	0.5292	0.5287	0.5282	0.5279	0.5276	0.5274	0.5272	0.5269	0.5264	0.5258	0.5250
11	30	7.8900	0.5070	0.5070	0.5069	0.5066	0.5063	0.5059	0.5054	0.5049	0.5042	0.5036	0.5028	0.5020	0.5011	0.5002	0.4994	0.4986
12	31	5.4600	0.5001	0.4999	0.4998	0.4998	0.4997	0.4995	0.4993	0.4991	0.4989	0.4988	0.4986	0.4984	0.4981	0.4976	0.4971	0.4965
13	32	1.0400	0.3967	0.3967	0.3967	0.3967	0.3966	0.3965	0.3963	0.3960	0.3958	0.3955	0.3952	0.3948	0.3945	0.3941	0.3938	0.3935
14	33	3.1300	0.5386	0.5393	0.5397	0.5397	0.5394	0.5389	0.5383	0.5376	0.5370	0.5367	0.5368	0.5374	0.5382	0.5391	0.5398	0.5403

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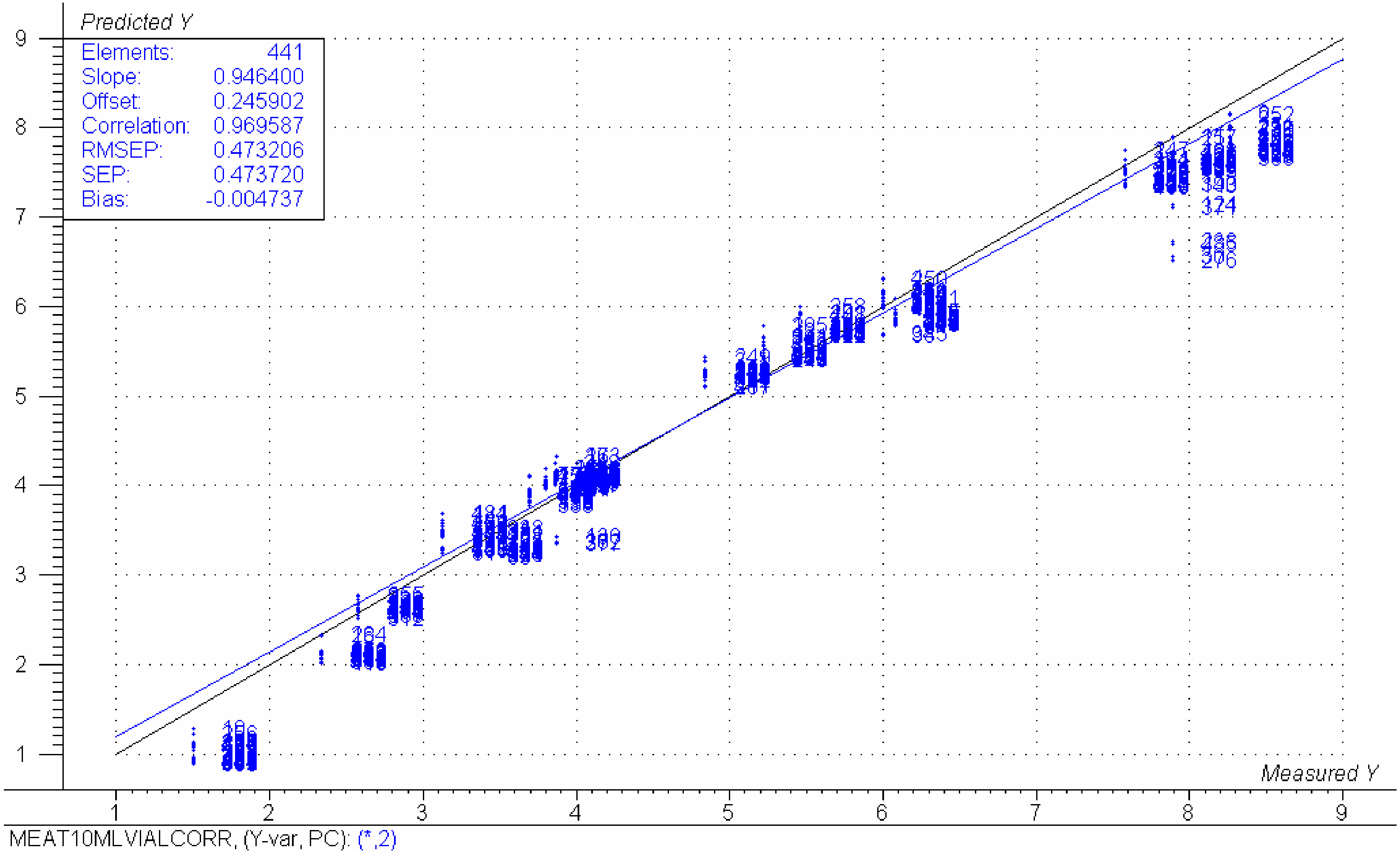
PLS1 model to extract the information 'hidden' in the spectra

