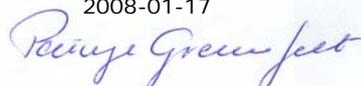# Ammonia slip measurements on ships with NO$_X$ converters

A study of different techniques

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Sammanfattning

Ett antal tekniker för att mäta ammoniakkoncentration i rökgaser har utvärderats. Syftet är att finna tillförlitliga metoder att analysera ammoniakslip från fartyg utrustade med SCR-utrustning för kväveoxidrening. Tester har gjorts ombord två fartyg samt i laboratoriemiljö. De testade metoderna är FTIR, laserabsorption, våtkemisk metod samt en metod, där ammoniak oxideras till NO_X över en katalysator. Lasermetoden är en *in-situ* metod, där sändare och mottagare placeras på flänsar på ömse sidor på avgaskanalen, emedan de övriga metoderna är *ex-situ*, dvs bygger på att en viss gasmängd sugs ut ur avgaskanalen till instrumenteringen. I fältstudierna fungerade lasermetoden bra och gav resultat med hög känslighet och bra tidsupplösning. FTIR fungerade ej bra för låga koncentrationer. Tidsupplösningen är bra men med en viss fördröjning. Vid stråkbildning fås varierande koncentration beroende på var sonden är placerad i rökgaskanalen. Vid laboratoriestudierna observerades ett stort inflytande av syre på den uppmätta ammoniakkoncentrationen. Den våtkemiska metoden gav tillförlitliga resultat. Tidsupplösningen är mycket dålig och metoden är känslig för stråkbildning. Katalysatormetoden fungerade i laboratoriet men inte i fält då katalysatorn deaktiverades, troligen av svavel i rökgasen.

Summary

A number of techniques to measure the concentration of ammonia in exhaust gas have been evaluated. The objective is to obtain reliable methods for measuring ammonia slip from ships equipped with SCR systems for cleaning of nitrogen oxide emissions. The methods tested are FTIR, laser absorption, a wet chemical method and a method where ammonia is oxidised into NO_X over a catalyst. The laser method is an *in-situ* technique, where the transmitter and receiver are positioned on opposite flanges at the exhaust channel, while the other methods are *ex-situ*, i. e., a probe volume of gas is taken from the exhaust channel into the instrumentation. The laser method worked well in the field studies and gave results with high sensitivity and good time resolution. FTIR did not work well for low concentrations. The time resolution is good but with a delay. In cases with an uneven distribution of ammonia throughout the exhaust channel, the concentration will vary depending on the location of the probe. A strong influence of the oxygen concentration on the observed ammonia concentration was found in the laboratory study. The wet chemical method gave reliable results. The time resolution is poor and the method is sensitive to uneven distribution in the exhaust channel. The method with the oxidation catalyst worked well in the lab but not in field where the catalyst was deactivated, probably by sulphur.

Content

1. Preface

Ten years from now, more than 50% of nitrogen oxides (NOX) emissions in Europe will originate from shipping. This calls for measures to take action and reduce these emissions. In Sweden, there is a system in operation since several years with reduced fairway dues for ships that have taken measures to reduce NOX emissions. The most effective way to achieve this is to use Selective Catalytic Reduction (SCR) units. In such systems, ammonia or urea is used as a reducing agent that reacts with NOX over a catalyst surface. These systems may therefore show a slip of ammonia emitted into the air with the exhaust. This slip is naturally not wanted and can be minimised through design improvements and fine-tuning of the system. In order to evaluate and improve SCR systems in this respect, reliable techniques to measure ammonia are called for.

This report is the result of a project where different ammonia measurement techniques were tested on ships equipped with catalysts for the reduction of nitrogen oxides using urea as reducing agent. The project was run in collaboration with Wärtsilä, Siemens Laser Analytics AB, DEC Marine AB, The Swedish Maritime Administration and The Swedish Environmental Protection Agency.

The objectives of the present study were:

- To evaluate three different techniques for ammonia measurements on ship engines equipped with SCR systems.

- To test these techniques onboard two ships.

- To collect time-resolved data for ammonium slip from ship engines equipped with SCR systems.

