

Mare Purum project report

Quantitative on-line characterisation of
wastewater in an laboratory scale
sewerage using near infrared
spectroscopy

Elena Sherman



Botnia-Atlantica 



EUROPEISKA
UNIONEN
Europeiska regionala
utvecklingsfonden

Gränsöverskridande samarbete över fjäll och hav

Contents

Contents.....	1
1. Introduction	3
1.1. History.....	3
1.2. Theory	3
1.3. Possibilities.....	4
2. Equipment.....	4
2.1. NIR spectroscopy	4
2.2. Modeling	4
3. Estimation of nitrogen ion	4
3.1. Method	4
3.2. Results	6
4. Estimation of phosphorous and calcium ions	7
4.1. Method	7
4.2. Results	9
5. Estimation of COD and suspended solids in wastewater	10
5.1. Method	10
5.3. Results	12
6. Estimation of nitrogen through the pipe system.....	12
6.1. Pipe system.....	12
6.2. Single component pulses	13
6.2.1. Description of the experiments and the results	13
6.2.2. Discussion	15
6.3. Ethanol pulses	15
6.3.1. Description of the experiments	15
6.3.2. Discussion	16
6.4. Pulses with several components.....	16
6.4.1. Description of the experiments and the results	16
6.4.2. Results.....	17

6.4.3. Discussion	18
6.5. Pulses with several components with big concentration.....	18
6.5.1. Results	18
6.5.2. Discussion	18
References.....	19
Internet	19
Bibliography.....	19
Appendixes.....	20
Appendix 1	20
Appendix 2	22
Appendix 3	23
Appendix 4	24
Appendix 5	34

1. Introduction

1.1. History

The history of NIR started with the discovery of the existence of infrared radiation in 1800 by Frederick William Herschel (1738-1822), a German astronomer, technical expert and a composer. (Jerry Workman, Jr. Lois Weyer 2008). Herschel have tried different shade glasses between the eye-piece of his telescope and the eye, in order to reduce the inordinate degree of heat and light transmitted by the instrument when directed towards the sun, and observed that at some combinations the amount of light was decreased but the amount of transmitted heat was increased and vice versa. By several experiments he concluded that the full red fell short of the maximum of heat, which, perhaps, lay even a little beyond the limits of the visible spectrum. (Edward Singleton Holden 2009)

1.2. Theory

The vibrations and bending of atomic nuclei of a molecules cause the periodic motions or vibrational spectroscopic activity or molecular spectra which can be measured using any kind of spectroscopic techniques. Each vibration considered harmonic and has a specific frequency accordingly at which it absorbs NIR energy. Here the amplitude of the wavelength or wave number is determined by its absorptivity and the number of molecules encountered within a path of the measuring instrument. (Jerry Workman, Jr. Lois Weyer 2008) Absorptions are generated by combinations and overtones of vibrational transitions.

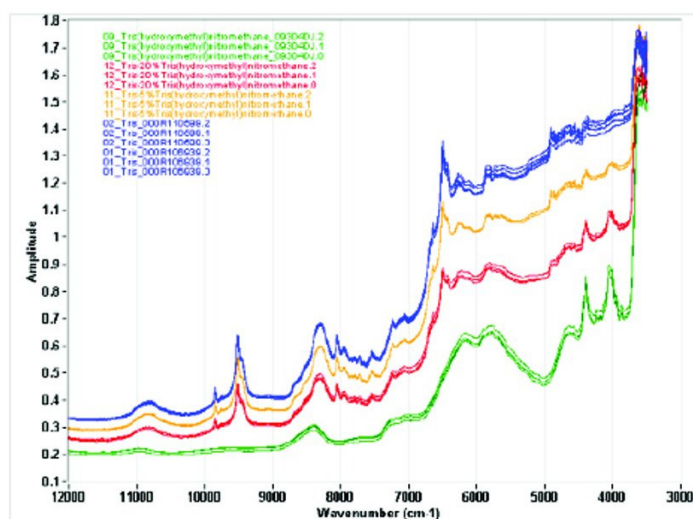


Figure 1. NIR spectra of pure Tris (blue), spiked with 5% (orange), 20% (red) of Tris (hydroxymethyl) nitromethane and NIR spectra of pure Tris (hydroxymethyl) nitromethane (green) (Zai-qing Wen, Ph.D., Guoxiang Chen, Ying Luo, Guiyang Li, Peter Masatani, Pavel Bondarenko, Joseph

Phillips, Ph.D., Dr. Xiaolin Cao, Ph.D. 2012 Assessment of Spectroscopic Techniques for Adulteration Detection of Raw Materials Used in Biopharmaceutical Manufacturing. Department of Drug Product Development. The Review of American Pharmaceutical Business and Technology).

1.3. Possibilities

NIR spectroscopy has a great potential in usage as an analysing monitoring technology. Firstly, NIR spectroscopy usage is non-destructive and non-invasive, fast, low maintenance cost where no use of reagents is needed and no residuals are produced. Secondly, it is fast, simple and inexpensive analysis technique that allow continuous and in situ monitoring that allows determining several parameters simultaneously. (Dias A. M. A., Moita I. 2008).

2. Equipment

2.1. NIR spectroscopy

The NIR spectra in the following experiments were collected with a GetSpec spectrometer, model #: NIR-256L-1.7T1 (Sentronic GmbH, Gostritzer Str. 61-63, D-01217 Dresden, Germany) with the spectral range 900-1700nm. This diode array instrument has an Indium-Gallium-Arsenide (InGaAs) detector with 256 elements. The spectrometer was equipped with a dip probe (getSpec.com, Gostritzer Str. 61-63, D-01217 Dresden, Germany), which was set to 1 mm gap size, and an AvaLight-HAL tungsten halogen light source (Avantes BV, Oude Apeldoornseweg 28, The Netherlands). The Spec32 v. 1.5.6.8 software was used as interface. (Pekka Stén)

2.2. Modeling

The partial least squares (PLS) models were calculated using the PLS_Toolbox v. 7.3.1 (Eigenvector Research, Inc. 3905 West Eaglerock Drive Wenatchee, WA 98801, USA), together with MATLAB R2011b (The MathWorks AB, Kista, Sweden). (Pekka Stén)

3. Estimation of nitrogen ion

3.1. Method

For measuring the nitrogen ion the salts of potassium nitrate (KNO_3), ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3) and carbamide or urea ($\text{CO}(\text{NH}_2)_2$) were used as sources. These salts were chosen according to the possibility to measure ammonium nitrogen, amid nitrogen and nitrate nitrogen ions which are common in wastewater. The concentrations of the salts solutions were chosen to be similar as in the wastewater. For example, carbamide or urea concentration in wastewater is around 2-6 mg/L in domestic sewage and 0,016-0,043 mg/L in primary sewage plant effluent. (Urea)

The concentration of nitrogen ion in the solution was calculated by the formula (1), where η is the number of moles (mole), C is the concentration (g/L), M is the atomic mass (g/mole) and V is the volume (L):

$$\eta = \frac{C * V}{M} \quad (1)$$

Table 1. Potassium nitrate solution.

Solution					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of nitrogen g/L	η of nitrogen, moles	η of salt, moles
0,361	0,5	0,722	0,10	0,00357	0,00357

Table 2. Ammonium chloride solution.

Solution					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of nitrogen g/L	η of nitrogen, moles	η of salt, moles
0,191	0,5	0,382	0,10	0,00357	0,00357

Table 3. Ammonium nitrate solution.

Solution					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of nitrogen g/L	η of nitrogen, moles	η of salt, moles
0,143	0,5	0,286	0,10	0,00357	0,00178

Table 4. Carbamide solution (urea).

Solution					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of nitrogen g/L	η of nitrogen, moles	η of salt, moles
0,107	0,5	0,214	0,10	0,00357	0,00178

Each salt was divided to ten samples with different concentrations from 10-100 mg of nitrogen ion per L. The solutions were prepared using distilled water.

Table 5. Dilutions.

Volume for diluted solution	50 ml									
Conc., g/L	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09	0,1
Water add, ml	45	40	35	30	25	20	15	10	5	0
Solution need, ml	5	10	15	20	25	30	35	40	45	50
Total solution need:	275 ml									

A total of 40 samples were measured each 3 times by the NIR spectroscopy. The spectra were collected as absorbance spectra with sample average 512 scans from 905 to 1682 nm. The measured data was analyzed using MATLAB and PLS quantitative analysis method.

The data was split into calibration and validation data for analysing total nitrogen, nitrate nitrogen, ammonium nitrogen and amid nitrogen concentrations.

3.2. Results

Table 6. PLS calibration models for total nitrogen, ammonium nitrogen, and nitrate nitrogen and amid nitrogen. The plotted diagrams of calibration are in Appendix 1.

	Total	NH ₃ -N	NO ₃ -N	NH ₂ -N (from urine)
# spectra in calibration	80	80	80	80
# spectra in validation	40	40	40	40
RMSEC (g/L)	0.00360	0.00987	0.00556	0.00827
RMSECV (g/L)	0.02443	0.01264	0.00949	0.01448
RMSEP (g/L)	0.00715	0.01643	0.00798	0.01348
R ²	0.972	0.802	0.947	0.869
CV Bias (g/L)	2.1958e-005	-1.2143e-0.16	0.000182	-9.019e-005
Latent Variables	8	3	4	4

4. Estimation of phosphorous and calcium ions

4.1. Method

Hardness of water plays an important role in metal toxicity, which varies depending on the concentration of Ca ion. Higher the hardness, lower the toxicity of Hg, Pb, Cu and Zn. Soft waters ($<24 \text{ mg/L CaCO}_3$) are more at risk from acidification due to their poor acid neutralizing capacity of water (ANC). (N.F. Gray)

Table 7. Hardness of water scale for CaCO_3 concentration.

Classification	hardness in mg/L
Soft	0–60
Moderately hard	61–120
Hard	121–180
Very hard	≥ 181

Phosphorous is one of the major nutrients causes the increase of eutrophication of surface waters. Its presence causes many water quality problems including increasing purification costs, decreasing recreational and conservation value of an impoundments, loss of livestock and the possible lethal effect of algal toxins on drinking water. (Linntech)

For measuring the calcium and phosphorous ions the salts of calcium hydrogen phosphate ($\text{CaH}_2\text{P}_2\text{O}_7$) and calcium carbonate (CaCO_3) were used as sources. The concentrations of the salts solutions were chosen to be similar as in the wastewater. The concentration of Ca and P ions in the solutions was calculated by the formula (1).

Table 8. Calcium hydrogen phosphate solution.

Calcium hydrogen phosphate Solution $\text{CaH}_2\text{P}_2\text{O}_7$					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of P g/L	η of P, moles	η of salt, moles
0,044	0,5	0,088	0,02	0,00032	0,00032

Table 9. Calcium carbonate solution.

Calcium carbonate CaCO_3 Solution					
Volume, L	0,5				
Mass of salt, g	V of water, L	Concentration of salt g/L	Concentration of Ca g/L	η of Ca, moles	η of salt, moles
0,100	0,5	0,200	0,08	0,0010	0,0010

Each salt was divided in to ten samples with different concentrations due to the dilution. The solutions were prepared using distilled water.

Table 10. Dilution for calcium hydrogen phosphate solution.

