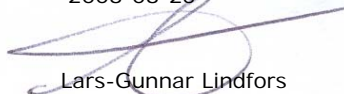


Determination of oil
content in bilge water
with acoustics in
combination with
multivariate data analysis

Sara Nilsson Anders Björk Erik Furusjö
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Lars-Gunnar Lindfors
Scientific Director

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Address P.O. Box 21060 SE-100 31 Stockholm	
Telephone +46 (0)8-598 563 00	
Author Sara Nilsson, Anders Björk, Erik Furusjö	
Title and subtitle of the report Determination of oil contents in bilge water with acoustics in combination with multivariate data analysis	
Summary <p>Bilge water is created when ship tanks are flushed and engine rooms are cleaned with water and detergents/degreaser. The resulting oil containing bilge water is usually treated in an on-ship waste water-treatment unit. To facilitate minimization of water-treatment chemicals and to assure that the oil concentration is low enough to allow discharge in the sea, it is important to know the oil concentration in the outflow. In this work we have tested and developed passive acoustic measurements for measurement of oil concentration in bilge water.</p> <p>The starting point was to make synthetic bilge water to test the concept and to get information about the system, including the properties of oils used and the specifics of applying acoustic measurement to them. We investigated the effect of salt in the bilge water by modelling synthetic bilge water with and without NaCl. The prediction errors obtained was 2.5 ppm oil (samples with salt), 0.6 ppm oil (samples without salt) and 4.5 ppm oil (samples with and without salt) (0.5-18 ppm calibration range). Thereafter real samples were collected from a ship. Since the samples had either high or low oil concentration, they were mixed in order to get a representative set of calibration samples with a large range of concentrations. The oil concentrations in the samples were determined by laboratory analysis, the experiments were performed and the calibration models developed. The best model was validated using a separate test set and yielded a test set prediction error of 7.3 ppm. This can be regarded as a good result, since the average absolute error for the laboratory measurement is around 5 ppm, and acoustic measurements is a promising technology to determine oil in bilge water.</p> <p>Recommendations for further work is to lower the error of the laboratory reference method used to determine the oil concentration, to improve the sampling handling chain and possibly also to improve the acoustic measurement equipment before new trials are performed.</p>	
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Summary

Bilge water is created when ship tanks are flushed and engine rooms are cleaned with water and detergents/degreaser. The resulting oil containing bilge water is usually treated in an on-ship waste water-treatment unit. To facilitate minimization of water-treatment chemicals and to assure that the oil concentration is low enough to allow discharge in the sea, it is important to know the oil concentration in the outflow. In this work we have tested and developed passive acoustic measurements for measurement of oil concentration in bilge water.

The starting point was to make synthetic bilge water to test the concept and to get information about the system, including the properties of oils used and the specifics of applying acoustic measurement to them. We investigated the effect of salt in the bilge water by modeling synthetic bilge water with and without NaCl, both separately and together. The prediction errors obtained was 2.5 ppm oil (samples with salt), 0.6 ppm oil (samples without salt) and 4.5 ppm oil (samples with and without salt) (0.5-18 ppm calibration range). Thereafter real samples were collected from a ship. Since the samples had either high or low oil concentration, they were mixed in order to get a representative set of calibration samples with a large range of concentrations. The oil concentrations in the samples were determined by laboratory analysis, the experiments were performed and the calibration models developed. The best model was validated using a separate test set and yielded a prediction error of 7.3 ppm. This can be regarded as a good result, since the average absolute error for the laboratory measurement is around 5 ppm, and acoustic measurements is a promising technology to determine oil in bilge water.

Recommendations for further work is to lower the error of the laboratory method used to determine the oil concentration, improve the sampling handling chain and possibly also improve the acoustic measurement equipment before new trials are performed.

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1 Introduction

The bilge water collected in the bilge of ships contains oil. The maximum allowable oil concentration in bilge water that is allowed to be released to the sea varies from region to region, in Swedish waters the limit is 15 ppm. Apart from the maximum limits in oil concentration there is also a measurement accuracy requirement of $\pm 5\%$. [1,2]. To reduce the environmental impact caused by oil on our seas and coastal waters it is important to ensure that the oil content does not exceed the limits. To do so it is essential to have a measuring technique that can monitor the oil concentration in the bilge water. Bilge water is a complex media and the traditional measuring techniques involving IR have difficulties with the varying contents of salt, oils, dispersants, detergents and solvents in the bilge water, leading to uncertain readings.

The aim of this project was to develop a technique for measuring oil concentration in bilge water that can meet the requirements stated above.

2 Material and methods

The method that was used to measure oil concentration in bilge water was acoustic measurements in combination with multivariate modeling.

2.1 Acoustic measurements

Characterisation of a fluid or multi-phase mixture with acoustic measurements is based on a number of steps according to Figure 1 below.

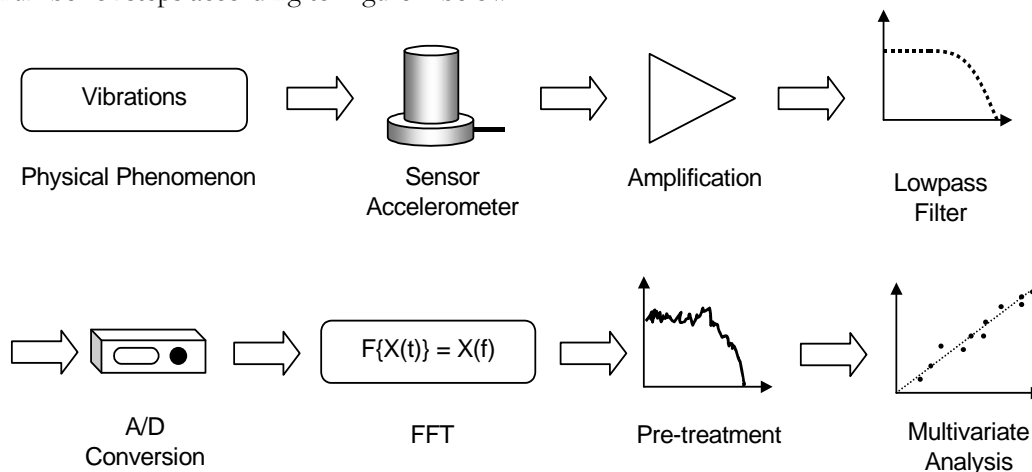


Figure 1. Visualization of the steps required for characterization of a fluid or multi-phase mixture with acoustic measurements.

The physical phenomenon that generates vibrations, i.e. the acoustic signal, is turbulence that is created by letting the process liquor flow through a constriction in a pipe or simply picking up sound from a pipe or process equipment. The former variant is usually accomplished by a

circulation loop that is connected to the process and returns the process liquor to the process after the measurement. Direct listening on process equipment could be efficient for monitoring mixing homogeneity in e.g. food and pharmaceutical processes.

An accelerometer attached to the pipe/process equipment or constriction is used to measure the vibrations in the frequency range 0-50 kHz. In this way, the characteristics of the turbulence are captured in the acoustic signal. Many physical and chemical parameters such as phase distribution, particle size, emulsion size distribution, viscosity and density of the different phases etc influence the turbulence and thus the signal. However, the signal from the accelerometer must pass several steps before useful information can be extracted.

Suitable signal processing, including amplification, filtering and signal transformation (e.g. Fast Fourier Transform FFT) is important to reduce irrelevant information and noise in order to facilitate the calibration process. The multitude of physical and chemical properties of the fluid that influence the signal necessitates the use of multivariate data analysis (MVDA) like Principal component analysis (PCA) [3,4] and Projection to latent structures (PLS) [3,5] (see “Multivariate data analysis” below).

Passive acoustic measurements have undergone a rapid development within the last 10 years [6]. Developments have been made related to mechanical design of the equipment, signal processing [7,13] and data analysis/calibration methodology [6,8]. These developments are necessarily at least partly application specific due to the different requirements in different applications. A number of applications based principally on the methodology described above have been published in the scientific literature or patents, including monitoring of powder properties during powder transportation [9,10,11], monitoring of crystallization [12], monitoring material properties in industrial pulp streams [7,13,14], detection of oil impurities in water [15], measurements of glycol in airport storm water [16], supervision of granulation processes both in biotech [17] and agriculture products [18] and for modeling of snack food texture [19].