2. Introduction

2.1 Emissions of nitrogen oxides from shipping

2.1.1 Emission inventories

Nitrogen oxides are formed in combustion engines mainly through the so-called Zeldovich mechanism where N_2 in air reacts to form NO. This process is strongly temperature dependent and also dependent on other factors such as type of fuel, air-to-fuel ratio and engine speed. The emission factors for larger engines, such as marine engines, are usually given as emitted mass of pollutant per engine power unit, i.e., in g/kWh. Table 1 gives some values of emission factors for NO_X for marine engines with different combinations of engine types, fuels, and operating conditions.

Table 1.   Emission factors for marine diesel engines from Cooper and Gustafsson[1]. SSD = slow speed diesel, MSD = medium speed diesel, HSD = high speed diesel, GT = gas turbine, ST = steam turbine, MD = marine diesel, RO = residual oil.

Engine type	Fuel type	NO_X-emission at sea (g/kWh)	NO_X-emission during manoeuvring (g/kWh)
SSD	MD	17.0	13.6
SSD	RO	18.1	14.5
MSD	MD	13.2	10.6
MSD	RO	14.0	11.2
HSD	MD	12.0	9.6
HSD	RO	12.7	10.2
GT	MD	5.9	3.0
GT	RO	6.1	3.1
ST	MD	2.0	1.6
ST	RO	2.1	1.7

The total emissions of NO_X from shipping sum up to considerable quantities. There are relatively large uncertainties in the volume of shipping on a global scale which leads to uncertainties in emission inventories. Eyring et al.[2] estimate that 21 Mton of NO_X (as NO_2) is emitted from shipping each year which is similar to the conclusion of Corbett and Köhler of 23 Mton, while a lower estimate is given by Endresen et al.[3] (12 Mton). In scenarios produced within the European CAFE programme, it is found that a significant part of future NO_X emissions in EU25 will originate from shipping (see Figure 1). At around 2020, shipping is expected to contribute with more NO_X emissions than all land-based sources combined.
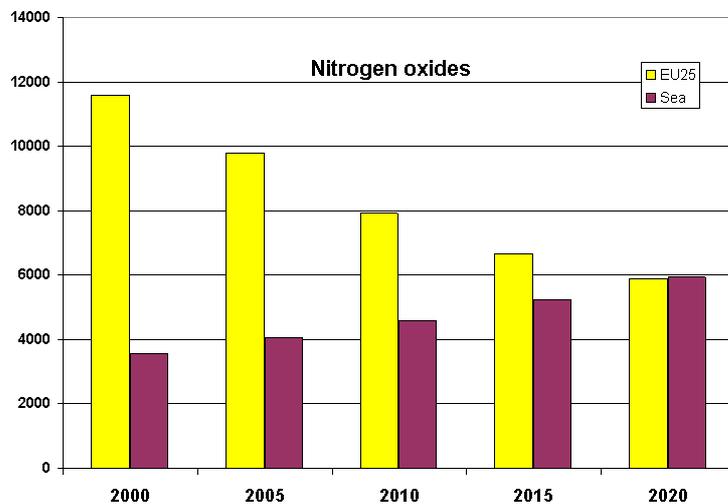
Figure 1.   Prognosis for emissions of NO_X from land based sources and shipping in Europe[4].

2.1.2 Regulations

According to IMO regulations, all ships constructed after January 1, 2000 must comply with the NO_X-emission standard in Figure 2, where the allowed emissions depend on engine speed. The impact of this regulation is limited since all new engines already comply. There are discussions about enforcing somewhat stricter regulations.
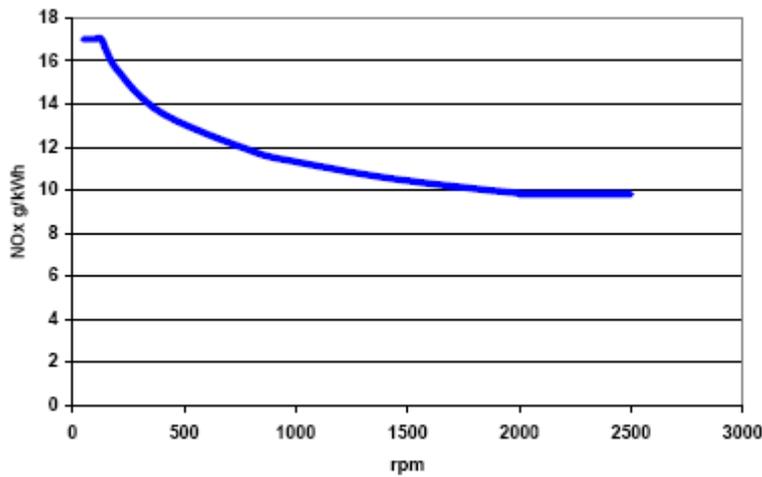
Figure 2.   Emission standard for NO_x according to IMO in g/kWh in relation to rotation speed (revolutions per min)[5].