Volume for diluted solution										
50 ml										
Conc., g/L	0,002	0,004	0,006	0,008	0,01	0,012	0,014	0,016	0,018	0,02
Water add, ml	45	40	35	30	25	20	15	10	5	0
Solution needed, ml	5	10	15	20	25	30	35	40	45	50
Total solution need: 275 ml										

Table 11. Dilution for calcium carbonate solution.

Volume for diluted solution										
50 ml										
Conc., g/L	0,008	0,016	0,024	0,032	0,04	0,048	0,056	0,064	0,072	0,08
Water add, ml	45	40	35	30	25	20	15	10	5	0
Solution needed, ml	5	10	15	20	25	30	35	40	45	50
Total solution need: 275 ml										

The spectra were collected as absorbance spectra with sample average 512 scans from 905 to 1682 nm as a single measurement. Measured data was analyzed using MATLAB and PLS quantitative analysis method.

4.2. Results

Table 12. PLS calibration models for phosphorous and calcium ions. The plotted diagrams of calibration are in Appendix 2.

	Phosphorous	Calcium
# spectra in calibration	20	20
# spectra in validation	10	9
<i>RMSEC (g/L)</i>	0.00038	0.00074
<i>RMSECV (g/L)</i>	0.00090	0.00151
<i>RMSEP (g/L)</i>	0.00063	0.00197
R^2	0.993	0.998
CV Bias (g/L)	8.4877e-005	-3.469e-017
<i>Laten Variables</i>	4	3

5. Estimation of COD and suspended solids in wastewater

5.1. Method

Table 13. Typical raw wastewater composition (N.F. Gray).

Parameter	US (mg/L)	UK (mg/L)
pH	7	7
BOD	250	350
COD	500	700
Suspended solids	250	400
Ammonia nitrogen	30	40
Nitrate nitrogen	<1	<1
Total phosphorus	10	15

For measuring the COD and suspended solids the wastewater from the Pått wastewater treatment plant was used. The water was analysed before the NIR measurements in the laboratory for the COD measurements.

The wastewater was diluted using distilled water to: 1: 5, 1: 10, 1: 25, 1: 50, 1: 70, and 1: 100.

Table 14. Concentrations of COD in wastewater.

Dilution	COD (mg/L)
1:0	378,7
1:5	75,7
1:10	37,9
1:25	15,1
1:50	7,6
1:70	5,4
1:100	3,8

Six wastewater solutions including the undiluted wastewater were divided to three samples each. And each sample was measured 3 times by the spectroscope.

For estimating the suspended solids by NIR the wastewater was boiled and the solid residuals were used for changing the concentration of suspended solids contamination in the wastewater samples. Nine solutions of wastewater were prepared by adding the solid residuals with different amount.

These nine wastewater solutions were divided to three samples each. And each sample was measured 3 times by the spectroscope. The spectra were collected as absorbance spectra with sample average 512 scans from 905 to 1682 nm as a single measurement.

Table 15. *Concentration of suspended solids in wastewater.*

	Add. Mass, g	Suspended solids concentration mg/L
C1	0,0082	614
C2	0,0137	834
C3	0,0149	882
C4	0,0216	1150
C5	0,0315	1546
C6	0,0372	1774
C7	0,0443	2058
C8	0,0511	2330
C9	0,0597	2674

The measured data was analyzed using MATLAB and PLS quantitative analysis method.

5.3. Results

Table 16. PLS calibration models for COD and suspended solids in wastewater. The plotted diagrams of calibration are in Appendix 3.

	COD	Suspended solids
# spectra in calibration	42	54
# spectra in validation	21	27
<i>RMSEC (mg/L)</i>	8.3235	95.8144
<i>RMSECV (mg/L)</i>	20.0333	205.3821
<i>RMSEP (mg/L)</i>	14.7441	122.5476
<i>R²</i>	0.993	0.976
CV Bias (mg/L)	-1.2206	1.7237
<i>Laten Variables</i>	8	8

6. Estimation of nitrogen through the pipe system

6.1. Pipe system

The laboratory scale sewerage system for detection of contaminants in wastewater was built by the students of European Project Semester (EPS) in 2013: Victor Benavides, Andreas Forsman, Wang Liangfu, Alicja Malik.

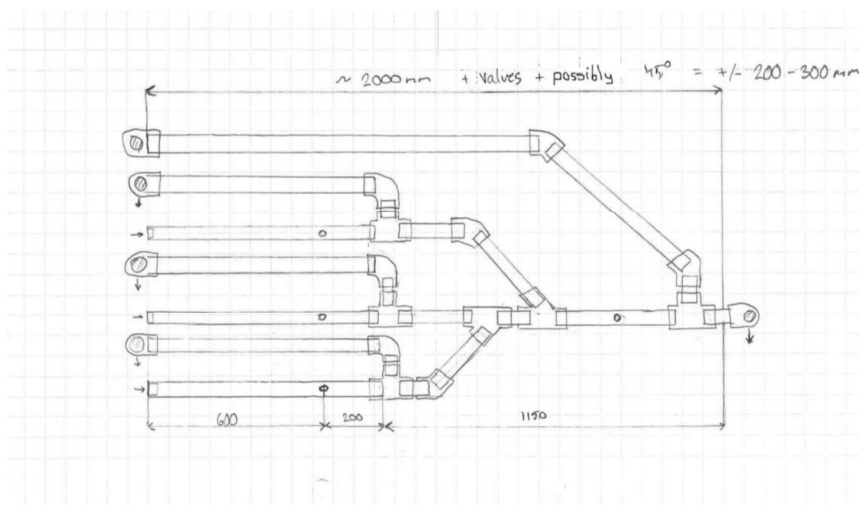


Figure 2. Pipe system.

Pipes are connected with the basins of 25, 25 and 50 liters supplied by 3 pumps to get the fluid flow by 4 possible circuits (3 small and 1 big which allows to mix the liquid from each 3 circuit). The system allows the use of the spectrometer for analyzing the contaminants of flowing liquid on-line. (Benavides, V. Forsman, A. Malik, A. Wang, L.)

6.2. Single component pulses

6.2.1. Description of the experiments and the results

For the first experiment ammonium chloride (NH_4Cl) with concentration of 1 g/L was chosen as an injecting liquid and tap water as a main circulating liquid. The injection was repeated for 3 times with the volume 100 ml to the 10 L of circulating water in the pipes. The probe of the spectrometer was inserted in the pipe system so that the measurements were taken directly from the pipe. The spectra were collected continuously as absorbance spectra with sample average 512 scans from 905 to 1682 nm and time interval 10 second. Injections were made at 10, 100 and 200 number of spectra.

The measured data was analyzed by MATLAB by using the earlier constructed model for ammonium nitrogen with pure samples. (Chapter 2. Estimation of nitrogen)

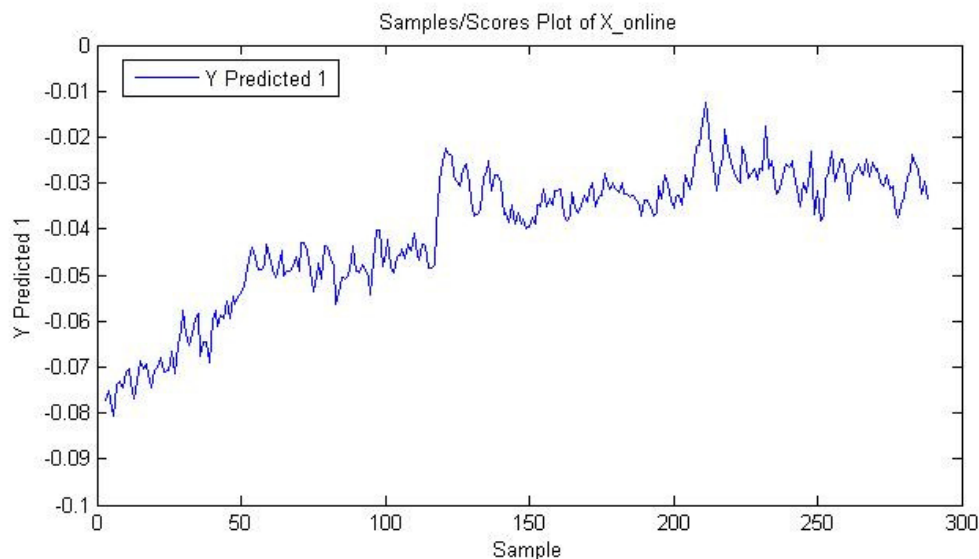


Figure 3. First experiment predictions.

For the second experiment it was decided to increase the time between the pulses to understand the behaviour of the injection dissolving process more clearly. The number of pulses, the concentration and the volume of the injected solution remained the same. The probe of the spectrometer was inserted in the pipe system so that the measurements were taken directly from the pipe. The spectra were collected continuously as absorbance spectra with sample average 512 scans from 905 to 1682 nm and time interval 10 second. Injections were made at 20,200 and 400 number of samples.

The measured data was analyzed by MATLAB by using the earlier constructed model for ammonium nitrogen with pure samples. (Chapter 2. Estimation of nitrogen)

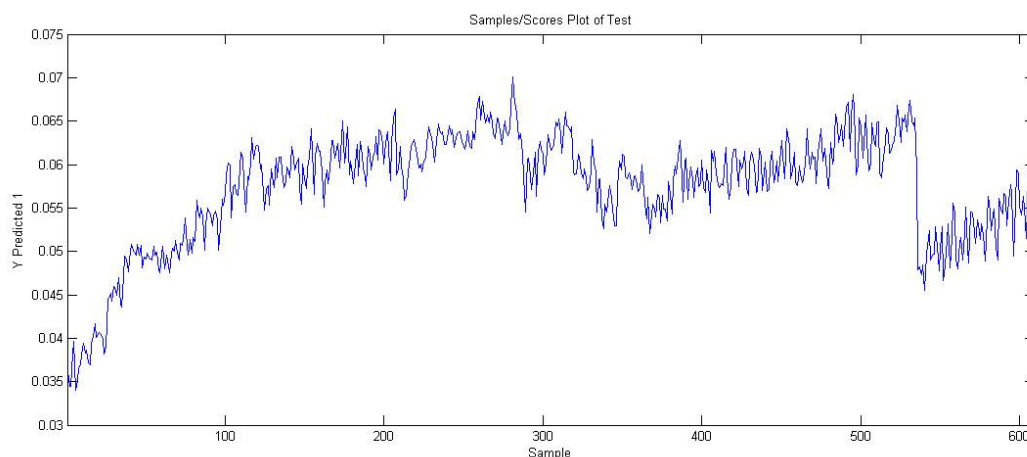


Figure 4. Second experiment predictions.

In the third experiment the number of pulses was increased to 5. However, the number of spectra in the beginning without any injection was increased to check the measurement of zero concentration. In addition the injection volume changed to 30 ml. All other characteristics remained constant. The injections were made at 100, 200, 300, 400 and 500 number of spectra. The probe of the spectrometer was inserted in the pipe system so that the measurements were taken directly from the pipe. The spectra were collected continuously as absorbance spectra with sample average 512 scans from 905 to 1682 nm and time interval 10 second.