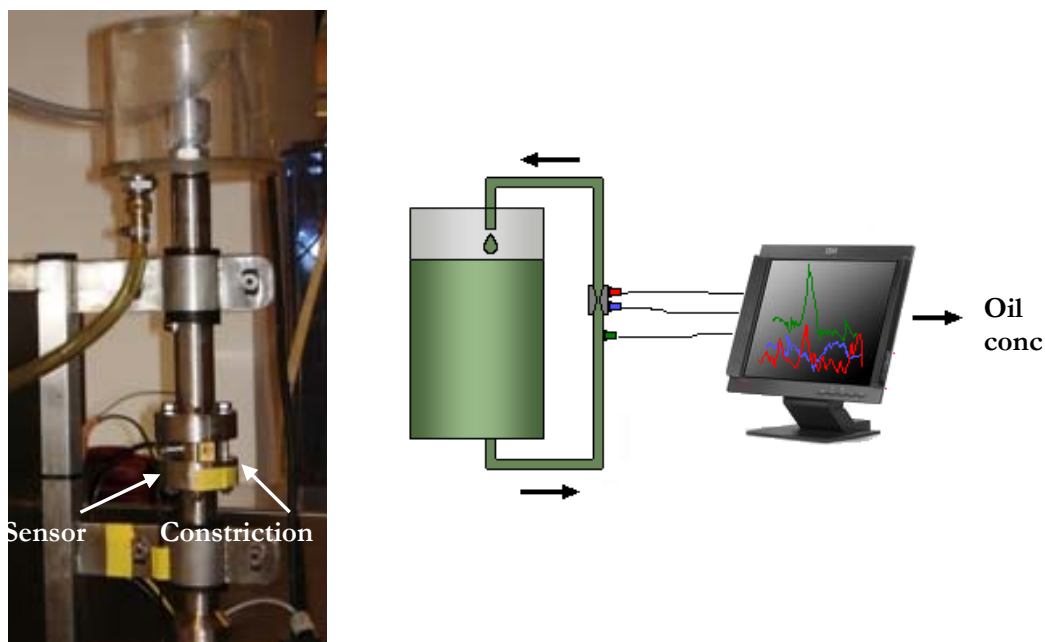


Figure 2. Picture of the measurement cell in acoustic measurement rig (left) and principal drawing of the acoustic measurement rig.

2.2 Multivariate data analysis

The spectra collected during the measurements are composed by a large number of frequencies that contain both information and noise. To extract the information in the acoustic spectra, multivariate data analysis (MVA) methods were used. Typical examples of MVA methods are principal component analysis (PCA) [3,4] and partial least squares (PLS) [3,5]. Both techniques reduce the multi-dimensional data set to lower dimensions by calculating so-called principal components (PCs) that describe the data. A PCA model is based on the X-block (i.e. the frequencies) and calculated in such a way that it describes as much variance as possible in the data, whilst a PLS model also takes the correlation to the response(s) of interest (oil content) into account. Results from PLS and PCA are often interpreted in score plots and loading plots. Score plots show how the samples are distributed and loading plots display the relationships between the variables (frequencies, oils content). Figure 3 below shows a geometric interpretation of PLS.

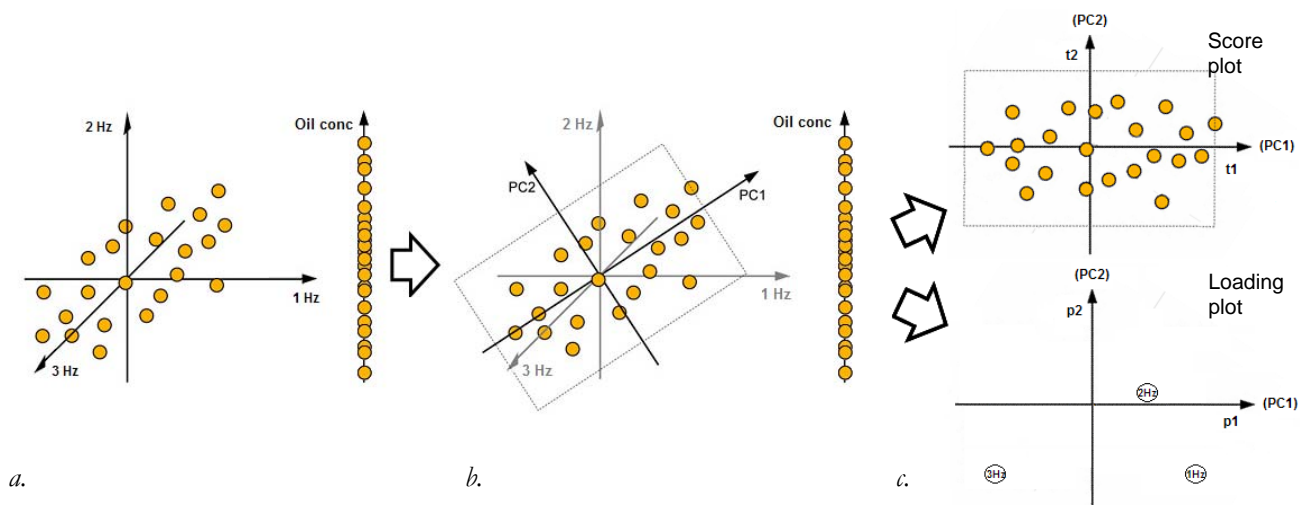


Figure 3. a Each sample has a value for each frequency, giving it a coordinate in the n -dimensional space (n = number of variables (frequencies), here $n = 3$). Each sample also has a corresponding oil concentration value. b A number of principal components (PCs) are placed in the n -dimensional space in such a way that they describe the data as good as possible. c. The score plot shows the projection of the samples on the PC plane and the loading plot shows the influence of each variable on the PCs.

One way to improve the PLS algorithm is the Orthogonal projections to latent structures, OPLS, where a one-component PLS is estimated and additional components that describe the Y-orthogonal part of the X-data are estimated [20].

2.3 Experiments

The work was divided into two parts; evaluation of synthetic bilge water samples and evaluation of real bilge water samples. The initial experiments were done on synthetic bilge water samples with known properties to gain information about the bilge water system and the acoustic measurement system. After the experiments with the synthetic samples, measurements on real bilge water samples were performed.

2.3.1 Synthetic bilge water samples

To, in a controlled manner, evaluate the acoustic measurement equipment, investigate which settings, e.g. pressure, in the measurement equipment that provides the best results and evaluate the possibility to measure the oil content in water, 15 different synthetic bilge waters were made and analyzed. The synthetic bilge water consisted of different concentrations of

- Tap water
- NaCl – 0 - 1 %
- Oil (bunker oil : lubricating oil : hydraulic oil ratio 8 : 1.5 : 0.5) – 0.5 - 18 ppm
- Detergent mix – 0 - 8.7 ppm

The constituents were mixed in such a way that the experimental space was spanned as much as possible (see Table 1). The recipes and a description of the mixing procedures can be found in Appendix 1. Ideas for the formulation design of the synthetic bilge water was found in [1,21].

Table 1. Contents in the synthetic bilge samples

NaCl [%]	Oil [ppm]	Detergent mix [ppm]
1	0.5	8.75
1	4	7
1	7.5	5.25
1	11	3.5
1	14.5	1.75
1	18	0
1	7.5	5.25
1	3	7.5
0	0.5	8.75
0	4	7
0	7.5	5.25
0	11	3.5
0	14.5	1.75
0	18	0
0	7.5	5.25

The samples were run in the acoustic rig according to the pressure scheme in Appendix 2 (Pump program for synthetic samples). The pressures investigated were 4, 5 6 and 7 bar and spectra were collected during 1 to 5 seconds. The spectral data was exported to Simca-P+ 11.5 for modeling.

2.3.2 Real bilge water samples

The ship Undine (Wallenius) collected 28 samples during 5.5 weeks (Nov 21 – Dec 29 2006). 4 samples were taken before the flocculation and 23 samples after the flocculation. Samples of all samples were sent to AIControl for determination of oil index. The sample taken after the flocculation (sample A-D Table 2) had an oil index value of 0.3 – 1.1 ppm and the samples taken before the flocculation (sample F-Å Table 2) varied between 150 and 210 ppm. The oil index of the samples is illustrated in the histograms in Figure 4.

Table 2. Oil index of the samples collected before (left) and after (right) flocculation. Samples written in red were used in the validation set.