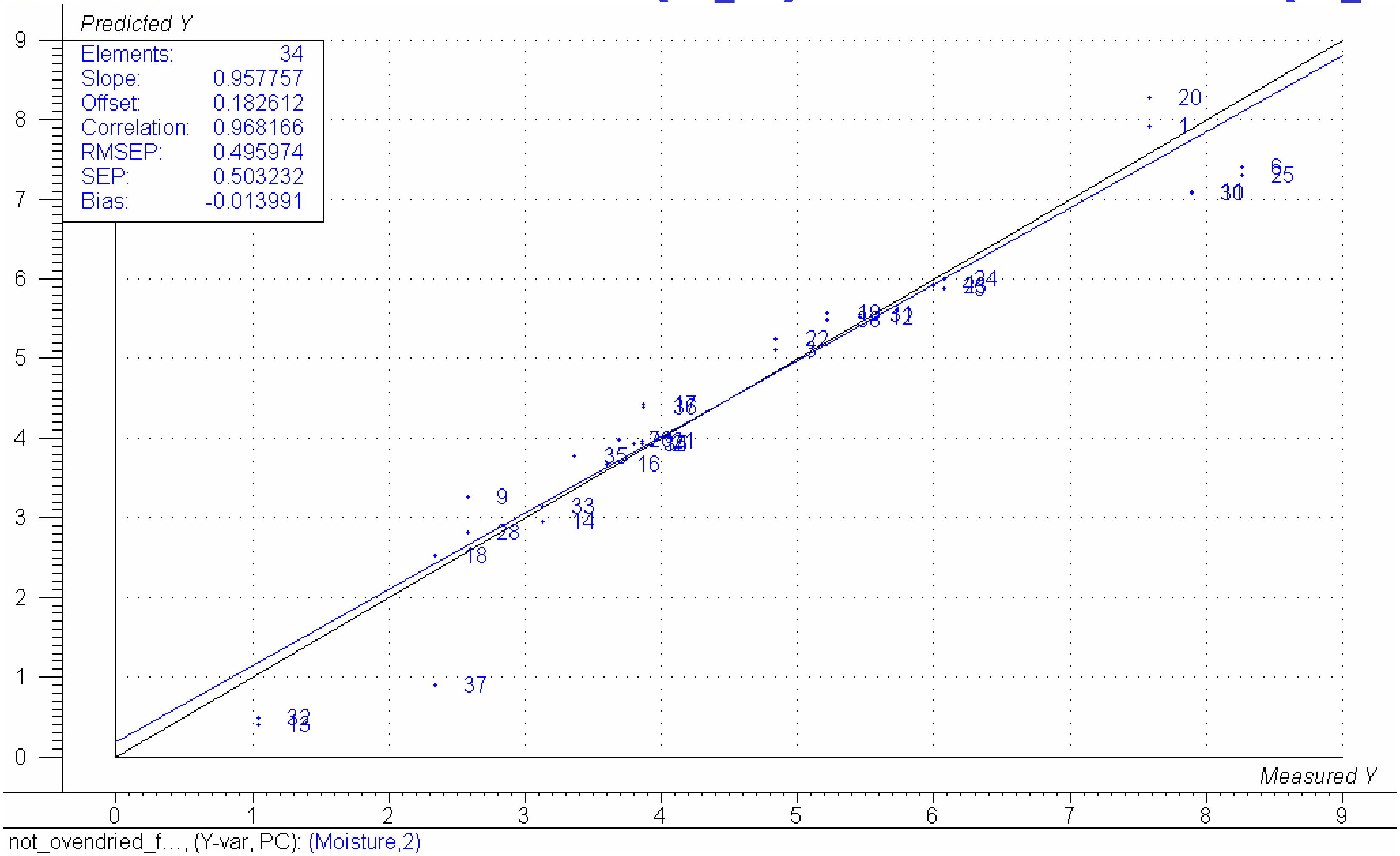
- 'Partial least squares' regression model or 'projection to latent structures' models both the X- and Y-matrices simultaneously to find latent variables in X (wavelength) that will best predict the latent variables in Y (water). PLS1 deals with only one response variable at a time (water) which the regression model tries to predict.