The measured data was analyzed by MATLAB by using the earlier constructed model for ammonium nitrogen with pure samples. (Chapter 2. Estimation of nitrogen)

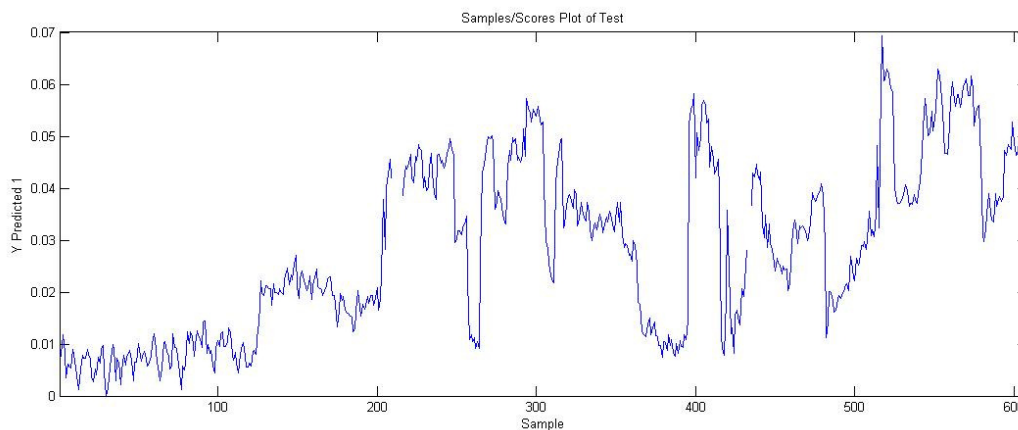


Figure 5. *Third experiment predictions.*

6.2.2. Discussion

The results showed that the predictions are not directly related to the changes of the nitrogen concentration in the pipe system. The cause of the problem might have been the low concentration of nitrogen that cannot be determined by such a model or the air bubbles. Air bubbles were getting stuck in the spectrometer probe disturbing the rate of light absorbance. Moreover, the mixing process in the pipes was not determined either.

6.3. Ethanol pulses

6.3.1. Description of the experiments

To determine the problem causing the wrong results and to understand the behaviour of the water in the pipes it was decided to change the injection solution to 99% ethanol (C_2H_5OH). As this compound is well known and easy to determine in NIR spectra. The dilution solution in the pipe system was the tap water. The probe of the spectrometer was inserted in the pipe system so that the measurements were taken directly from the pipe. The spectra were collected continuously as absorbance spectra with sample average 512 scans from 905 to 1682 nm and time interval 10 second.

6.3.2. Discussion

After analyzing the results it became clear that the problem was caused by the air bubbles. As the spectroscopy probe was inserted in the pipe system the air bubbles were getting stuck in the probe messing the measurements.

To reduce this problem new way of measuring was suggested. The probe should be located under the flow of falling water which would push the collected air bubbles. The average number of scans was changed to 64 and the time interval to 1 second during the measurements for more precise data. This method was proved by the following experiments with the 99% ethanol.

6.4. Pulses with several components

6.4.1. Description of the experiments and the results

When the problem with the air bubbles was fixed it was decided to run more complicated experiments with injections of several components into the pipe system. The compounds were chosen according to the wastewater contamination and the earlier constructed PLS models for the prediction. So for these experiments the salts of potassium nitrate (KNO_3), ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3) and carbamide or urea ($\text{CO}(\text{NH}_2)_2$) were used. The dilution solution in the pipe system was the tap water. The system of injections of solutions of these salts was initially decided so that the increase or the decrease or the concentration of nitrogen ions can be observed. The total amount of experiments performed was three. The difference between the first and the second experiments is the system of the injections. The third experiment is the repeated second one.

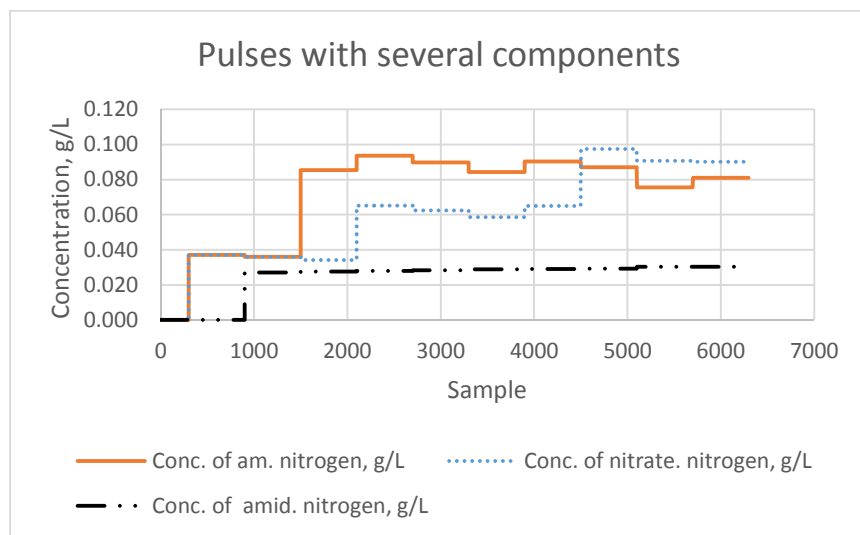


Figure 6. Concentration of the nitrogen ions in the first experiment.

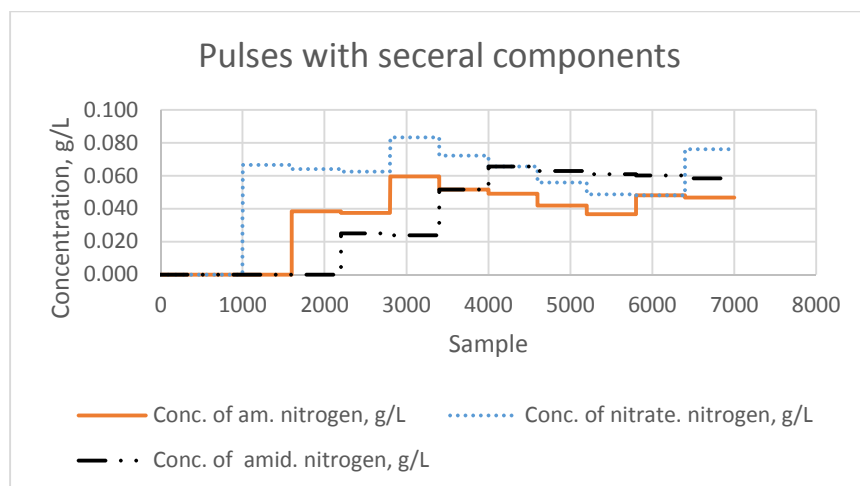


Figure 7. Concentration of the nitrogen ions in the second and third experiment.

The table of the injections and the plots of the calculated prediction of the concentrations of the nitrogen ions are in the Appendix 4.

The probe of the NIR spectroscope was located under the flow of falling water. The spectra were collected continuously as absorbance spectra with sample average 64 scans from 905 to 1682 nm and time interval 1 second.

6.4.2. Results

The results of the predictions from the first experiment made by the earlier constructed model for the nitrogen ions with pure samples (Chapter 2. Estimation of nitrogen) were not satisfying. The predicted concentrations were not related to the calculated ones numerically and the graphs of calculated concentration to the number of samples and the predicted concentrations to the number of samples were not graphically similar either. The plots with the predictions from the PLS quantitative analysis method are in the Appendix 4.

The results for the second experiment had the same quality as the first one, which predictions plots made by the earlier constructed model for the nitrogen ions with pure samples (Chapter 2. Estimation of nitrogen) can be found in the Appendix 4.

The second experiment was repeated as the third experiment. The collected spectra from the third experiment were analysed for prediction with PLS by using the model based on the first experiment. These models were based on the calculated concentrations of the solution after the injection. The results of these predictions did not give reliable information either. The plots of the models from the first experiment and the plots of the predicted results by these models are in the Appendix 4. The collected spectra from the second experiment were analysed for prediction with PLS by using the model based on the third experiment also.

6.4.3. Discussion

The predictions made in MATHLAB by using pure samples models were not related to the actual concentration of the nitrogen ions in the water. This can be caused by the too small concentrations of the nitrogen ions and the spectra measured are mainly of a water molecule.

The models based on the experiments are quite good and reasonable. However, when these models are applied for the predictions for the concentration no relation is observed.

6.5. Pulses with several components with big concentration

This experiment purpose is to observe the prediction for the larger concentration of the nitrogen ions in the water. The compounds were chosen to be same as the previous several components experiments. The dilution solution in the pipe system was the tap water. The concentration of the injecting solutions was dramatically increased and chosen according to the solubility properties of the salts.

Table 17. Concentration of the injecting solutions.

Name	Chemical formula	Conc. g/L
Potassium nitrate	KNO ₃	30
Ammonium chloride	NH ₄ Cl	30
Ammonium nitrate	NH ₄ NO ₃	15
Carbamide	CO(NH ₂) ₂	10

The table of the injections and the plots of the calculated prediction of the concentrations of the nitrogen ions are in the Appendix 5.

The probe of the NIR spectroscope was located under the flow of falling water. The spectra were collected continuously as absorbance spectra with sample average 64 scans from 905 to 1682 nm and time interval 1 second.

6.5.1. Results

The collected spectra were analysed for the prediction by the earlier constructed model for the nitrogen ions with pure samples (Chapter 2. Estimation of nitrogen). The plots with the predictions from the PLS quantitative analysis method are in the Appendix 5.

6.5.2. Discussion

The results of the prediction from this experiment shows are more exact the predictions of the experiments with smaller concentration of the nitrogen ions. Each injection can be easily observed on the plots with the predicted data. However, the concentration values from the prediction are not as the calculated one which can be explained due to the model.

References

Internet

Urea. Identifiers, Physical and Chemical properties. *UNEP Publications. IRPTIC Data Profile.*

<http://www.inchem.org/documents/sids/sids/57136.pdf>

Lenntech. Phosphorous removal.

<http://www.lenntech.com/phosphorous-removal.htm>

Benavides, V. Forsman, A. Malik, A. Wang, L. Laboratory scale sewerage system for detection of contaminants in wastewater, Report, European Project Semester (2013)

http://www.mare-purum.eu/publications/EPS_2013_Final_Report.pdf

Bibliography

Dias A. M. A., Moita I., Páscoa R., Alves M. M., Lopes J. A. and Ferreira E. C. 2008 Activated sludge process monitoring through in situ near-infrared spectral analysis. *Water Science and Technology*, **57**(10), 1643–1650.