In Sweden the fairway dues for ships give discounts for ships with reduced emissions of NO_X since 1998. The fairway dues follow the curves in Figure 3. This system has had an impact mainly on ships that spend most of their time in Swedish waters. In Norway a system with a tax on each emitted kg of NO_X was introduced in 2007.

Figure 3.   Fairway dues in Sweden in relation to NO_x emissions for different types of vessels[5].

2.1.3 Methods to reduce emissions

There are several different alternatives to reduce the emissions of nitrogen oxides from marine engines. The most common are engine modifications, water injection techniques, and catalytic reduction of the exhaust.

The engine modifications aim at improving the combustion in the combustion chamber. This is usually done by replacing the fuel valves in order to change the distributi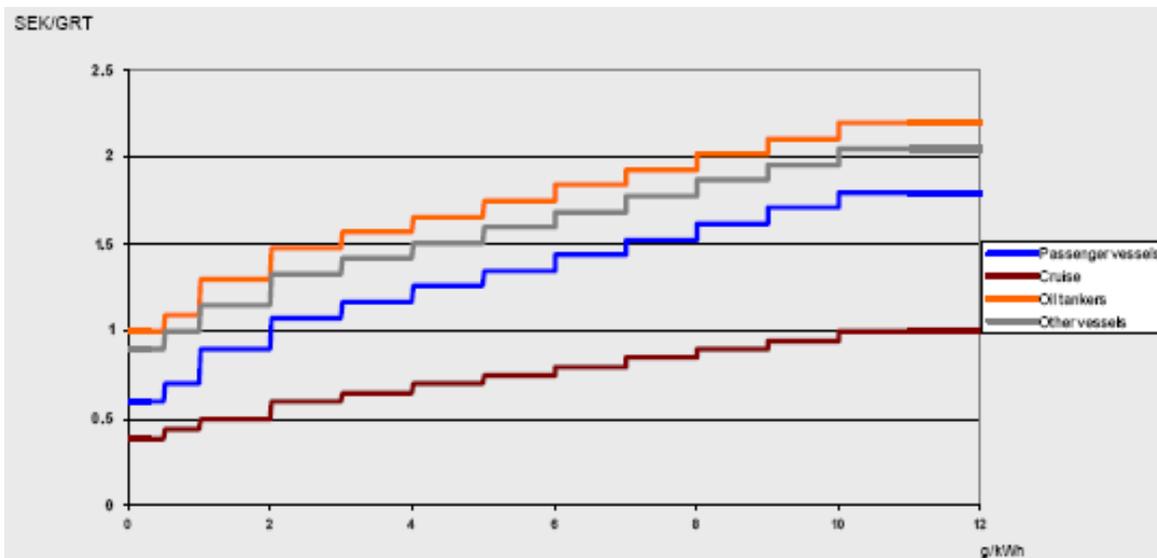on of fuel in the combustion chamber. This results in a somewhat lower maximum temperature during the combustion cycle, which lowers the formation of NO. The reduction potential is about 20% at present but may increase somewhat in the future.
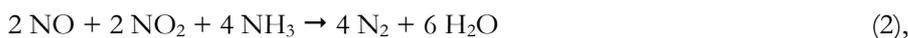
By introducing water during the combustion, the temperature can be lowered. This can be done with direct injection of fresh water or by humidifying the inlet air. The reduction efficiency can be up to 80% but is typically around 30%.

There are several different catalytic techniques available for treatment of diesel exhaust. However, due to the high levels of sulphur and other impurities in marine fuels many of them are inapplicable. The one catalytic technique that is available is Selective Catalytic Reduction (SCR) which is described below.