Measured Y (H_2O) vs. Predicted Y (H_2O)



Regression model for 10 mL vials. The 19 meat calibrants measured in duplicate over 7 days together with 12777 potato samples. r = 0.969 and a with Standard Error of Prediction of 0.47 % water

Measured Y (H_2O) vs. Predicted Y (H_2O)



Regression model for 100 mL vials. The 19 meat calibrants measured in duplicate, r = 0.968 and a with Standard Error of Prediction of 0.50 % water,

CRMs measured by AOTF-NIR and V-KFT

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- Pork muscle (a CRM for dietary properties and some elements, 100 mL vial, also the calibrant in this case)
- Rye grass (a CRM for trace metals, 100 mL vial)
- Non-GMO potatoes (a blank material, 10 mL vial)
- GMO-potatoes (a CRM with 100 % genetically modified potato, 10 mL vial)

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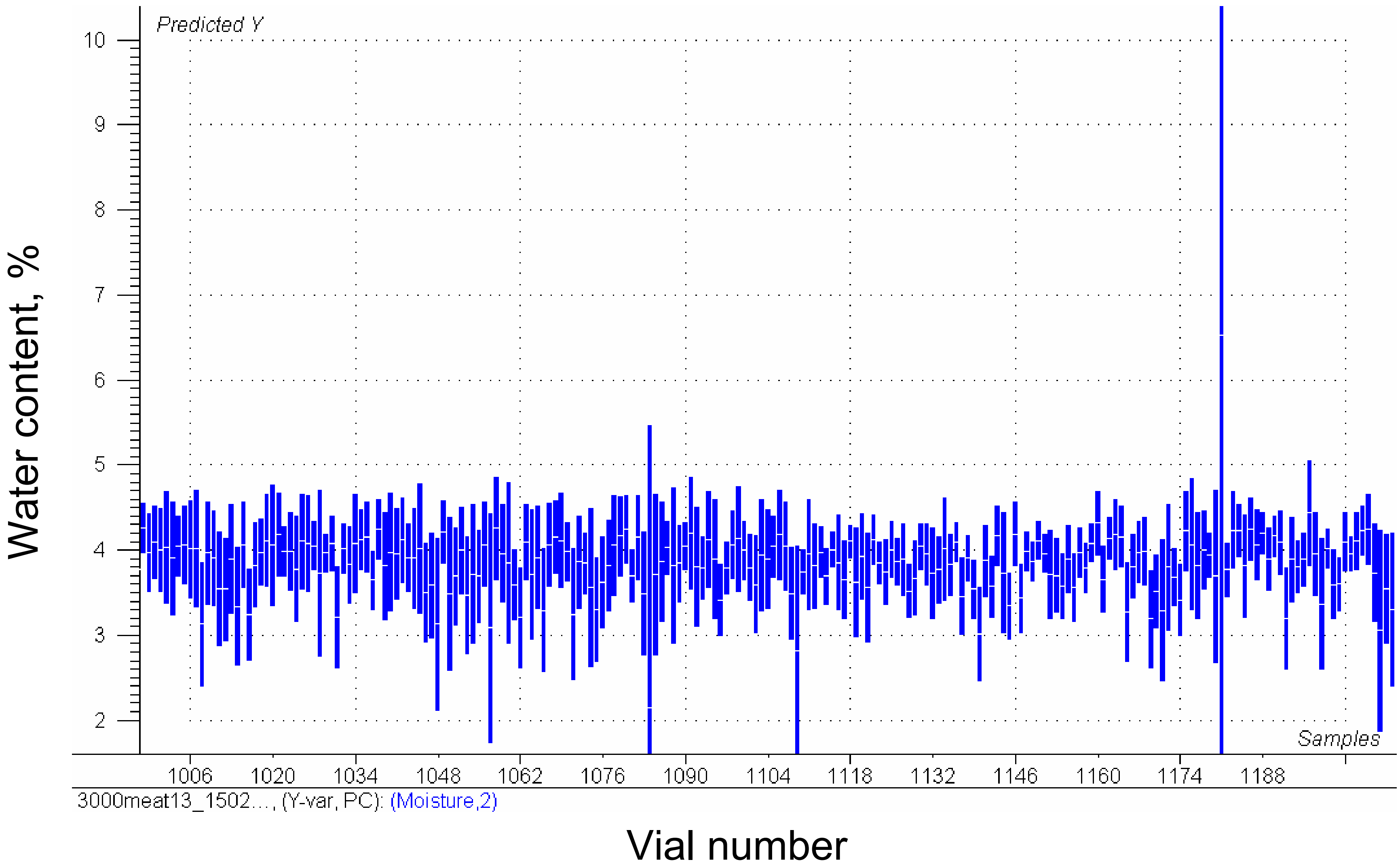
Water content in % (m/m) in the meat samples using the 100 mL vial PLS model