Jerry Workman, Jr. Lois Weyer 2008 Practical guide to interpretive near-infrared spectroscopy. *Taylor and Francis Group, LLC* **1**(1.1-1.3) 1-3, **13**(13.1-13.3) 107-109

Edward Singleton Holden 2009 Sir William Herschel: His Life and Works. *The Project Gutenberg EBook of Sir William Herschel: His Life and Works* **4** 199-202

N.F. Gray Ph.D.,Sc.D. 2010 Water technology. An introduction for environmental scientists and engineers. Third edition. *Elsevier Ltd.*, **13**(13.1) 403-411

Pekka Stén, John Dahlbacka, Tom Lillhonga, Steven Ulbricht, Sonja Heikkilä, Juha Nieminen 2014 Transient responses of a laboratory-scale activated sludge plant to momentary high sludge loads. *The 9th International Conference “ENVIRONMENTAL ENGINEERING”* **2**(2.1)

Appendixes

Appendix 1

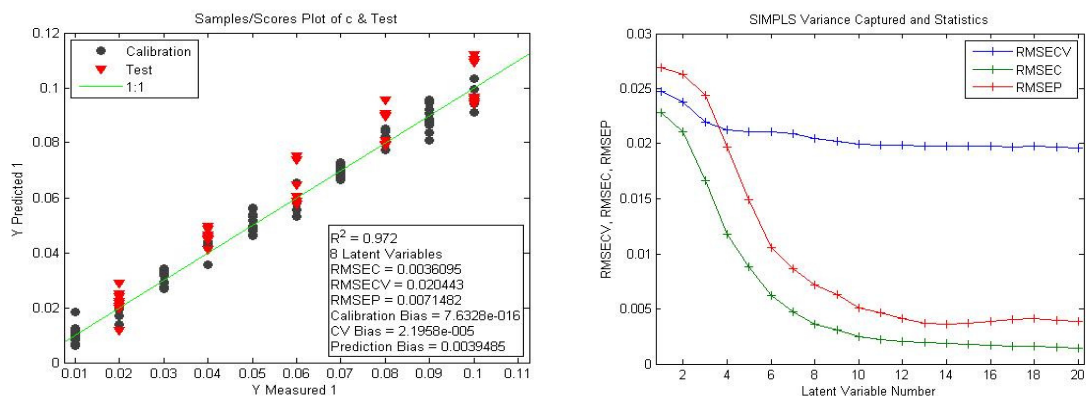


Figure 8. Total nitrogen.

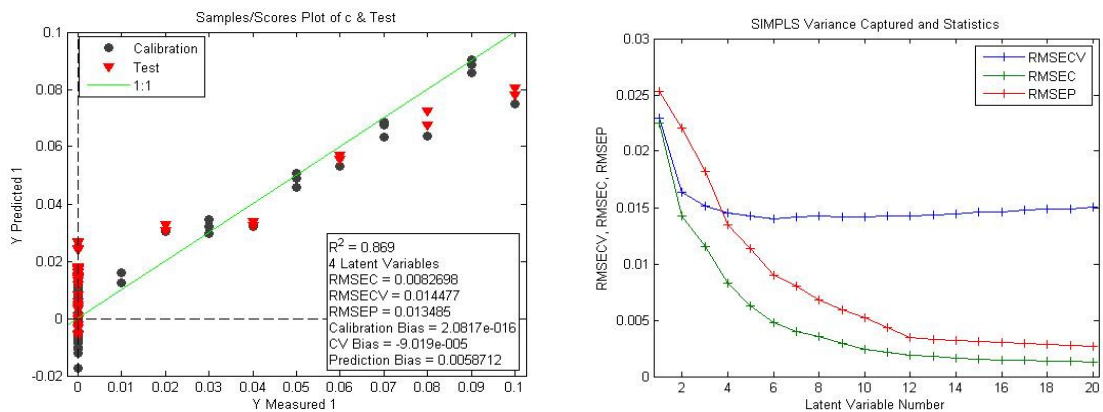


Figure 9. NH_2 -nitrogen.

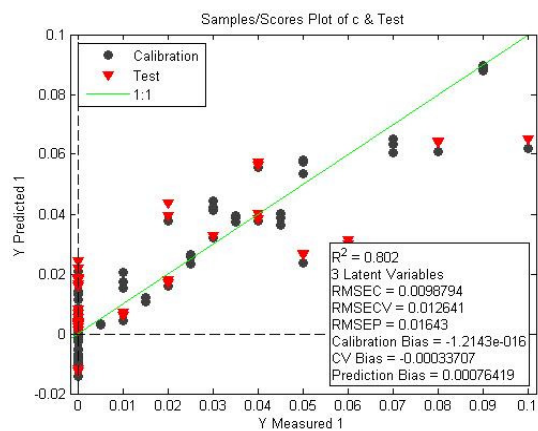


Figure 10. NH_3 nitrogen.

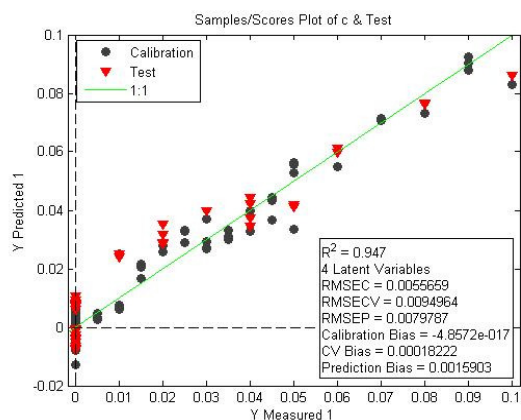
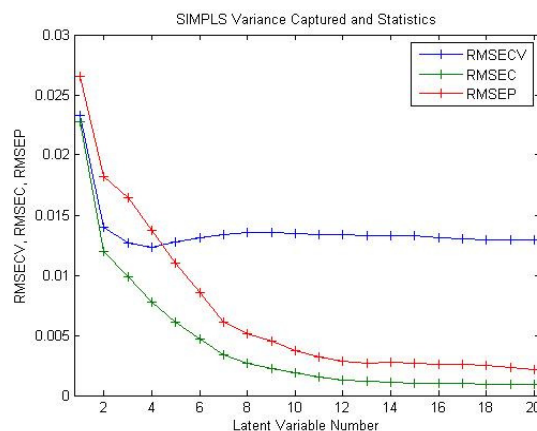
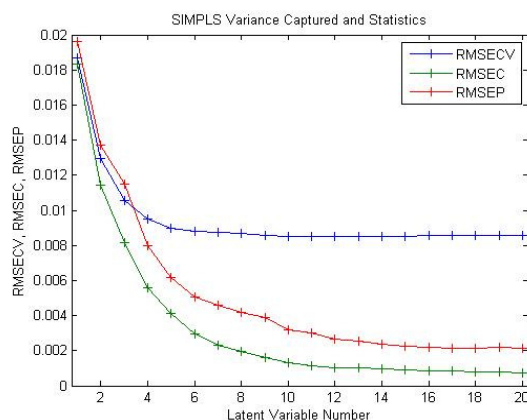


Figure 11. NO_3 nitrogen.



Appendix 2

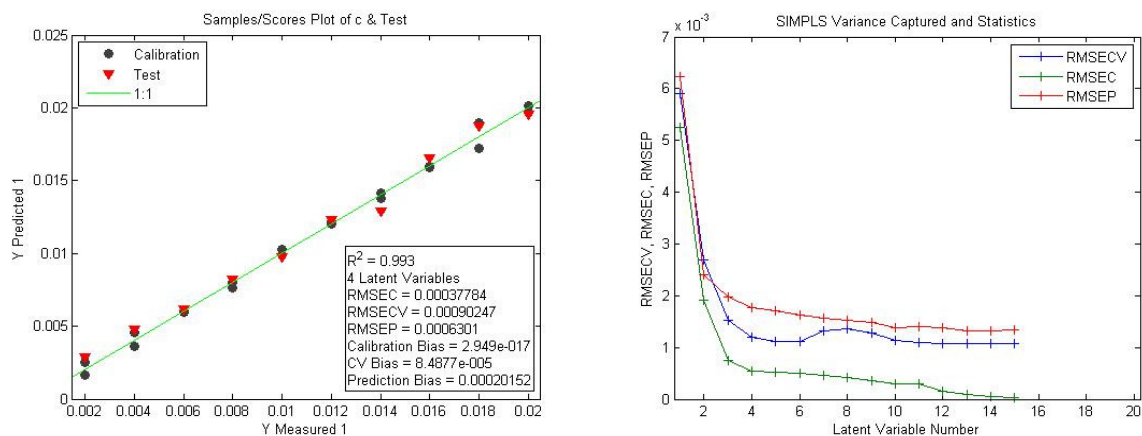


Figure 12. Phosphorous.

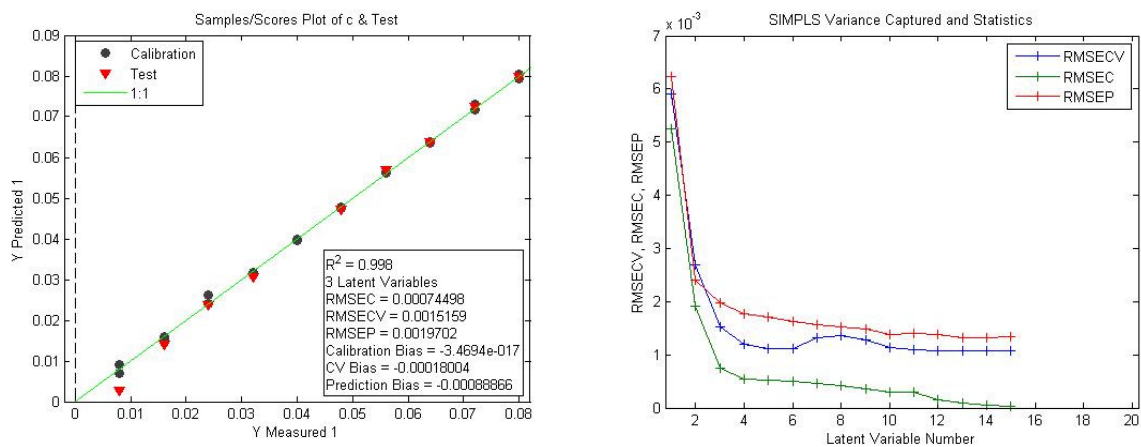


Figure 13. Calcium.

Appendix 3

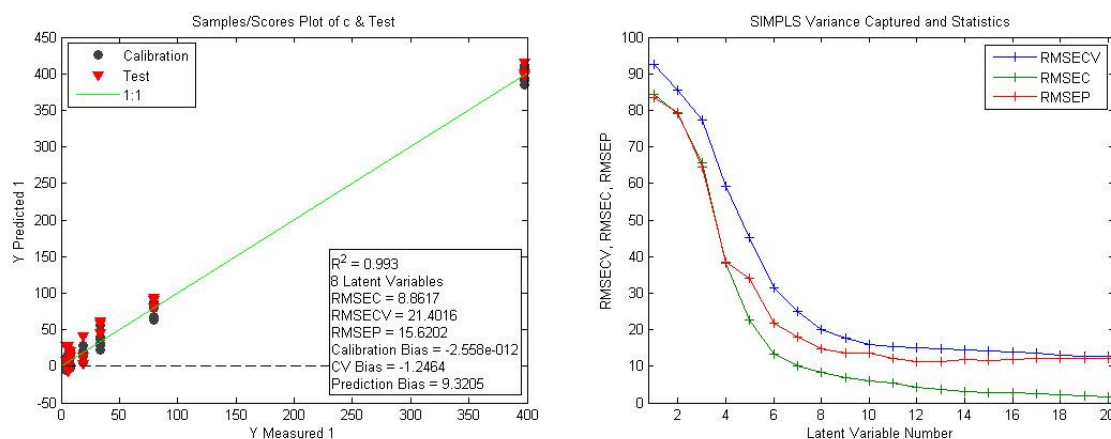


Figure 14. Wastewater, COD.