Oil index before flocculation [ppm]		Oil index after flocculation [ppm]	
A	170	F	0.7
B	140	G	0.3
C	210	H	0.8
D	150	I	0.4
		J	0.5
		K	0.7
		L	0.6
		M	0.7
		N	0.7
		O	0.6
		P	0.7
		Q	1.1
		R	0.7
		S	0.9
		T	0.4
		U	0.5
		V	0.6
		W	0.5
		X	0.6
		Y	0.5
		Z	0.5
		Å	0.3
		Ä	0.3

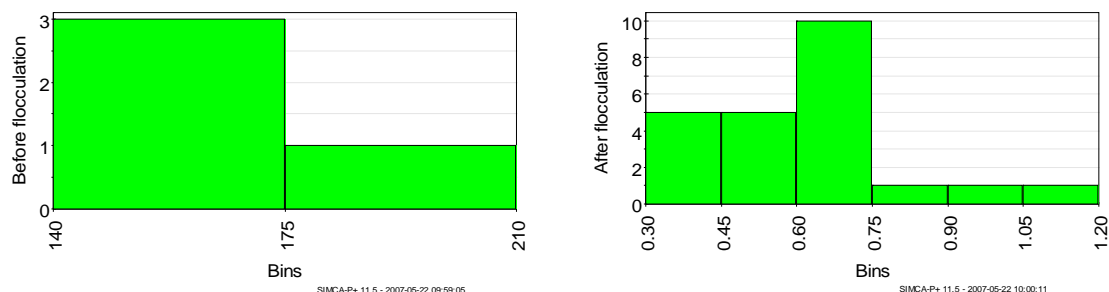


Figure 4. Histograms of oil index [ppm] in the samples collected before flocculation (left) and after flocculation (right).

The samples collected after the flocculation did not vary very much in oil concentration and had a relatively low oil concentration compared to the Swedish emission limit 15 ppm. To facilitate modeling of a greater oil concentration span, samples collected after the flocculation were mixed with samples collected before the flocculation to create 23 samples with an oil concentration of 2 to 50 ppm oil, see Table 3 for further information. This resulted in a total of 46 samples.

Table 3. "New" samples were created by mixing samples collected before the flocculation (left column) with samples collected after flocculation (middle column) to expand the oil concentration region. Samples written in red were used as validation set.

Used sample(s) before flocculation	Used sample after flocculation	Resulting oil conc after mxing
B+C	+F	2
A+D	+K	2
A+D	+H	4
B+D	+J	6
B+D	+M	6
A+C	+L	8
C+D	+P	10
A+C	+N	10
A+B	+S	12
A	+T	14
C+D	+Q	14
B	+X	15
A+B	+R	16
C	+Z	16
D	+Å	18
A+B+C	+W	20
A	+U	20
B+C+D	+O	25
A+B+C+D	+G	30
B	+V	30
A+B	+Y	35
C	+Å	40
C+D	+I	50

3 Results

3.1.1 Synthetic bilge water samples

The 9 measurement runs resulted in a dataset with the following properties:

Parameter name	Range	Comment
Trial no:	1-2	1: 0% NaCl 2: 1% NaCl
Run:	1-15	The fifteen runs/samples.
Pump step:	1-151	The pump program was built on 151 steps (see Appendix 2, Pump program for synthetic samples)
Sensor:	1-4	1: The accelerometer placed on the constriction 2: The accelerometer sensor placed approx 15 cm in front of the constriction 3: The acoustic emission sensor placed on the constriction 4: Cross spectra based on sensor 1 and 2
Temp:	43-51°C	The temperature measured by the temperature sensor placed approx 15 cm before the constriction
Pressure MV:	0-7 bar	The measured pressure
Pressure SP:	0-7 bar	Pressure set-point defined by the pump program
Settling time:	0-65 s	Acquired time when the pressure must be within the relative control error
Measurement time:	1-5 s	The time during which the spectra are measured
Number of spectra:	46-276	The number of spectra collected at each measurement time
Oil:	0 – 18 ppm	The oil content of the samples presented in ppm
NaCl:	0-1%	The salt content of the samples
0, 0.05, 0.1, ..., 102	0-	The amplitude at 0, 0.05, 0.1, ..., 102 kHz

A PCA model (5 comp, R2 0.572, Q2 0.540) based on the spectra (0-102 kHz) from Sensor 1 was calculated. Observations with a pressure set-point of 0 bar were not included in the model. To investigate the effect of pressure a score plot colored according to pressure (Figure 5) was studied. It was clear that high pressures resulted in a large variability than low pressures. From a score plot colored according to oil concentration (Figure 6) it was possible to conclude that the scattering at high pressures was random rather than caused by oil content. This implies that the measurements should be performed under relatively low pressures, e.g. 4 - 5 bar. Also a clear effect of salt content

could be seen in the NaCl colored score plot (Figure 7), which caused the grouping within each pressure that could be seen in Figure 5. This could indicate the necessity of a variable that reflects the salt content, e.g. conductivity, which can be relatively easily and inexpensively, measured both on-line and off-line.

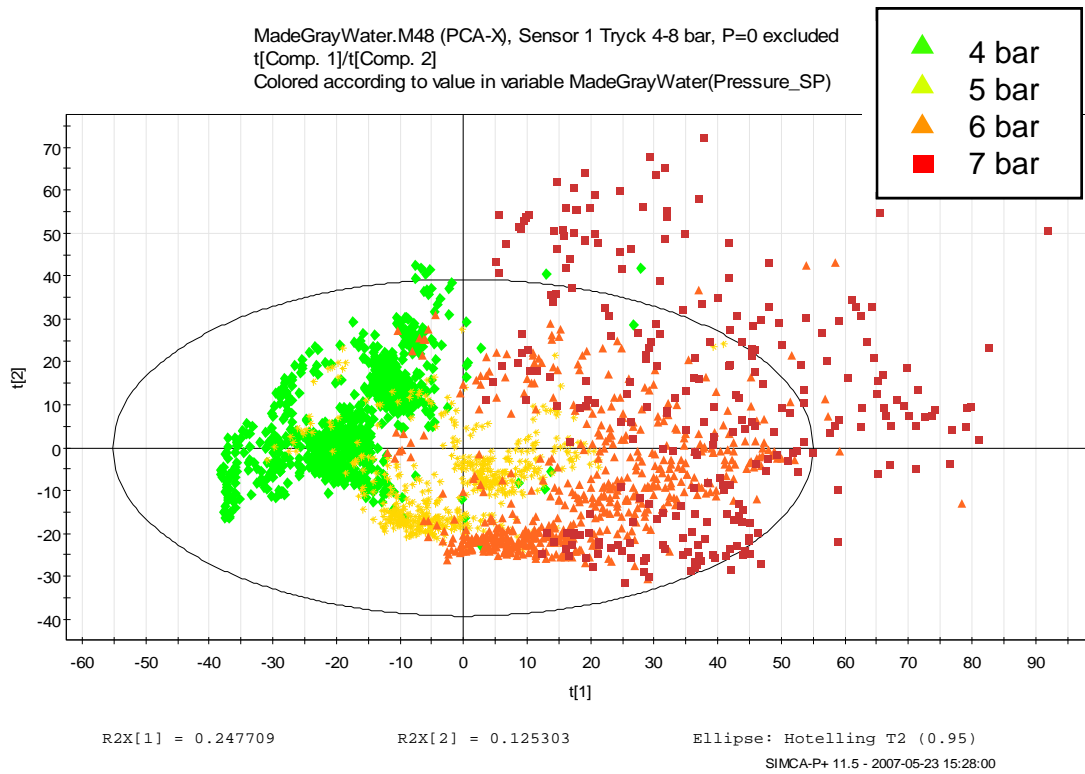


Figure 5. Score plot colored with respect to pressure.