$H_2O = 3.9 \pm 0.3$ %

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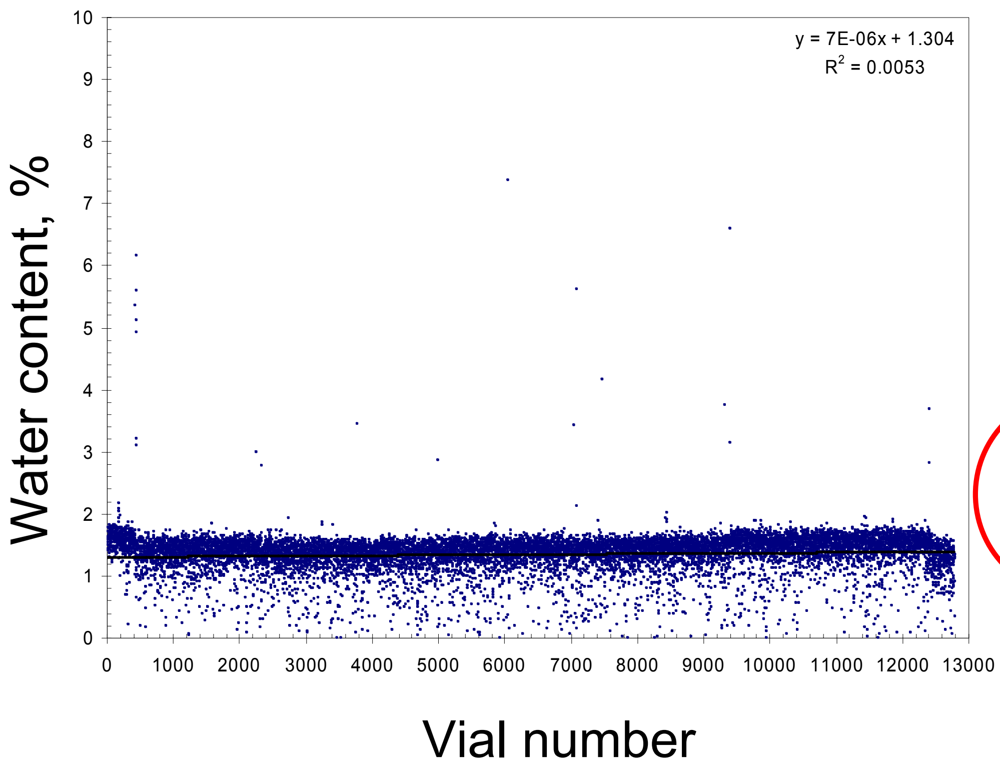
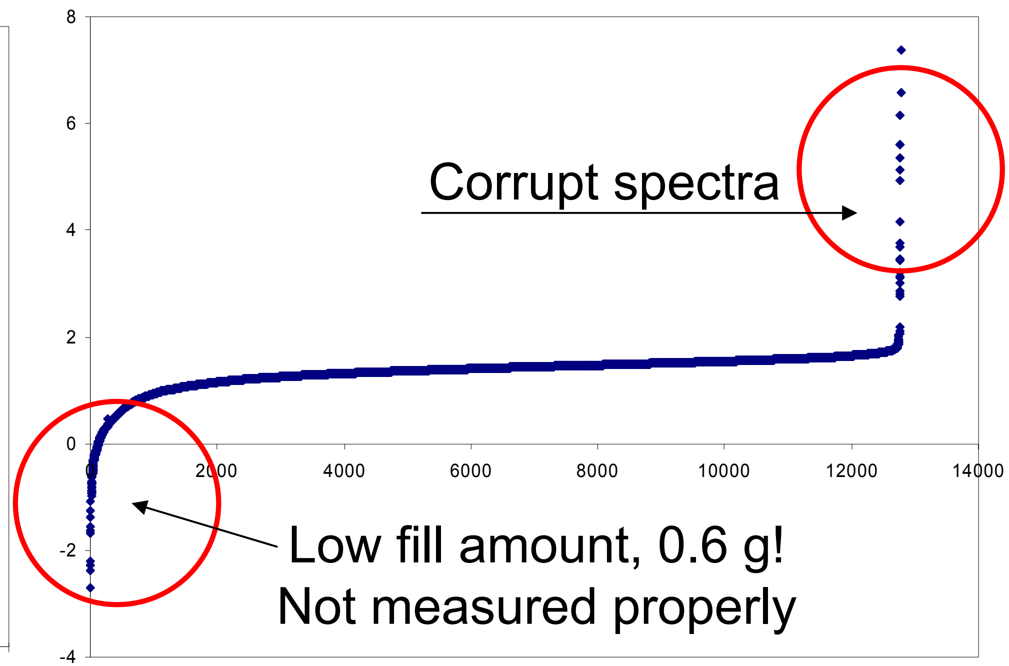
Water content in % (m/m) in the GMO potatoes using the 10 mL vial PLS model