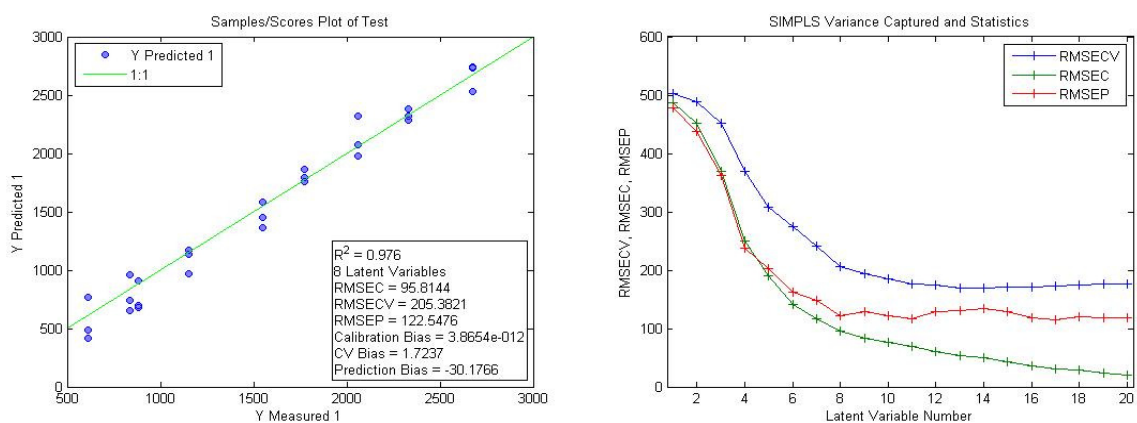


Figure 15. Wastewater, suspended solids.

Appendix 4

Table 18. Experiment 1 table of injections in the first experiment.

# of pulse	# of spectra	Total volume, L	Add of water	Add. Volume of Potassium nitrate	Add. Volume of Amm. chloride ,L	Add. Volume of Ammonium nitrate	Add. Volume of Carbamide,L	Conc. of am. nitrogen, g/L	Conc. of nitrate. nitrogen, g/L	Conc. of amid. nitrogen, g/L	Total, g/L
	0	10,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
0	300	10,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
1	301	10,8	0,0	0,000	0,000	0,800	0,000	0,037	0,037	0,000	0,074
2	900	10,8	0,0	0,000	0,000	0,000	0,000	0,037	0,037	0,000	0,074
3	901	11,1	0,0	0,000	0,000	0,000	0,300	0,036	0,036	0,027	0,099
4	1500	11,1	0,0	0,000	0,000	0,000	0,000	0,036	0,036	0,027	0,099
5	1501	11,7	0,0	0,000	0,600	0,000	0,023	0,085	0,034	0,028	0,147
6	2100	11,7	0,0	0,000	0,000	0,000	0,000	0,085	0,034	0,028	0,147
7	2101	12,3	0,0	0,400	0,150	0,000	0,021	0,094	0,065	0,028	0,187
8	2700	12,3	0,0	0,000	0,000	0,000	0,000	0,094	0,065	0,028	0,187
9	2701	12,8	0,5	0,000	0,000	0,000	0,019	0,090	0,062	0,028	0,181
10	3300	12,8	0,0	0,000	0,000	0,000	0,000	0,090	0,062	0,028	0,181
11	3301	13,6	0,8	0,000	0,000	0,000	0,031	0,084	0,059	0,029	0,172
12	3900	13,6	0,0	0,000	0,000	0,000	0,000	0,084	0,059	0,029	0,172
13	3901	13,9	0,0	0,000	0,000	0,200	0,008	0,090	0,065	0,029	0,184
14	4500	13,9	0,0	0,000	0,000	0,000	0,000	0,090	0,065	0,029	0,184
15	4501	14,4	0,0	0,500	0,000	0,000	0,019	0,087	0,097	0,029	0,214
16	5100	14,4	0,0	0,000	0,000	0,000	0,000	0,087	0,097	0,029	0,214
17	5101	16,6	2,0	0,100	0,000	0,000	0,081	0,076	0,091	0,030	0,196
18	5700	16,6	0,0	0,000	0,000	0,000	0,000	0,076	0,091	0,030	0,196
19	5701	16,7	0,0	0,000	0,100	0,000	0,004	0,081	0,090	0,030	0,201
20	6300	16,7	0,0	0,000	0,000	0,000	0,000	0,081	0,090	0,030	0,201
				1,0	0,9	1,0	0,5				

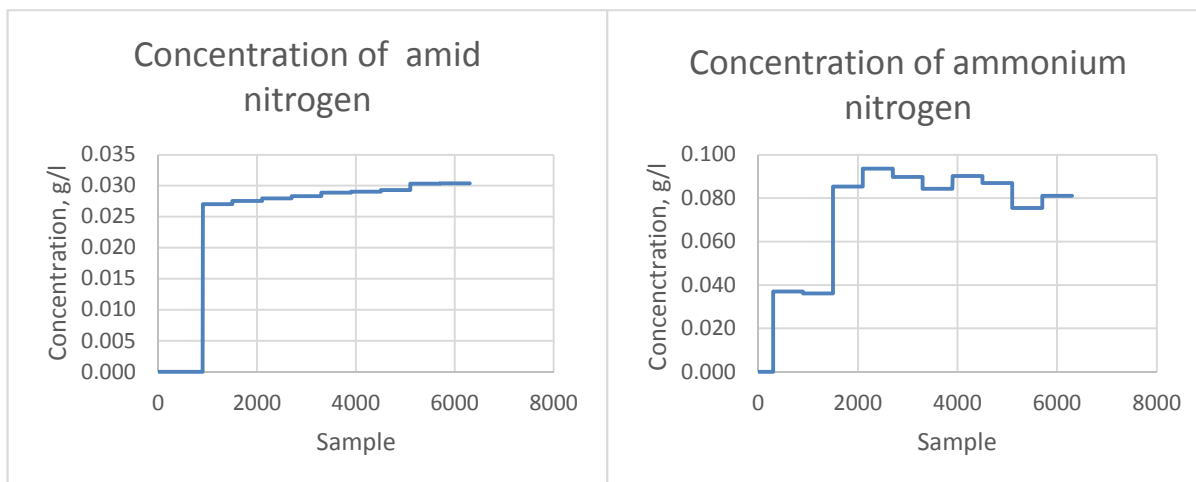


Figure 16. Calculated concentrations during injections in the first experiment.

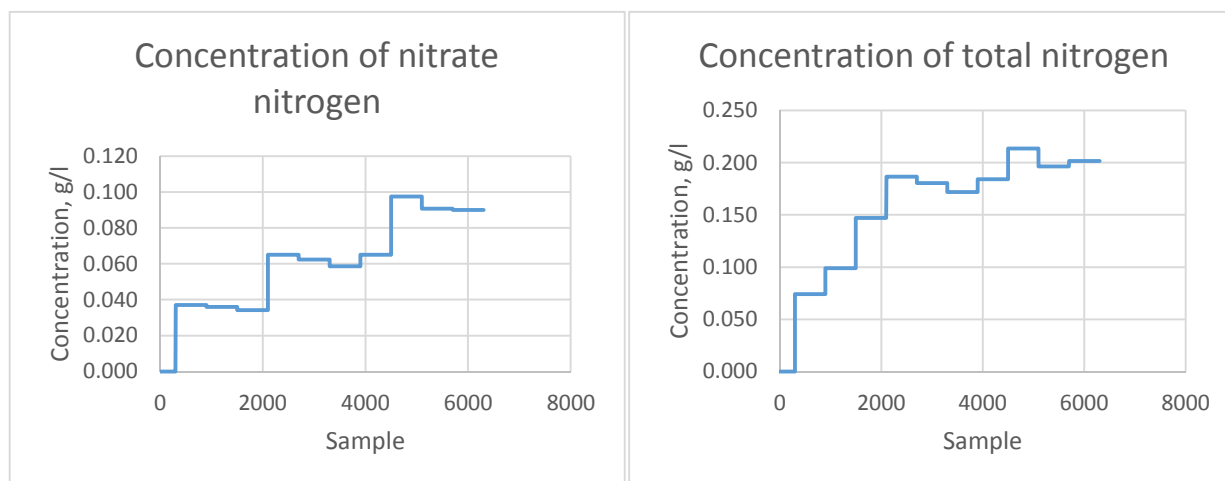


Figure 17. Calculated concentrations during injections in the first experiment.

Table 19. Experiment 2 table of injections in the first experiment.

# of pulse	# of spectra	Total volume, L	Add of water	Add. Volume of Potassium nitrate	Add. Volume of Amm. chloride ,L	Add. Volume of Ammonium nitrate	Add. Volume of Carbamide,L	Conc. of am. nitrogen, g/L	Conc. of nitrate. nitrogen, g/L	Conc. of amid. nitrogen, g/L	Total, g/L
	0	7,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
0	1000	7,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
1	1001	7,5	0,0	0,500	0,000	0,000	0,000	0,000	0,067	0,000	0,067
2	1600	7,5	0,0	0,000	0,000	0,000	0,000	0,000	0,067	0,000	0,067
3	1601	7,8	0,0	0,000	0,300	0,000	0,000	0,038	0,064	0,000	0,103
4	2200	7,8	0,0	0,000	0,000	0,000	0,000	0,038	0,064	0,000	0,103
5	2201	8,0	0,0	0,000	0,000	0,000	0,200	0,038	0,063	0,025	0,125
6	2800	8,0	0,0	0,000	0,000	0,000	0,000	0,038	0,063	0,025	0,125
7	2801	8,4	0,0	0,000	0,000	0,400	0,000	0,060	0,083	0,024	0,167
8	3400	8,4	0,0	0,000	0,000	0,000	0,000	0,060	0,083	0,024	0,167
9	3401	9,7	1,0	0,000	0,000	0,000	0,300	0,052	0,072	0,052	0,175
10	4000	9,7	0,0	0,000	0,000	0,000	0,000	0,052	0,072	0,052	0,175
11	4001	12,2	2,0	0,000	0,000	0,200	0,300	0,049	0,066	0,066	0,180
12	4600	12,2	0,0	0,000	0,000	0,000	0,000	0,049	0,066	0,066	0,180
13	4601	14,3	2,0	0,000	0,000	0,000	0,100	0,042	0,056	0,063	0,161
14	5200	14,3	0,0	0,000	0,000	0,000	0,000	0,042	0,056	0,063	0,161
15	5201	16,4	2,0	0,000	0,000	0,000	0,100	0,037	0,049	0,061	0,146
16	5800	16,4	0,0	0,000	0,000	0,000	0,000	0,037	0,049	0,061	0,146
17	5801	16,6	0,0	0,000	0,200	0,000	0,000	0,048	0,048	0,060	0,157
18	6400	16,6	0,0	0,000	0,000	0,000	0,000	0,048	0,048	0,060	0,157
19	6401	17,1	0,0	0,500	0,000	0,000	0,000	0,047	0,076	0,058	0,181
20	7000	17,1	0,0	0,000	0,000	0,000	0,000	0,047	0,076	0,058	0,181
				1,0	0,5	0,6	1,0				

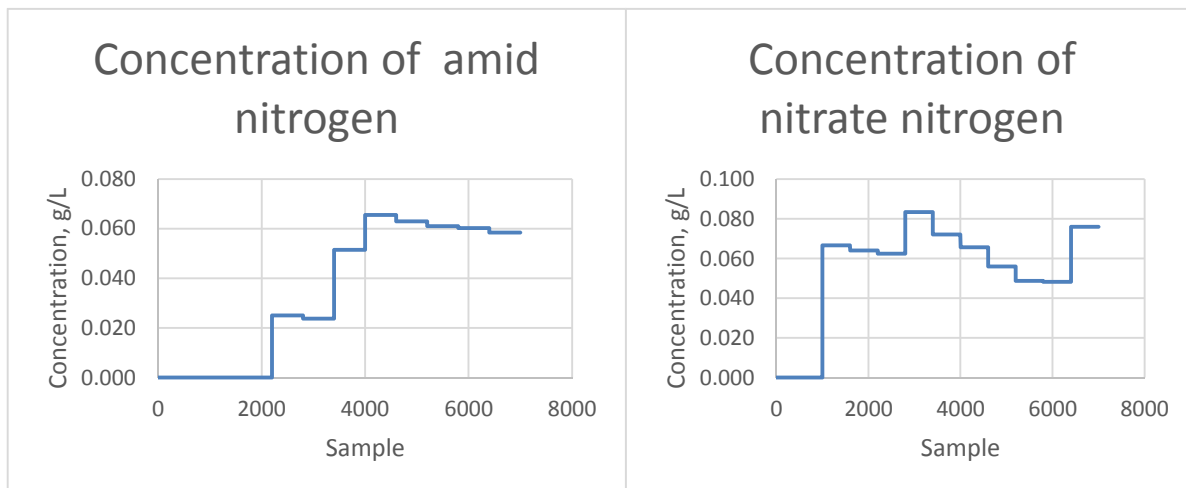


Figure 18. Calculated concentrations during injections in the second and third experiment.