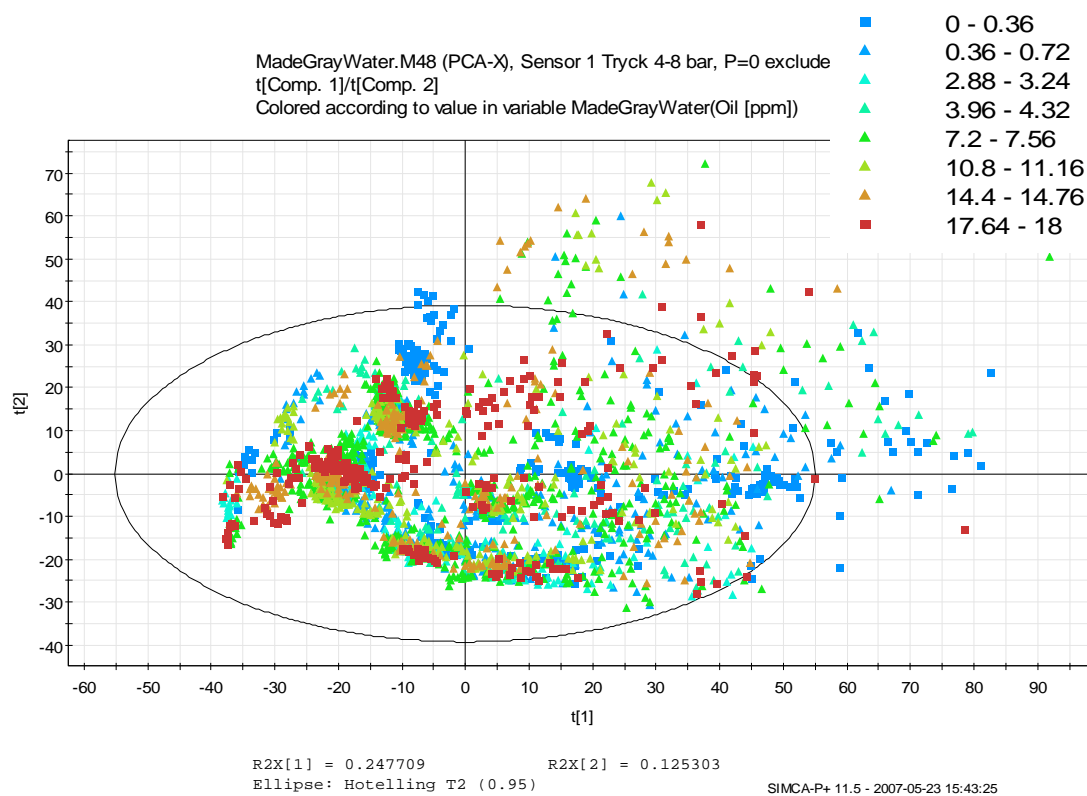


Figure 6. Score plot colored according to oil concentration

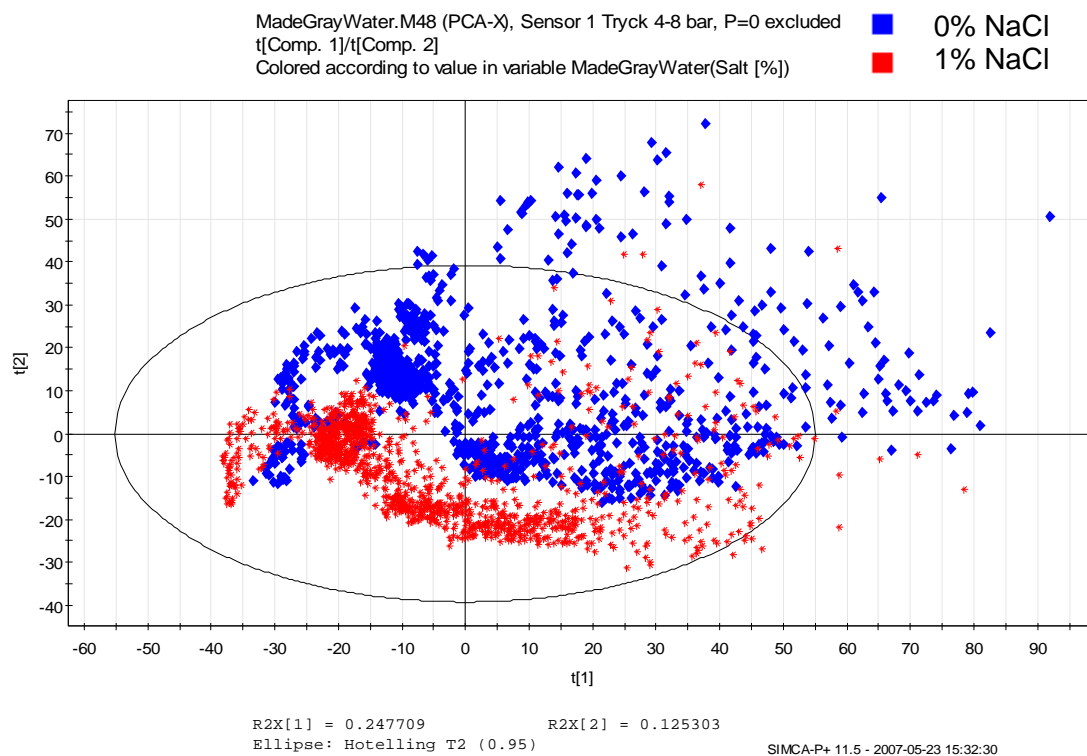


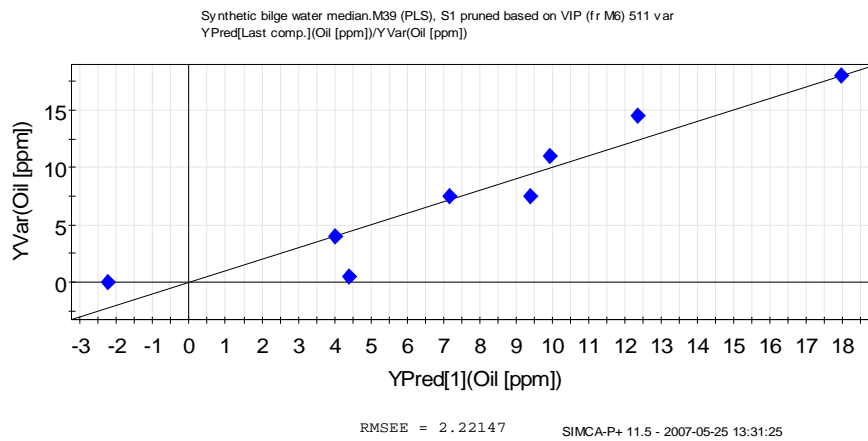
Figure 7. Score plot colored according to salt content.

PLS models for oil content were calculated. The models were based on a pressure of 4 bar. First it was investigated if there were any frequency ranges that did not contribute as positively to the models as the others by calculating PLS models on data where 10 Hz ranges (0 – 10 Hz, 10 – 20 Hz and so on) had been excluded and comparing corresponding Q2 values. None of the 10 ranges seemed to contribute to the model in an unconstructive way, wherefore all the frequencies were decided to be used in coming models.

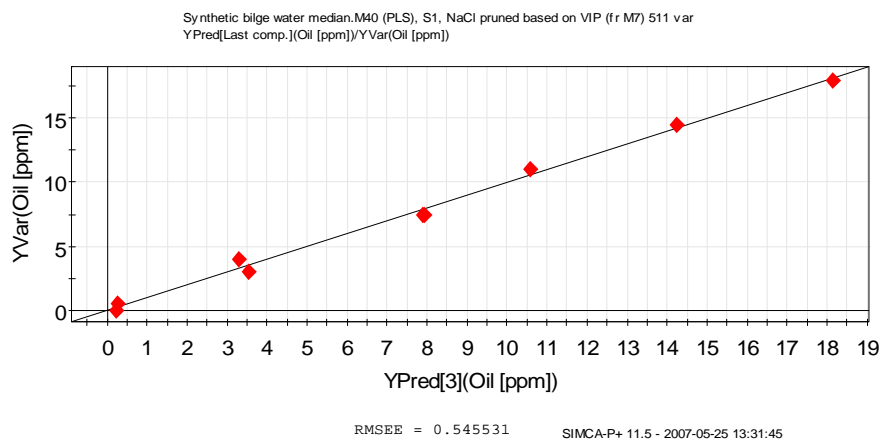
Median values for the spectra collected during 5 seconds were calculated for each sample. Separate PLS models for bilge water samples containing NaCl and not containing NaCl as well as models for samples both with and without NaCl were calculated. Also a comparison of using data from Sensor 1 (i.e. the sensor placed on the constriction) and sensor 4 (i.e. cross spectra based on Sensor 1 and the sensor placed in front of the constriction) was done. All models were improved when the data sets were pruned to contain 25% (511) of the frequencies. The frequencies that were excluded were the ones that had the lowest Variable importance plot (VIP) value. The VIP value reflects the importance of a frequency in the model both with respect to Y, i.e. its correlation to all the responses, and with respect to X (the projection). In general it could be concluded that the pruning significantly increased Q2 and reduced the over-fit in all cases and that data from Sensor 4 did not result in better models than Sensor 1. The pruned models for samples with NaCl and the pruned models for samples without NaCl had a Q2 of 0.9 and the Q2 values of the models for samples both containing NaCl and not containing NaCl were 0.7 (Sensor 1) and 0.5 (Sensor 4). Table 4 shows the properties of all the models and Figure 8 illustrates the results from Sensor 1.