Filled during 7 days, -no trend

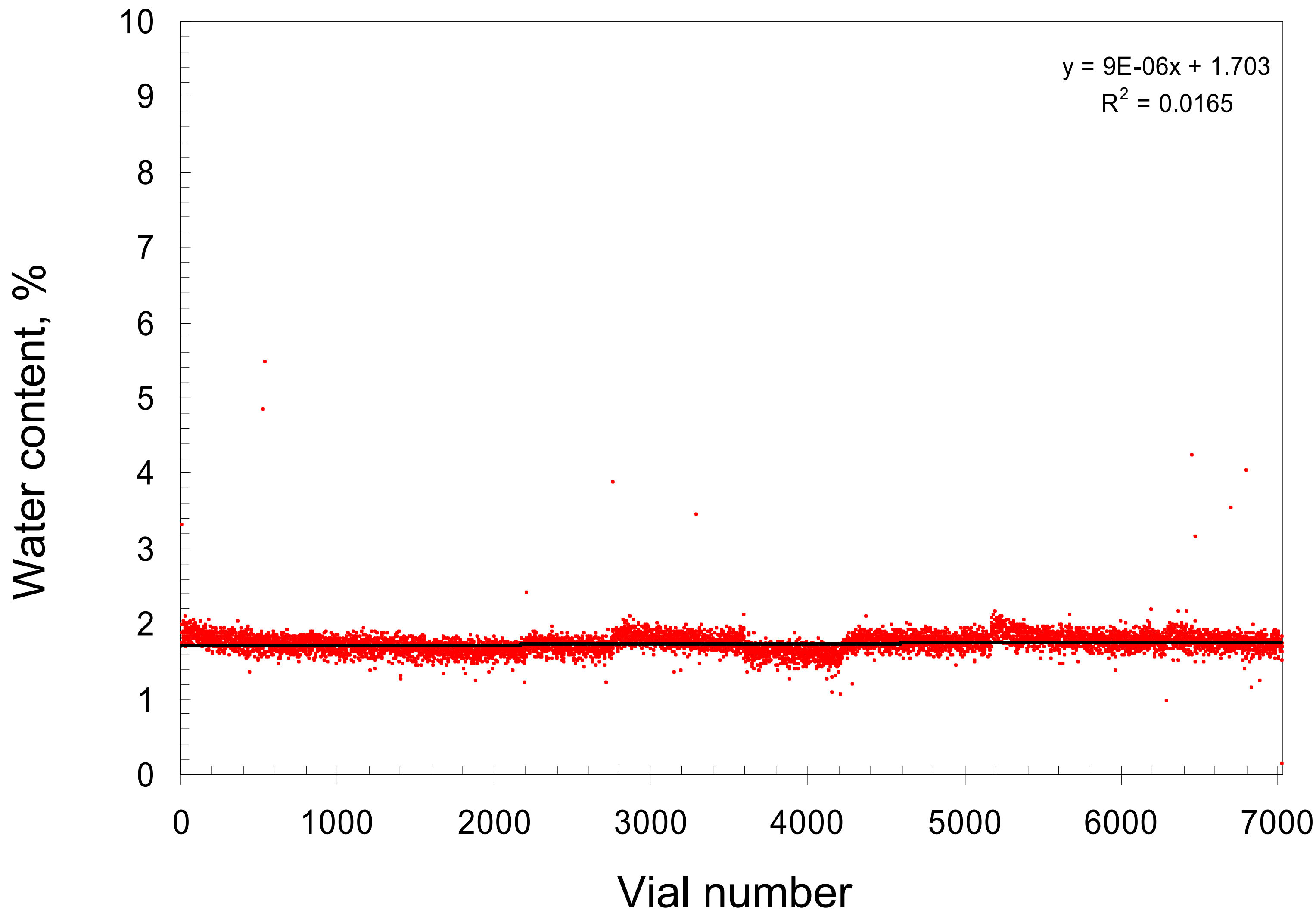


Sorted data



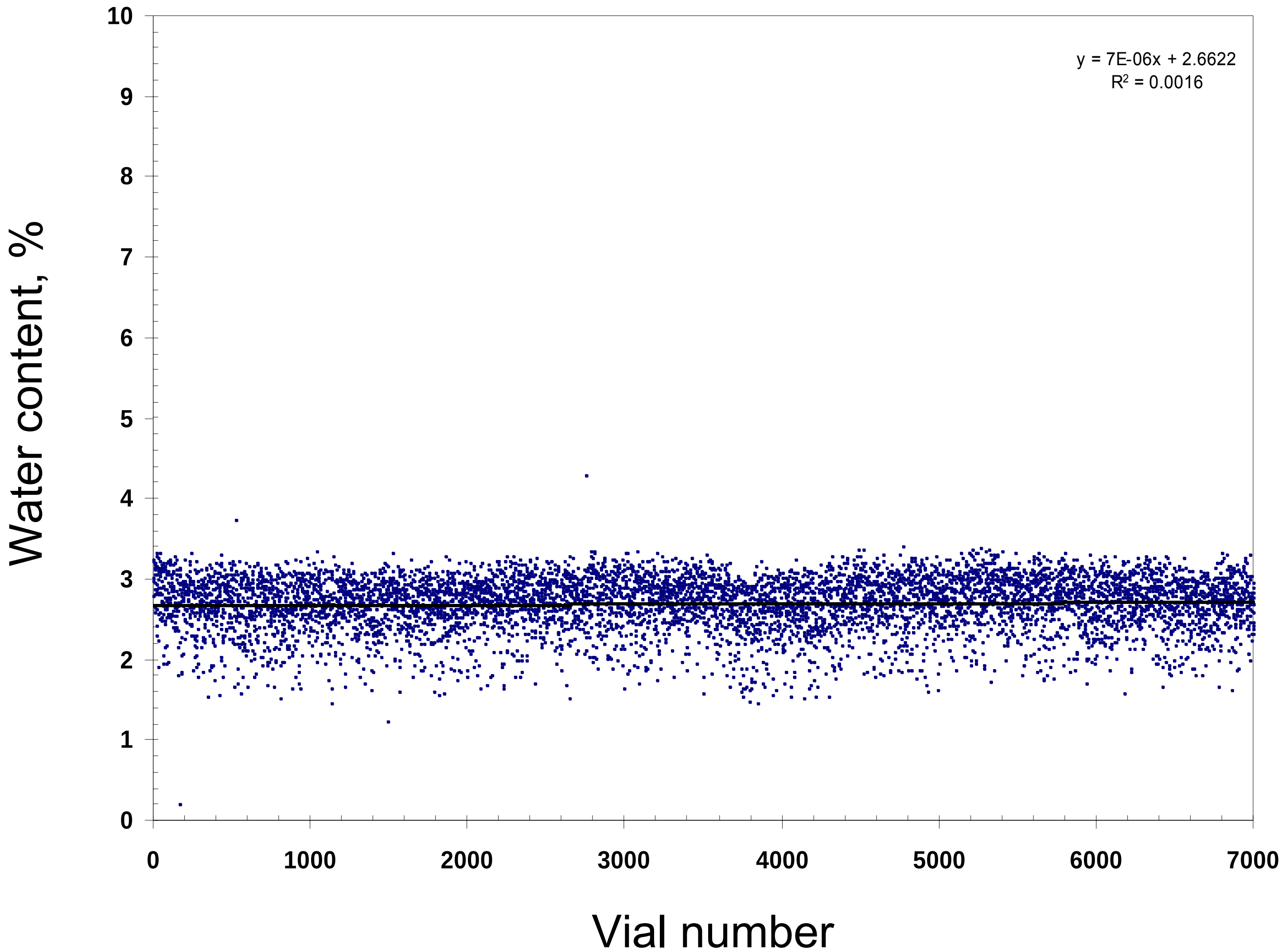