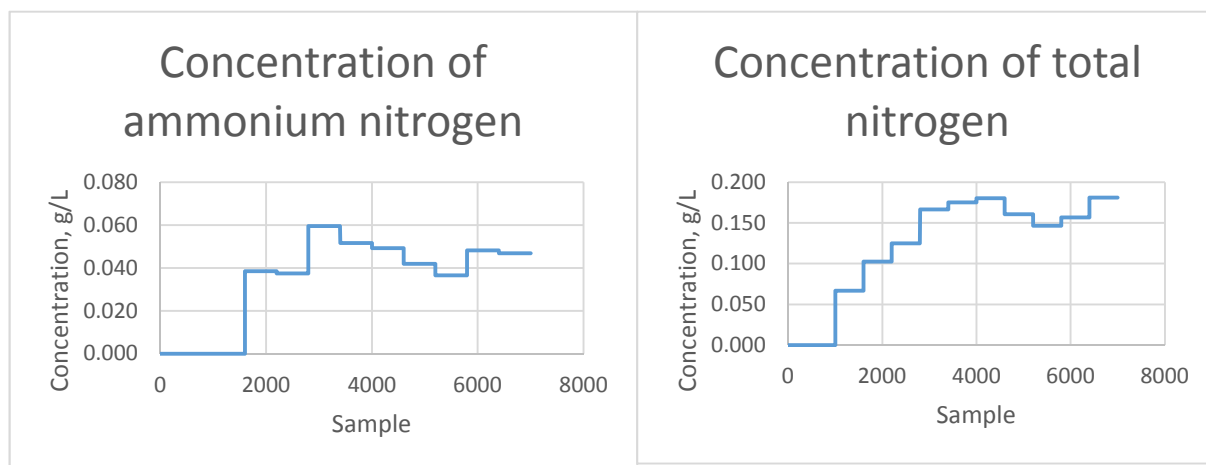


Figure 19. Calculated concentrations during injections in the second and third experiment.

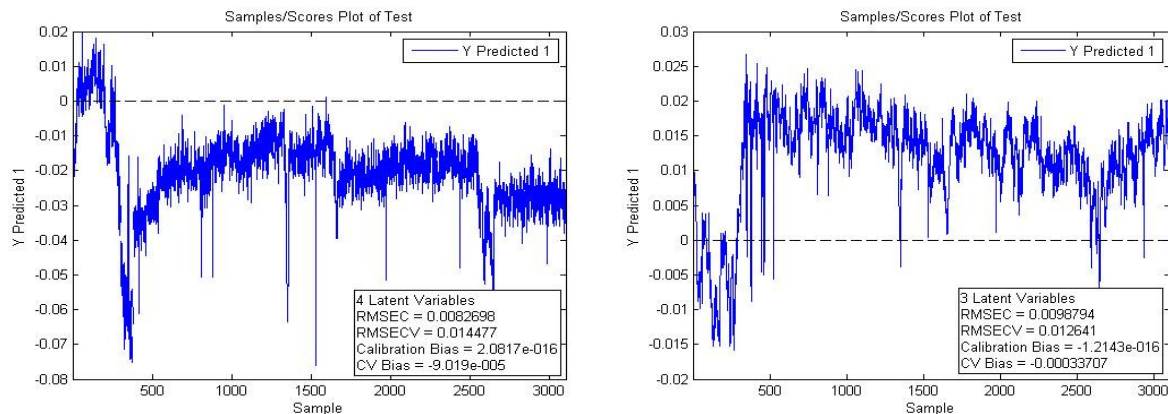


Figure 20. Predicted concentration of amid and ammonium nitrogen in the first experiment based on the model from pure samples.

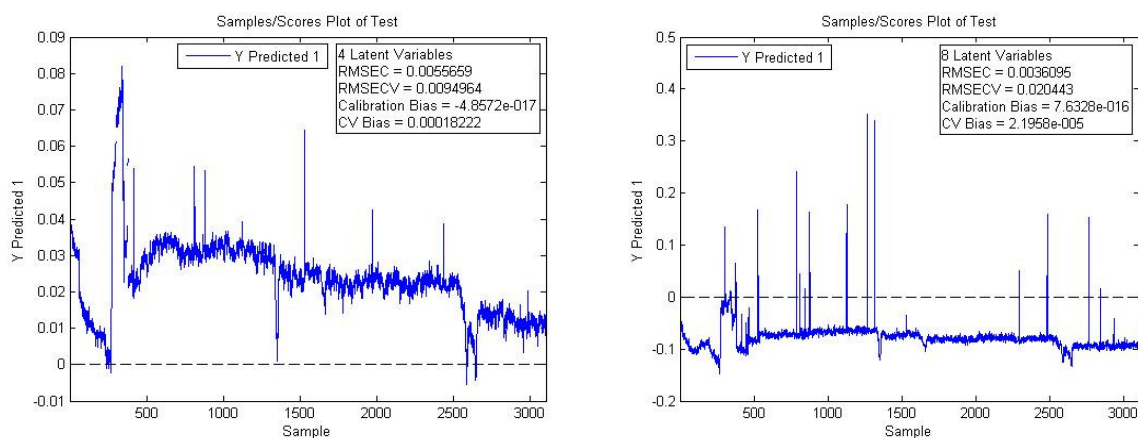


Figure 21. Predicted concentration of nitrate and total nitrogen in the first experiment based on the model from pure samples.

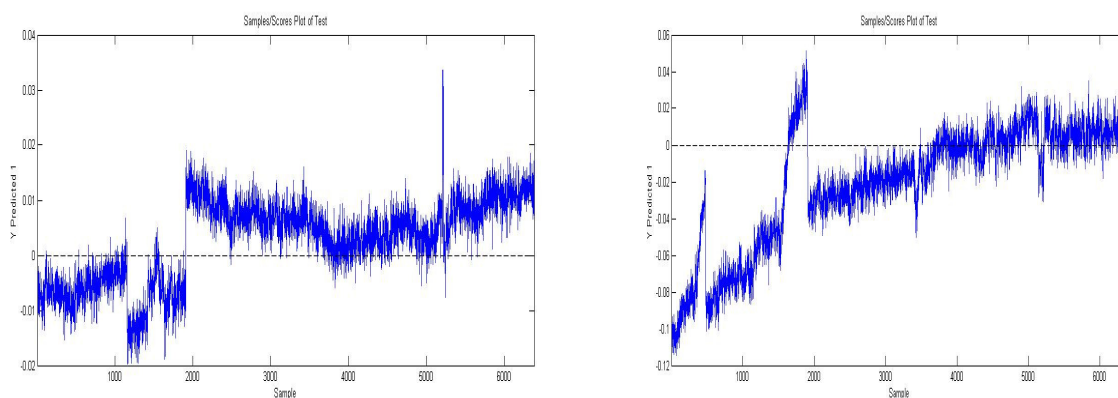


Figure 22. Predicted concentration of amid and ammonium nitrogen in the second experiment based on the model from pure samples.

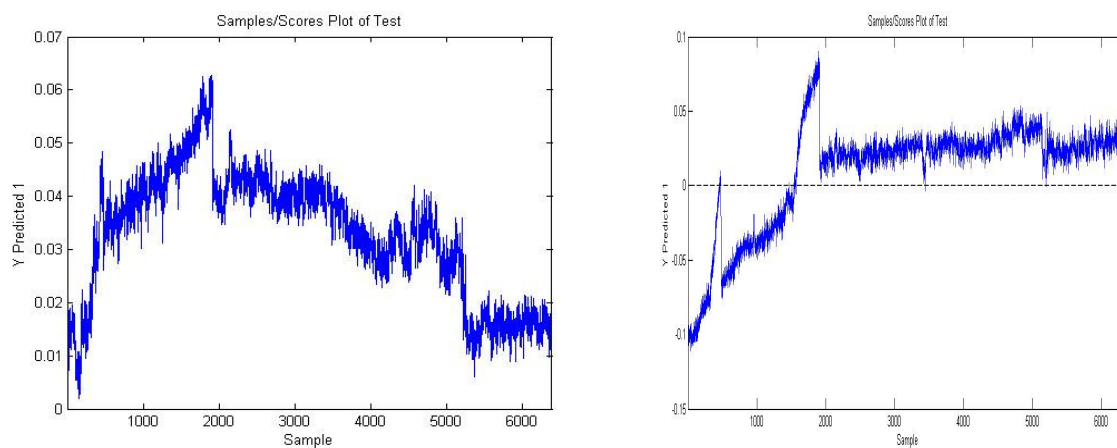


Figure 23. Predicted concentration of nitrate and total nitrogen in the second experiment based on the model from pure samples.

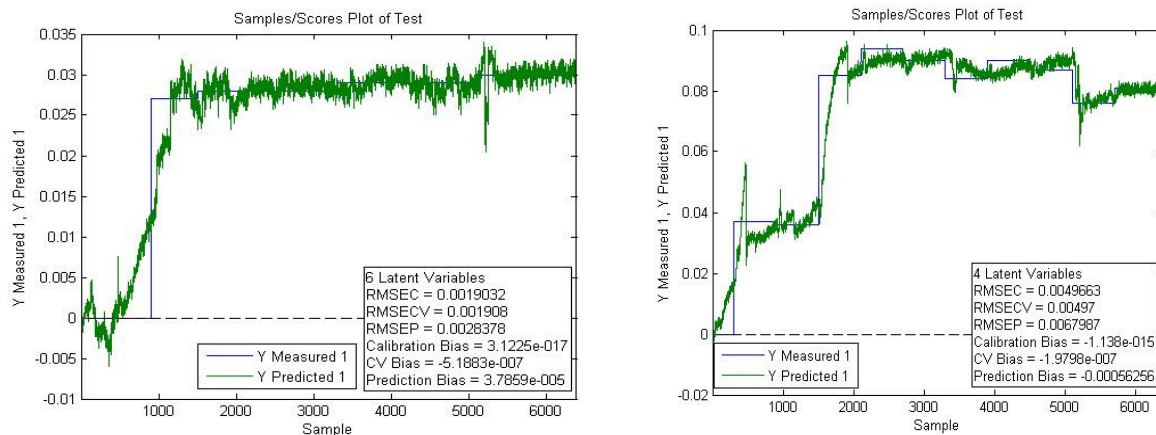


Figure 24. PLS model for concentration of amid and ammonium nitrogen based on the calculated concentrations from the first experiment.