Table 4. Properties of the PLS models for oil concentration. Models based on samples containing salt and/or not containing salt were calculated from median spectra from sensor 1 and sensor 4. A = number of principal components.

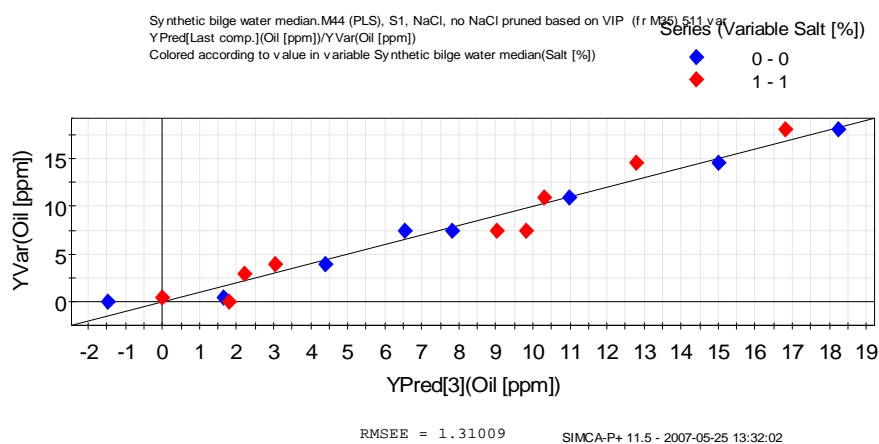
NaCl [%]	Sensor	Original (2048 frequencies)				Pruned (511 frequencies)			
		A	R2	Q2	RMSEE [ppm]	A	R2	Q2	RMSEE [ppm]
0	1	1	0.873	0.777	2.47	1	0.897	0.89	2.22
1	1	4	0.995	0.686	0.6	3	0.995	0.901	0.55
0 & 1	1	1	0.564	0.279	4.17	3	0.963	0.745	1.31
0	4	1	0.875	0.806	2.45	1	0.903	0.898	2.16
1	4	3	0.995	0.647	0.54	3	0.998	0.883	0.39
0 & 1	4	1	0.483	0.283	4.54	1	0.552	0.522	4.22



a. 0% NaCl



b. 1% NaCl



c. 0% NaCl (blue) and 1% NaCl (red)

Figure 8a-c. The oil concentrations predicted by the PLS models (sensor 1) on the x-axis and real oil concentrations on the y-axis.

It would be of great interest to validate the model with an external data set that is unknown to the model, but the number of samples was too low.

3.1.2 Real bilge water samples

The 46 measurement runs resulted in a dataset with the following properties:

Parameter name	Range	Comment
Run:	1-46	46 samples
Pump step:	1-22	The pump program was built on 22 steps (see Appendix 2, Pump program for real bilge water samples)
Sensor:	1-4	1: The accelerometer placed on the constriction 2: The accelerometer sensor placed approx 15 cm in front of the constriction 3: The acoustic emission sensor placed on the constriction 4: Cross spectra based on sensor 1 and 2
Temp:	19-23°C	The temperature measured by the temperature sensor placed approx 15 cm before the constriction
Pressure MV:	0-5.7 bar	The measured pressure
Pressure SP:	0-5.0 bar	Pressure set-point defined by the pump program
Settling time:	1-30 s	Acquired time when the pressure must be within the relative control error
Measurement time:	1-30 s	The time during which the spectra are measured
Number of spectra:	35-1500	The number of spectra collected at each measurement time
Oil:	0.3-50 ppm	The oil content of the samples presented in ppm
Conductivity:	1508-1745 uS	The measured conductivity of the bilge water
0, 0.05, 0.1, ..., 102	0-102 kHz	The amplitude at 0, 0.05, 0.1, ..., 102 kHz

In addition to the variables that were measured in the synthetic bilge water case, conductivity was measured to reflect the contents of NaCl in the water.

As mentioned earlier, the data set was divided into one training set, upon which the models were calculated, and one validation set that was used for external validation of the models. The data set consisted of 23 samples with oil concentration 0.3 - 1.1 ppm and 23 samples with oil concentration 2 - 50 ppm. To avoid fitting the models disproportionately much to samples with low oil concentrations, 21 of the 0.3 – 1.1 ppm samples were excluded from the data set before modeling. After the exclusion of the low concentrations, the training set consisted of 17 samples and the validation set of 10 samples. The validation set was selected in such a way that the concentrations were as representative as possible for the data set.

When validating the models with the external validation set, it was clear that excluding variables based on VIP values did not improve the predictive ability of the models and that the predictive

ability of the models based on data from Sensor 1 and the models based on data from sensor 4 was of the same order of magnitude.

Data preprocessing in some cases improve the models. Therefore different methods for data preprocessing were investigated:

- Logarithm transformation of the frequencies (X)
- Logarithm transformation of the oil concentration (Y)
- SNV (Standard Normal Variate) – spectral filter (X)
- wavelet compression – spectral filter (X)

None of the above mentioned methods increased the predictive ability of the models.

In addition to previously mentioned pre-processing methods, Orthogonal Projection to Latent Structures (OPLS) was also used on the data as the best PLS model (M14). A further pruned variant of the OPLS model was also estimated. Results from the first OPLS model and from the final OPLS model are shown in Figure 11 - Figure 13. An overview of all presented models for real bilge water is shown in Table 5.

Table 5. Properties of the PLS and OPLS models for oil concentration of real bilge water samples. Models based on spectra from sensor 1 and sensor 4. A = number of principal components.

Model No.	PLS/OPLS	Sensor	A	R2	Q2	RMSEE [ppm]	All variables or pruned
M14	PLS	1	3	0.946	0.750	10.3	All (2048 X-var.)
M30	OPLS	1	2	0.888	0.727	9.2	All (2048 X-var.)
M33	OPLS	1	2	0.900	0.779	7.3	Pruned (890 X-var.)

The best PLS model was the model based on data from Sensor 1. This model had a Q2 value of 0.75, and the external validation resulted in a RMESP value of 10.3. The results are displayed in form of an observed vs. predicted plot (Figure 9) where the predicted value of the oil concentration can be found on the x-axis and the corresponding measured value can be found on the y-axis. This model was based on the training set consisting of the 17 samples that constituted the training set and was externally validated with the 10 samples that was selected as validation set. The score values of the training and validation set can be seen in the PCA score plot below (Figure 10).

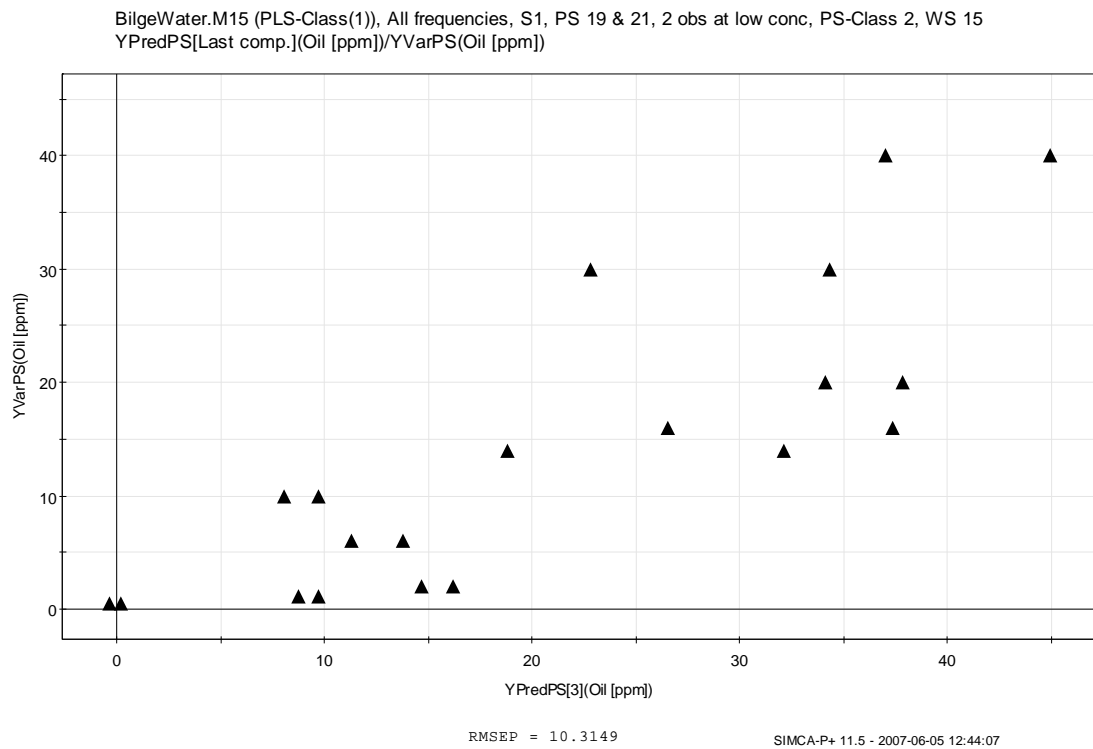


Figure 9. Observed vs. predicted. PLS model based on data from Sensor 1 (contains 2 observations between 0.3 and 1.1 ppm) predicting the oil concentration in the validation set samples.