$H_2O = 1.3 \pm 0.4$ %

Water content in % (m/m) in the non-GMO potatoes using the 10 mL vial PLS model



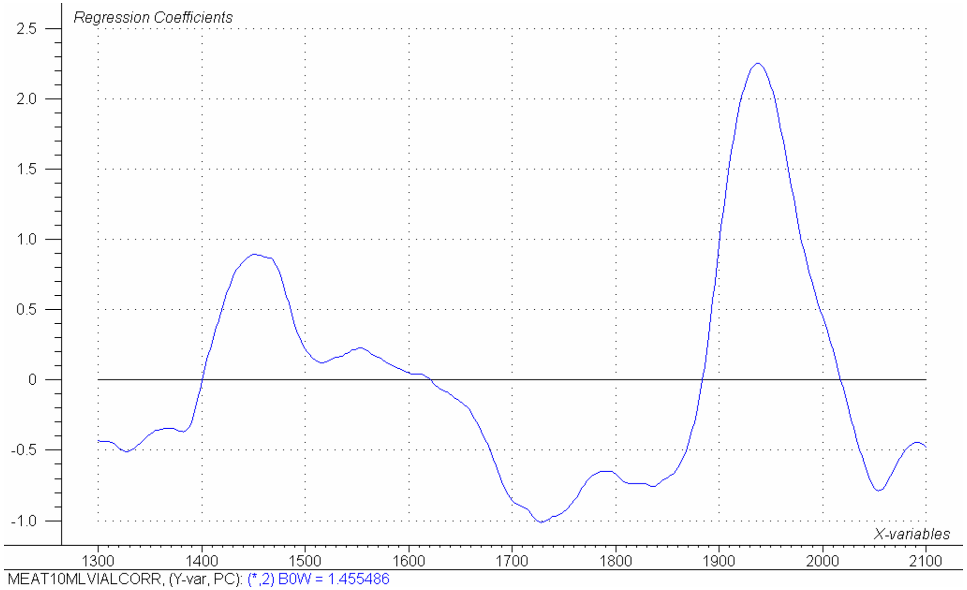