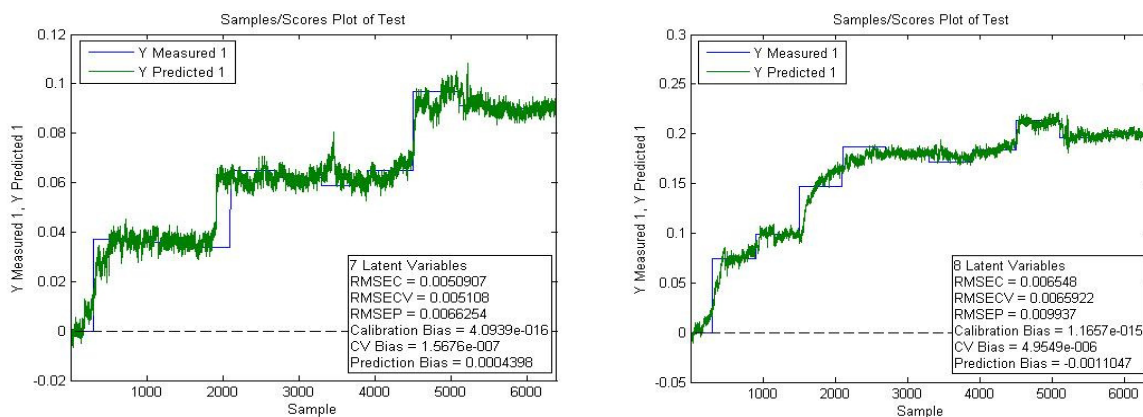


Figure 25. PLS model for concentration of nitrate and total nitrogen based on the calculated concentrations from the first experiment.

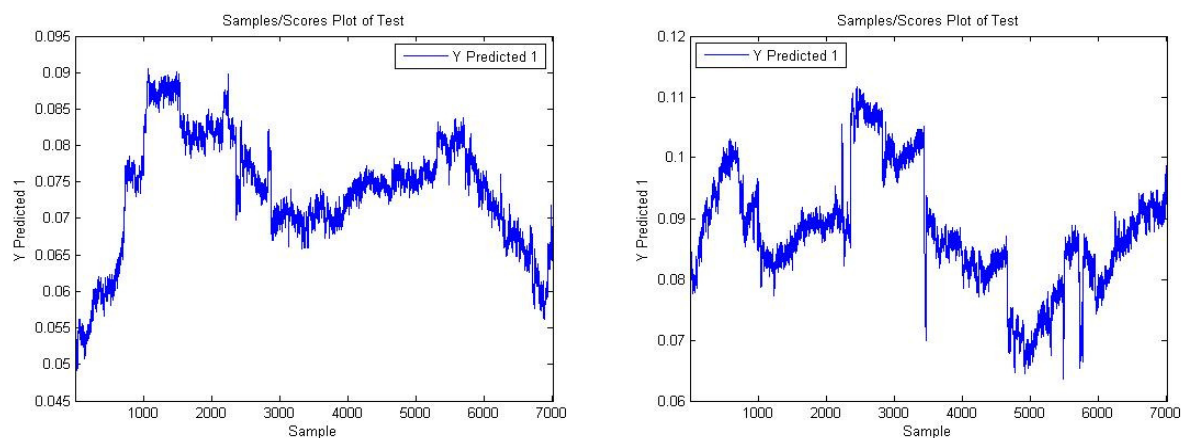


Figure 26. Predicted concentration of amid and ammonium nitrogen by PLS in the third experiment based on the model from the first experiment.

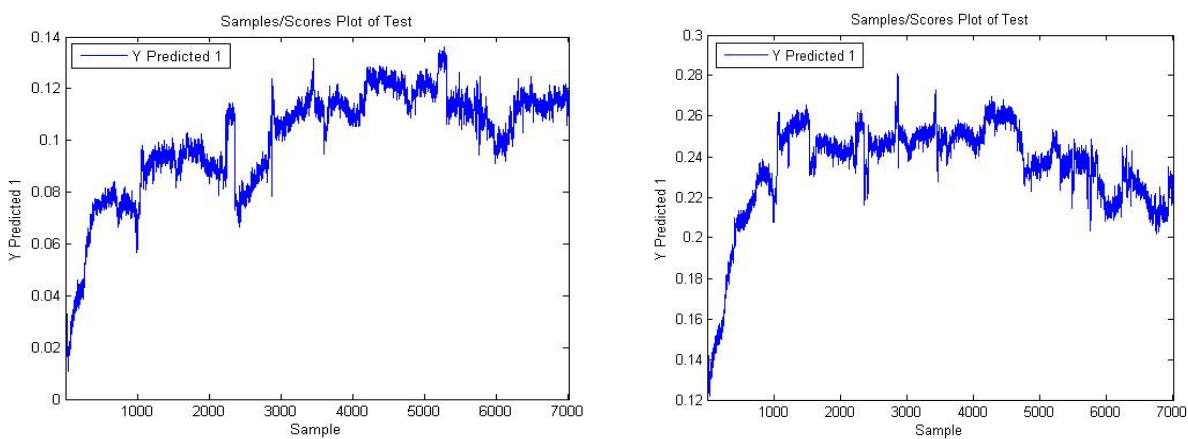


Figure 27. Predicted concentration of nitrate and total nitrogen by PLS in the third experiment based on the model from the first experiment.

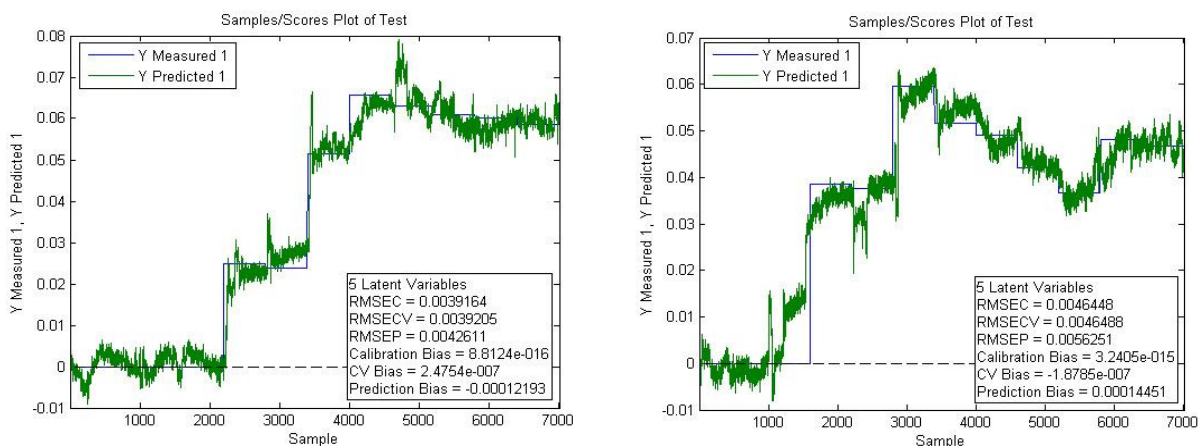


Figure 28. PLS model for concentration of amid and ammonium nitrogen based on the calculated concentrations from the third experiment.

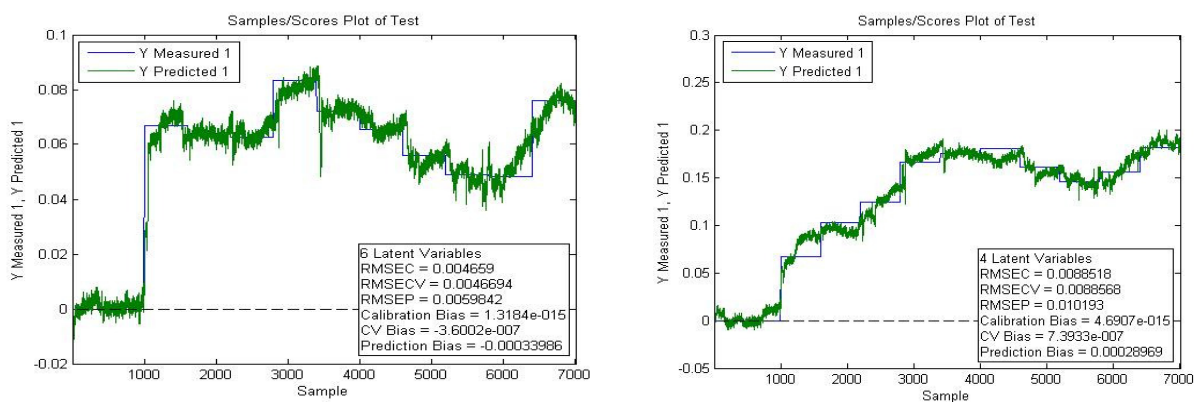


Figure 29. PLS model for concentration of nitrate and total nitrogen based on the calculated concentrations from the third experiment.

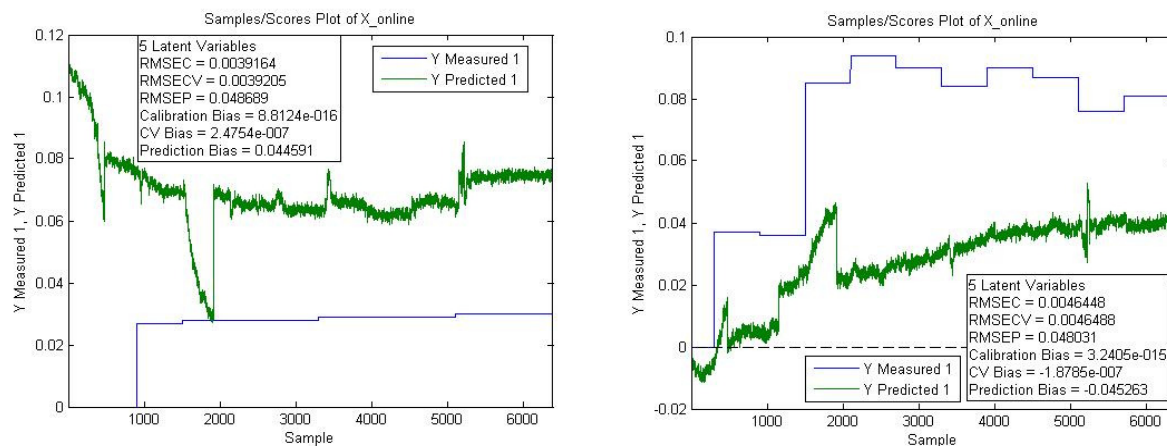


Figure 30. Predicted concentration of amid and ammonium nitrogen by PLS in the second experiment based on the model from the third experiment.