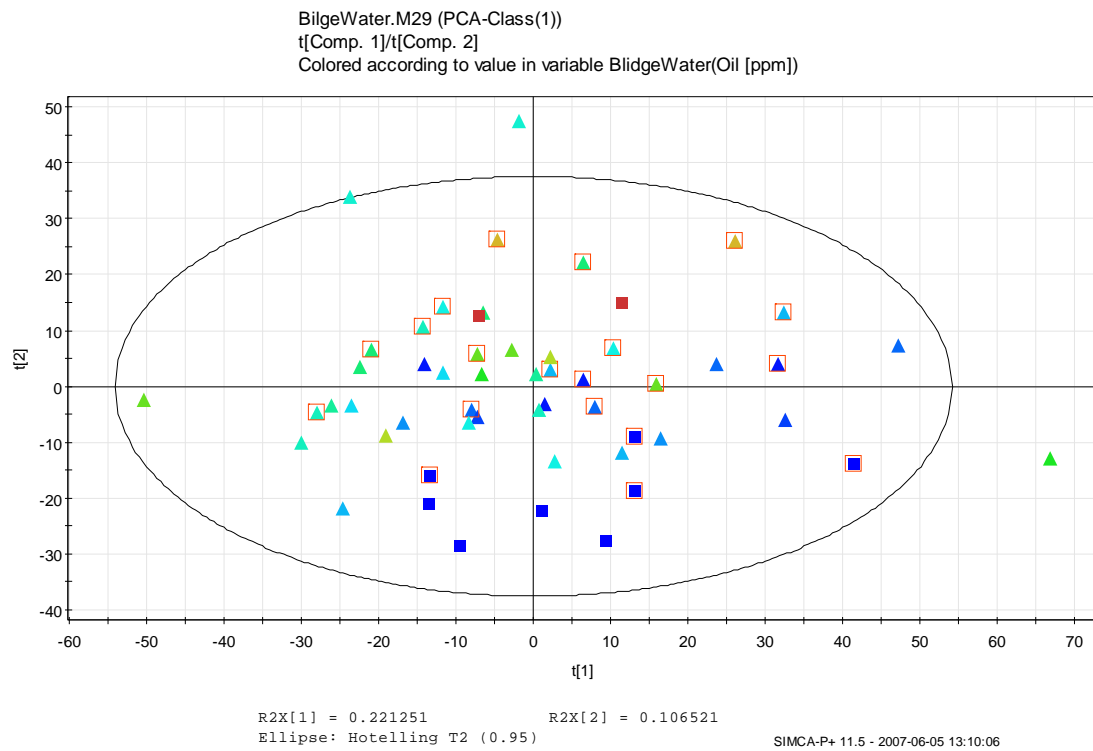


Figure 10. PCA score plot coloured according to oil concentration, Sensor 1, 2 observations between 0.3 and 1.1 ppm oil concentration. Marked observations were selected as validation set.

The OPLS model that was based on same data as the best PLS model had a Q2 value of 0.727, and the external validation resulted in a RMESP value of 9.19. The predicted vs. measured for the test-set is shown in Figure 11.

The pruning was done in the opposite way to regular PLS, where variables with small coefficients are removed, i.e. variables with low importance for the prediction. In the OPLS case the variables with large coefficients were removed, i.e. variables with high importance for the unrelated information (noise). The idea is that the OPLS model can not completely remove the Y-orthogonal information. Therefore, removing these variables from the model eliminates the contribution to the prediction error caused by the uncorrected disturbances in these variables. How the selection of pruned variables was done is shown in Figure 12.

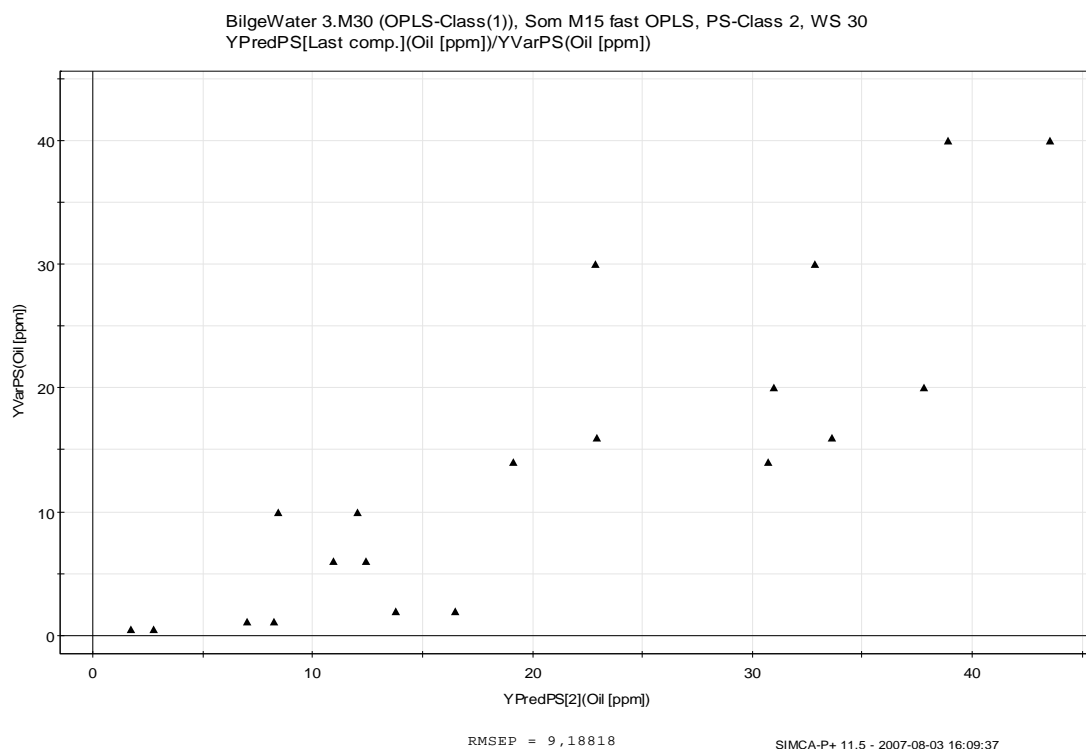


Figure 11. Observed vs. predicted. OPLS model based on data from Sensor 1 (contains 2 observations between 0.3 and 1.1 ppm) predicting the oil concentration in the validation set samples.

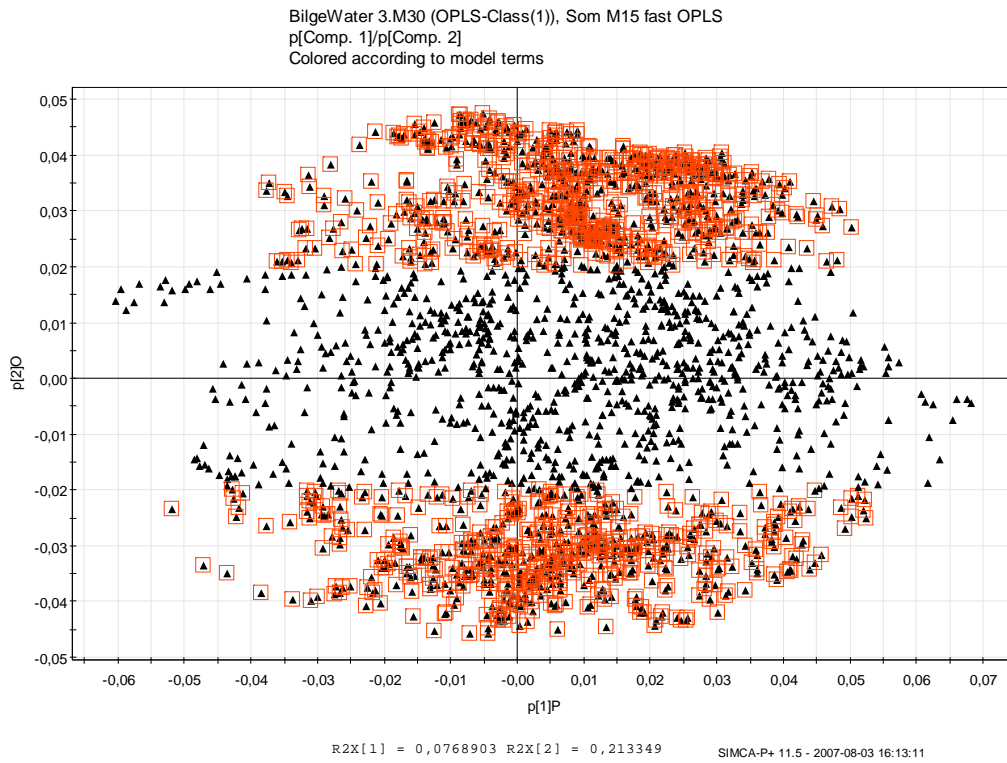


Figure 12. Loadings from OPLS model, pruning based on magnitude in p-orthogonal.