$H_2O = 1.7 \pm 0.2$ %

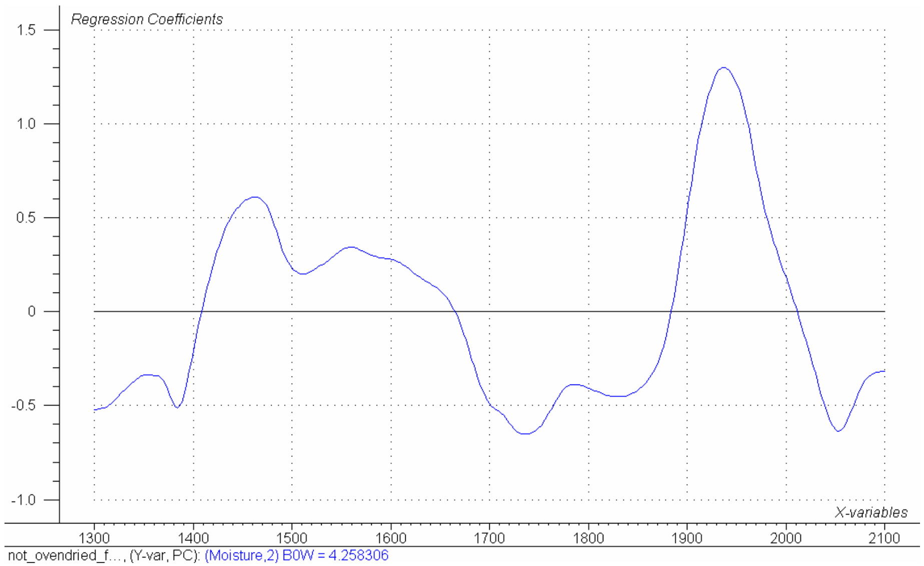
Water content in % (m/m) in the non-GMO potatoes using the 100 mL vial PLS model