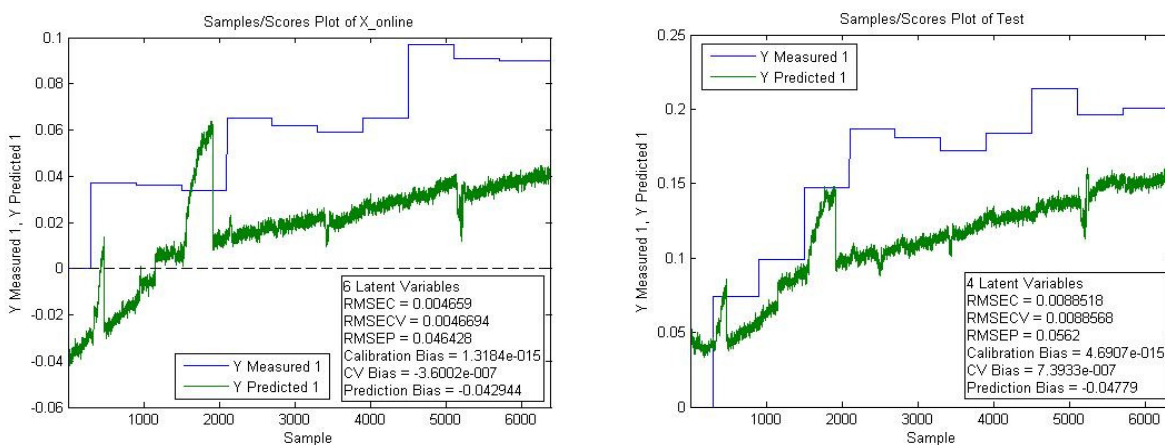


Figure 31. Predicted concentration of nitrate and total nitrogen by PLS in the second experiment based on the model from the third experiment.

Appendix 5

Table 20. Table of injections.

# of pulse	# of spectra	Total volume, L	Add of water	Add. Volume of Potassium nitrate, L	Add. Volume of Ammonium chloride, L	Add. Volume of Ammonium nitrate, L	Add. Volume of Carbamide, L	Conc. of am. nitrogen, g/L	Conc. of nitrate. nitrogen, g/L	Conc. of amid. nitrogen, g/L	Total, g/L
	0	7,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
0	1000	7,0	0,0	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
1	1001	7,5	0,0	0,500	0,000	0,000	0,000	0,000	2,000	0,000	2,000
2	1600	7,5	0,0	0,000	0,000	0,000	0,000	0,000	2,000	0,000	2,000
3	1601	7,8	0,0	0,000	0,300	0,000	0,000	1,154	1,923	0,000	3,077
4	2200	7,8	0,0	0,000	0,000	0,000	0,000	1,154	1,923	0,000	3,077
5	2201	8,0	0,0	0,000	0,000	0,000	0,200	1,125	1,875	0,250	3,250
6	2800	8,0	0,0	0,000	0,000	0,000	0,000	1,125	1,875	0,250	3,250
7	2801	8,4	0,0	0,000	0,000	0,400	0,000	1,429	2,143	0,238	3,810
8	3400	8,4	0,0	0,000	0,000	0,000	0,000	1,429	2,143	0,238	3,810
9	3401	9,7	1,0	0,000	0,000	0,000	0,300	1,237	1,856	0,515	3,608
10	4000	9,7	0,0	0,000	0,000	0,000	0,000	1,237	1,856	0,515	3,608
11	4001	12,2	2,0	0,000	0,000	0,200	0,300	1,107	1,598	0,656	3,361
12	4600	12,2	0,0	0,000	0,000	0,000	0,000	1,107	1,598	0,656	3,361
13	4601	14,3	2,0	0,000	0,000	0,000	0,100	0,944	1,364	0,629	2,937
14	5200	14,3	0,0	0,000	0,000	0,000	0,000	0,944	1,364	0,629	2,937
15	5201	16,4	2,0	0,000	0,000	0,000	0,100	0,823	1,189	0,610	2,622
16	5800	16,4	0,0	0,000	0,000	0,000	0,000	0,823	1,189	0,610	2,622
17	5801	16,6	0,0	0,000	0,200	0,000	0,000	1,175	1,175	0,602	2,952
18	6400	16,6	0,0	0,000	0,000	0,000	0,000	1,175	1,175	0,602	2,952
19	6401	17,1	0,0	0,500	0,000	0,000	0,000	1,140	2,018	0,585	3,743
20	7000	17,1	0,0	0,000	0,000	0,000	0,000	1,140	2,018	0,585	3,743
				1,0	0,5	0,6	1,0				

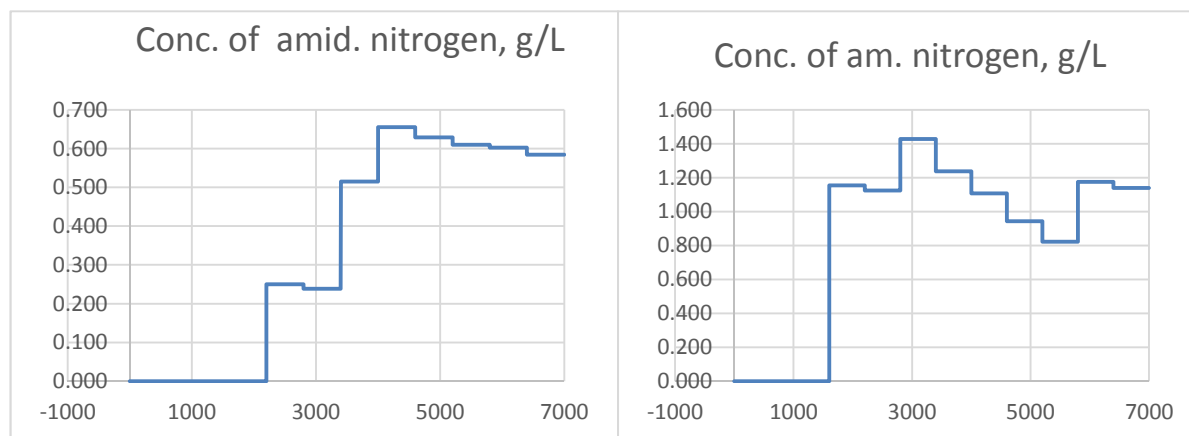


Figure 32. Calculated concentration of amid and ammonium nitrogen.

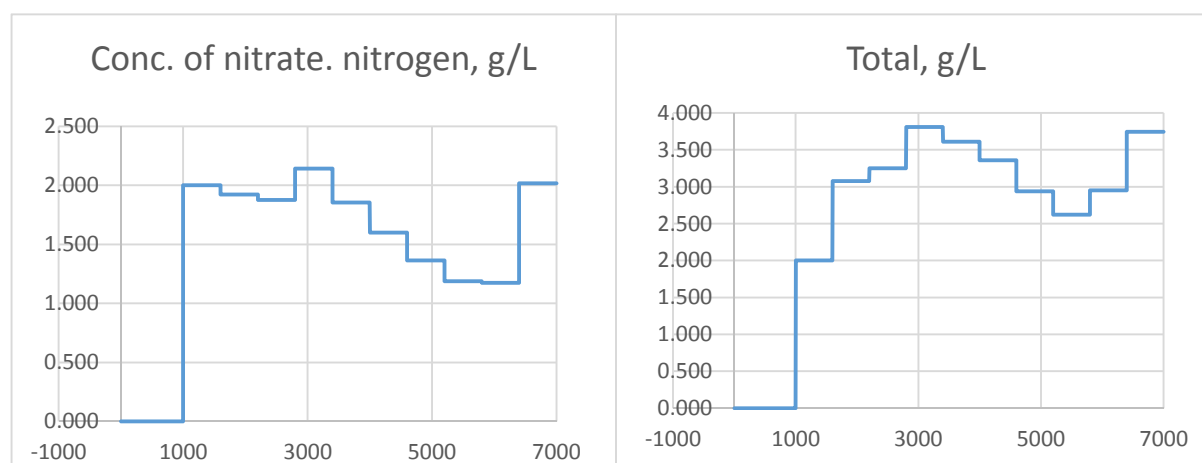


Figure 33. Calculated concentration of nitrate and total nitrogen.

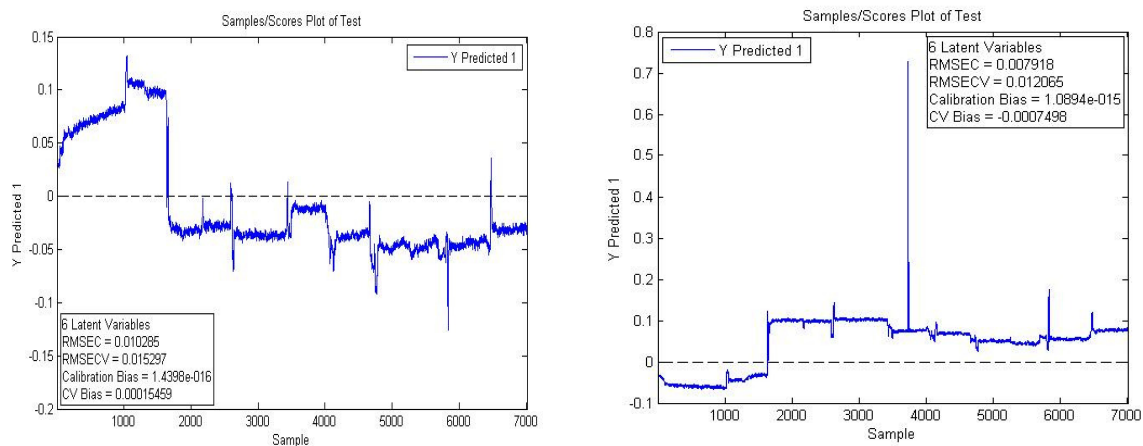


Figure 34. Predicted concentration of amid and ammonium nitrogen by PLS in the high concentration experiment based on the model constructed from the first experiment.

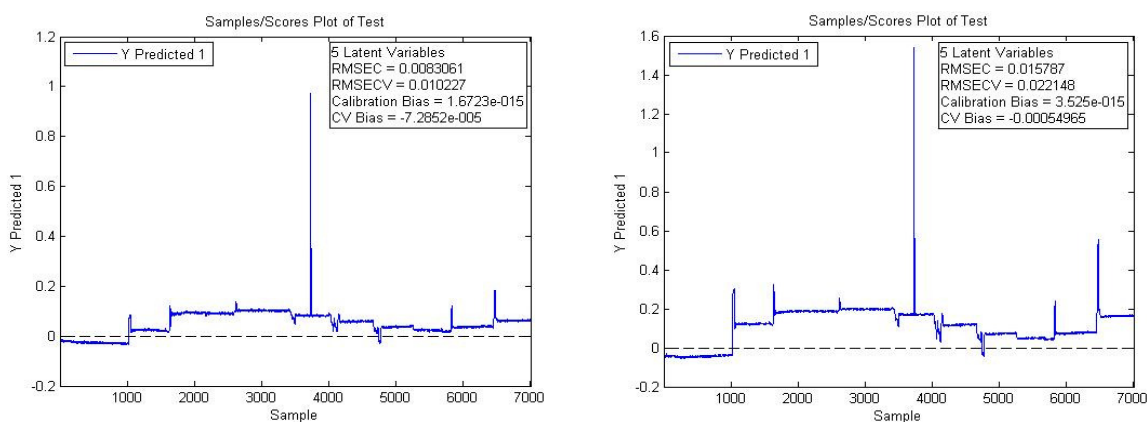


Figure 35. Predicted concentration of nitrate and total nitrogen by PLS in the high concentration experiment based on the model constructed from the first experiment.