The best OPLS model was the model based on data from Sensor 1. This model had a Q2 value of 0.779, and the external validation resulted in a RMESP value of 7.33. The predicted vs. measured is shown in Figure 13.

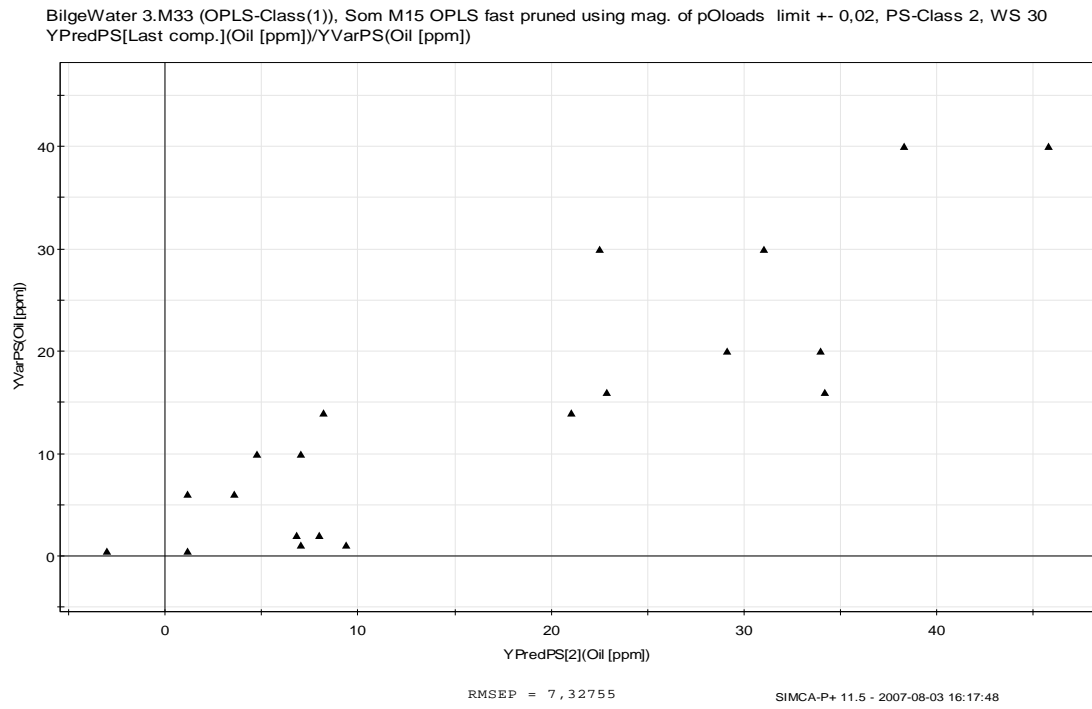


Figure 13. Observed vs. predicted. for a pruned OPLS model based on data from Sensor 1 (contains 2 observations between 0.3 and 1.1 ppm) predicting the oil concentration in the validation set samples.

4 Discussion

Synthetic bilge water was produced to gain information about the bilge water system and the acoustic measurement system. Measurement parameter, such as pressure level, was optimized. The effects of salt in bilge water was investigated. Models were built on salt-free bilge water, bilge water with salt and both salt and salt-free bilge water. The prediction errors obtained were 2.5 ppm, 0.6 ppm and 4.5 ppm respectively (0.5-18 ppm calibration range). It is possible that the salt makes the oil droplets in the bilge water more stable, therefore it is not surprising that the prediction error is large when both salt and salt-free solutions are included in the same model.

Since the emission limit is 15 ppm, the most important oil concentration range to investigate for real bilge water was approximately 10-20 ppm. The oil concentration in the samples collected after the flocculation onboard Undine was low (0.3 – 1.1 ppm) compared to the emission limit. Oil could also have stuck on the walls of the plastic containers, which might have contributed to lower the oil concentrations in the samples even further. Therefore it is preferable to shorten the storage time of the samples before they are used for measurements, but it might be hard to achieve in practice. An alternative is to select a different container material.

To facilitate modeling of higher concentrations the samples were mixed with samples collected before the flocculation. It would have been more realistic if the oil concentration range of the “original” samples was wider. Also, it would have been preferable to include samples from more than one ship, but due to practical circumstances this was not possible.

The lowest prediction error, 7.3 ppm, was obtained when using an OPLS model in combination with clever pruning of frequencies with disturbances orthogonal to oil concentration in the bilge water. Measurement uncertainty or disturbances in the measurement rig seem to prevent the possibility to calculate a model with lower prediction error than we now obtained.

The measurement uncertainty in the analyses performed by the external lab was high; 25%. This has most certainly contributed to a significant uncertainty of the models. A more precise analysis method would have been preferable. With the uncertainty of 25% in mind and recalling that the average oil concentration was around 20 ppm this would mean that in average the absolute error would be 5 ppm! In that perspective, a prediction error of 7 ppm is an acceptable result, since it is obtained from a comparison to the lab determinations.

Further work should include improving the uncertainty of the laboratory method used to determine the oil concentration in the bilge water. More background material about the water-treatment and inlet water could give additional information. To ensure always measuring on fresh samples it is important to continuously collect, transport and measure samples. In addition, it is also important that representative samples are acquired over the complete calibration range. Mixing samples with high oil concentration with low concentration samples might cause additional disturbances. It might also be possible to improve the acoustic measurement equipment. There are reasons to believe that the acoustic equipment is more robust than conventional IR systems. Therefore, an interesting approach for further research is to compare results from the acoustic equipment with corresponding results from a conventional IR system. Preferably, the comparisons will be done with samples with different (known) concentrations of oil, salt and detergents. To expand the experimental range, different amounts of for example oil and detergent could be added.

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6 References

1. International Maritime Organisation, Marine Environment Protection Committee, Report Marpol 73/78 Annex 1, 2002 (ISBN 92-801-51-25-8)
2. Resolution MEPC.107(49), Adopted on July 2003
3. Martens, H. och Naes, T. , *Multivariate calibration*, John Wiley and Sons, Chichester 1989.
4. Wold, S., Esbensen, K. och Geladi, P., *Principal Component Analysis*, Chemom. Intell. Lab. Syst. (1987), 2, 37-52
5. Geladi, P. and Kowalski, B R., *Partial least-squares regression: a tutorial*, Anal. Chim. Acta (1986), 185, 1-17
6. A Björk, 'Chemometric and signal processing methods for real time monitoring and modeling using acoustic sensors.Applications in the pulp and paper industry.', PhD Thesis, Kungl. Tekniska Högskolan, Royal Institute of Technology, 2007.
7. Björk A and Danielsson L-G, *Spectra of wavelet scale coefficients from process Acoustic Measurements as input for PLS modelling of pulp quality*, J. Chemometrics 16 (2002), 521-528
8. Flåten, G.-R., Belchamber, R. Collins M. and Walmsley Anthony D., Caterpillar—an adaptive algorithm for detecting process changes from acoustic emission signals Analytica Chimica Acta, Volume 544, Issues 1-2, 15 July 2005, Pages 280-291
9. Esbensen, Kim H.; Halstensen, Maths; Tonnesen Lied, Thorbjorn; Saudland, Arild; Svalestuen, Jorild; de Silva, Sunil och Hope, Bjorn. *Acoustic chemometrics - from noise to information*, Chemom. Intell. Lab. Syst. (1998), 44(1,2), 61-76
10. Halstensen M. och Esbensen K., *New developments in acoustic chemometric prediction of particle size distribution - 'the problem is the solution'* J. Chemometrics (2000),14(5-6), 463-481.
11. Halstensen, M. de Silva, S. and Esbensen K. (1998) "Acoustic Monitoring of Pneumatic Transport Lines: From Noise to Information", KONA Powder and Particle No. 16. Telemark College/Tel-Tek, Porsgrunn, Norway.
12. Bouchard, J. G., Payne, P. A. och Szyzko, S., *Non-invasive measurement of process states using acoustic emission techniques couple with advanced signal processing*, Trans IChemE, Vol 72, Part A, January 1994
13. . Björk och L-G Danielsson, *Extraction of Distribution Curves from Process Acoustic Measurements on a TMP-Process*, Pulp and Paper Canada 105 No.11 (2004), T260-T264.
14. A Björk, L-G Danielsson, 'Pulp Quality And Performance Indicators For Pressure Screens Based On Process Acoustic Measurements', Proceedings Control Systems 2002, June 3-5, Stockholm, Sweden (2002), 175-179; A Björk, L-G Danielsson, 'Predicting Pulp Quality from Process Acoustic Measurements on a Medium Consistency Pulp Stream', Proceedings Control Systems 2002, June 3-5, Stockholm, Sweden (2002), 49-53
15. Esbensen, Kim H.; Hope, Bjorn; Lied, Thorbjorn T.; Halstensen, Maths; Gravermoen, Tore; Sundberg, Kenneth. *Acoustic chemometrics for fluid flow quantifications - II: a small constriction will go a long way*, J. Chemometrics (1999), 13(3-4), 209-236
16. Sensorteknikk A/S, FPS - Fluid Purity System, <http://www.sensorteknikk.no/environment.htm> [2007-04-27]
17. Frank R. and Paash M. in U.S. Pat.Application 2002/0189358 A1 (7 Mars2002), Prior 8 Mars 2001 (DK Appl.), Novozymes A/S. 2002