H_2O = 2.7 ± 0.3 %

Regression coefficient plots of H_20 calibrants as a function of wavelength

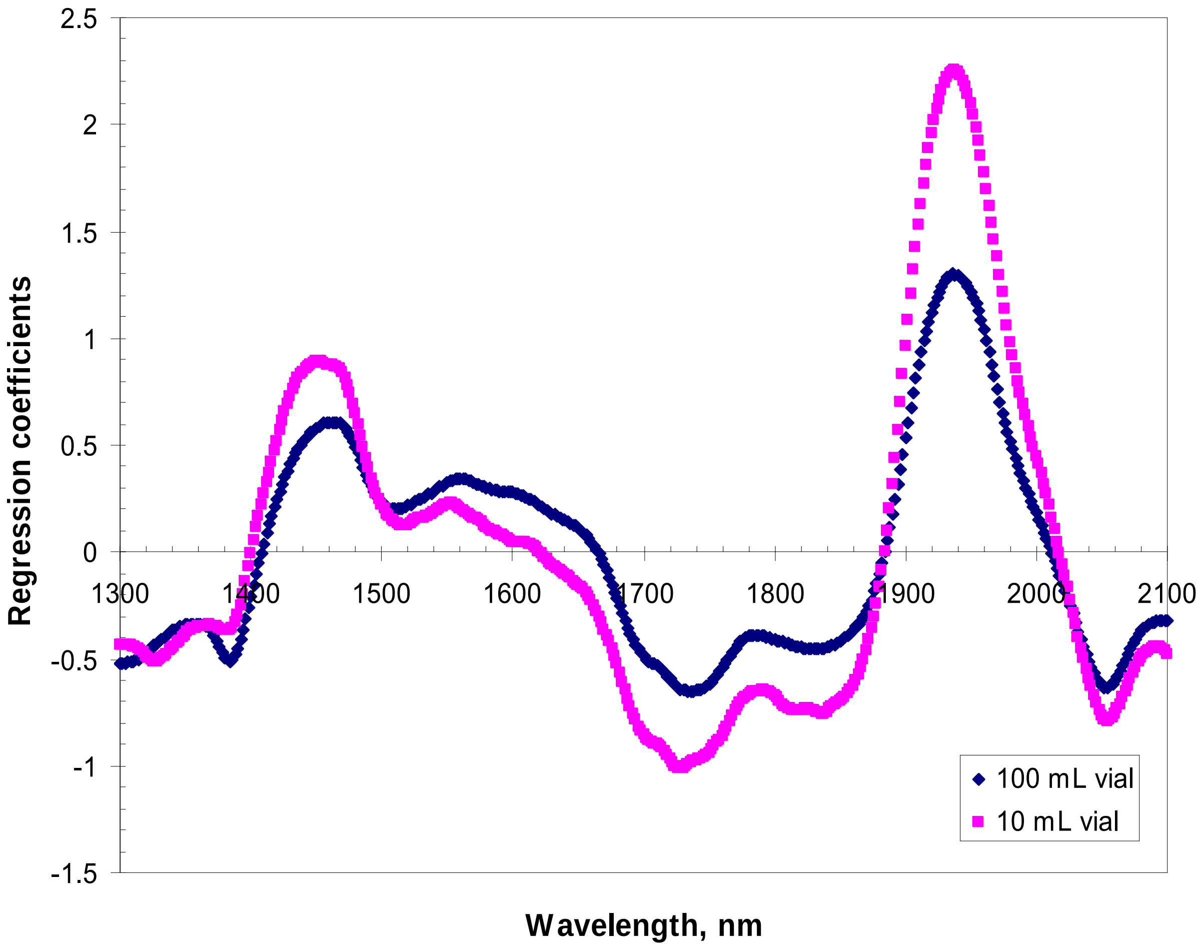




10 mL vial

100 mL vial

Overlay of regression coefficient plots



Small differences observed for the meat powder calibrants contained in different vials sizes despite MSC

Direct comparison with V-KFT

MATRIX	% H_2O (m/m) AOTF-NIR	% H_2O (m/m) V-KFT
Pork muscle (meat)	3.9 ± 0.3 (3000)	4.0 ± 0.3 (3)
GMO Potatoes	1.3 ± 0.4 (12777)	1.2 ± 0.2 (3)
Non-GMO Potatoes	1.7 ± 0.2 (7021)	1.7 ± 0.1 (3)
Rye grass	2.7 ± 0.2 (2425)	2.6 ± 0.1 (3)

Comparison of results between AOTF-NIR and V-KFT (ISO 17025). Results are reported as mean ± one standard deviation for the number of samples given

CONCLUSIONS

- The AOTF-NIR clearly has the potential of monitoring a large number of samples with good accuracy and reasonable precision.
- It is necessary to expand the number of calibration models for different vial sizes as it turns out that MSC cannot correct for the influence of light scattering due the different vial sizes.
- To a lesser extent there is also an influence of the matrix but the meat calibrants can be used for all three matrices investigated as a universal calibrant.

CONCLUSIONS

- The AOTF-NIR provides true on-line control of water content in all samples leaving the material processing improving the overall quality control
- Other parameters like fat and proteins can be also be measured
- Trends in water content in a CRM batch can from now on be detected
- Matrix degradation over time can probably also be monitored

Acknowledgements

- Thanks to the processing team who has performed all the measurements and operated the capping / labelling machine in which the AOTF-NIR is installed
- Jean Charoud-Got
- Andrea Bau
- Paul De Vos
- Albert Oostra
- Katharina Teipel
- Alberto Perez Sordo

You all know from this picture that NIR and water has something to do with each other even if you have not been convinced by this talk!