18. Halstensen M., de Bakker P. and Esbensen K.H. "Acoustic chemometric monitoring of an industrial granulation production process--a PAT feasibility study", *Chemometr. Intellig. Lab. Syst.* 84 (2006), 88-97.
19. Bruwer M.-J., MacGregor J.F. and Bourg W.M. "Soft Sensor for Snack Food Textural Properties Using On-Line Vibrational Measurements", *Indust. Eng. Chem. Res.* 46 (2007), 864-870.
20. Trygg J, Wold S. Orthogonal projections to latent structures, O-PLS. *J. Chemometrics*, 2002; 16: 119-128. [<http://www3.interscience.wiley.com/cgi-bin/abstract/89015377/>]
21. Marco Nottegar, "The Effects Of Particulates On The Ultrafiltration Bilge (Oily) Wastewater Containing New Or Used Lubricating Oil", Master of Science Thesis, Department of Chemical Engineering University of Ottawa, 2000.

Appendix 1

Preparation of stock solutions

20% NaCl: 1 kg NaCl/5L

Detergent mix: QS (1):Terra (2):OC (2)

1% Oil-mix: (Bunker oil (8) : Lubricating oil (1.5) : Hydraulic oil (0.5)):

4g	Bunker oil	}	Mix	}	Mix approx 1 min at low speed, then mix 2 + 2 min at high speed
0.75g	Lubricating oil				
0.25g	Hydraulic oil				
2.5g	Detergent mix				
500mL	Warm water				

Sample preparation

1. 8L water (50°C) (incl 20% NaCl) is added to the tank of the acoustic measurement rig.
2. 2L (50°C) water and detergent mix is added to the mixer. Oil-mix is added and the mixture is mixed at relatively low speed.
3. The water-oil-detergent mixture is added to the tank of the acoustic measurement rig.

Sample recipes

15 samples were prepared according to the recipes below.

NaCl 20% [L]	Oil mix 1% [mL]	Detergent mix [uL]	Water [L]
0.5	0.5	87.5	9.5
0.5	4	70	9.5
0.5	7.5	52.5	9.5
0.5	11	35	9.5
0.5	14.5	17.5	9.5
0.5	18	0	9.5
0.5	7.5	52.5	9.5
0.5	3	75	9.5
0	0.5	87.5	10
0	4	70	10
0	7.5	52.5	10
0	11	35	10
0	14.5	17.5	10
0	18	0	10
0	7.5	52.5	10

The report is based on the assumption that oil has a density of 1. Usually oil has a density of 0.85 – 0.99.

Appendix 2

Pump program for synthetic samples

Table. The program used for the acoustic measurements of the synthetic bilge water samples.

Pump step	Pressure [bar]	Settling time [s]	Measurement time [s]	Pump step	Pressure [bar]	Settling time [s]	Measurement time [s]
1	0	10	1	75	0	10	1
2	4	65	1	76	4	5	1
3	4	1	1	77	4	1	1
4	4	1	1	78	4	1	1
5	4	1	1	79	4	1	1
6	4	1	1	80	4	1	1
7	4	1	5	81	4	1	5
8	4	1	5	82	4	1	5
9	4	1	5	83	4	1	5
10	4	5	1	84	4	5	1
11	4	1	1	85	4	1	1
12	4	1	1	86	4	1	1
13	4	1	1	87	4	1	1
14	4	1	1	88	4	1	1
15	4	1	5	89	4	1	5
16	4	1	5	90	4	1	5
17	4	1	5	91	4	1	5
18	5	5	1	92	5	5	1
19	5	1	1	93	5	1	1
20	5	1	1	94	5	1	1
21	5	1	1	95	5	1	1
22	5	1	1	96	5	1	1
23	5	1	5	97	5	1	5
24	5	1	5	98	5	1	5
25	5	1	5	99	5	1	5
26	6	5	1	100	6	5	1
27	6	1	1	101	6	1	1
28	6	1	1	102	6	1	1
29	6	1	1	103	6	1	1
30	6	1	1	104	6	1	1
31	6	1	5	105	6	1	5
32	6	1	5	106	6	1	5
33	6	1	5	107	6	1	5
34	7	5	1	108	7	5	1
35	7	1	1	109	7	1	1
36	7	1	1	110	7	1	1
37	7	1	1	111	7	1	1
38	7	1	1	112	7	1	1
39	7	1	5	113	7	1	5
40	7	1	5	114	7	1	5
41	7	1	5	115	7	1	5
42	6	5	1	116	6	5	1
43	6	1	1	117	6	1	1
44	6	1	1	118	6	1	1
45	6	1	1	119	6	1	1
46	6	1	1	120	6	1	1
47	6	1	5	121	6	1	5
48	6	1	5	122	6	1	5

Pump step	Pressure [bar]	Settling time [s]	Measurement time [s]	Pump step	Pressure [bar]	Settling time [s]	Measurement time [s]
49	6	1	5	123	6	1	5
50	5	5	1	124	5	5	1
51	5	1	1	125	5	1	1
52	5	1	1	126	5	1	1
53	5	1	1	127	5	1	1
54	5	1	1	128	5	1	1
55	5	1	5	129	5	1	5
56	5	1	5	130	5	1	5
57	5	1	5	131	5	1	5
58	4	5	1	132	4	5	1
59	4	1	1	133	4	1	1
60	4	1	1	134	4	1	1
61	4	1	1	135	4	1	1
62	4	1	1	136	4	1	1
63	4	1	5	137	4	1	5
64	4	1	5	138	4	1	5
65	4	1	5	139	4	1	5
66	4	5	1	140	4	5	1
67	4	1	1	141	4	1	1
68	4	1	1	142	4	1	1
69	4	1	1	143	4	1	1
70	4	1	1	144	4	1	1
71	4	1	5	145	4	1	5
72	4	1	5	146	4	1	5
73	4	1	5	147	4	1	5
74	0	10	1	148	0	10	1

Pressure – *pressure set point*
Settling time – *acquired time when the pressure must be within the relative control error*
Measurement time – *time during which the acoustic spectrum is measured*

Pump program for real bilge water samples

Table. The program used for the acoustic measurements of the real bilge water samples.

Pump step	Pressure [bar]	Settling time [s]	Measurement time [s]
1	0	1	1
2	1.5	30	1
3	4.5	30	1
4	4.5	1	1
5	4.5	1	1
6	4.5	1	1
7	4.5	1	1
8	4.5	1	1
9	4.5	1	1
10	4.5	1	1
11	4.5	1	1
12	4.5	1	1
13	4.5	1	5
14	4.5	1	5
15	4.5	1	5
16	4.5	1	5
17	4.5	1	5
18	5	5	30
19	4.5	5	30
20	4	5	30
21	4.5	5	30
22	0	1	1