2.2 Selective catalytic reduction

In the selective catalytic reaction NO and NO_2 react with an added reducing agent over a catalyst surface. The reducing agent used in marine applications is either ammonia or urea ($(NH_2)_2CO$). The latter is most frequently used since urea is easier to handle. Urea reacts to form NH_3 either over a hydrolysis catalyst (which can be the same catalyst as is used for the SCR reaction) or thermally. The presence of a single nitrogen atom makes ammonia react quickly with NO_X to form N_2, rather than being oxidised by the large amounts of oxygen present in diesel exhaust. The active catalyst is normally a combination of oxides of vanadium and titanium. Also a number of zeolites can be used but these are not suitable for marine applications due to their sensitivity to sulphur deactivation.

The reaction between NO_X and NH_3 over the catalyst follows two different paths:

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad\qquad\qquad (1)$$

$$2\,NO + 2\,NO_2 + 4\,NH_3 \rightarrow 4\,N_2 + 6\,H_2O \qquad\qquad\qquad (2),$$

where reaction 2 is much faster. It is thus beneficial if the exhaust contains a mixture of NO and NO_2. This is normally not the case for the exhaust from large diesel engines where the NO_X content is dominated by NO.

A key parameter for a high NO_X reduction rate is the temperature over the catalyst. Figure 4 shows a comparison for different NO_X reduction techniques for applications on truck diesel engines[6]. As can be seen the SCR reaction is not really effective until the temperature reaches almost 300°C. This has the effect that an SCR system on a ship cannot be used immediately after start-up or before the catalyst has reached operational temperature.
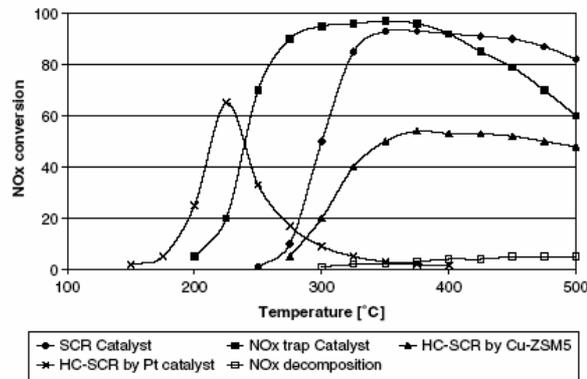
Figure 4.   Comparison of NO_X reduction for some deNO_X catalysts.

A schematic diagram of a SCR system is shown in Figure 5. The initial oxidation catalyst, which may also be placed further back in the system, is used to oxidise remaining hydrocarbons and CO and is normally not used in marine applications. Further, the urea hydrolysis catalyst and the actual SCR catalyst are often present as one catalyst. The slip catalyst is sometimes used in marine applications in order to oxidise unreacted ammonia.
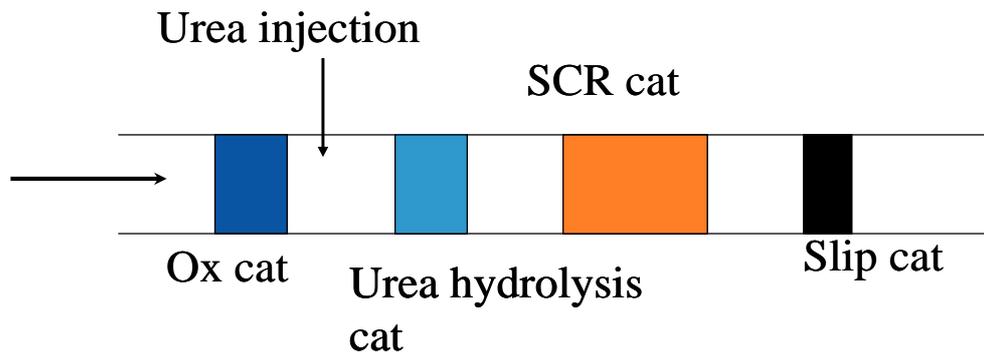
Figure 5.   Schematic diagram of SCR system

2.3 Ammonia slip

2.3.1 Occurrence

In situations with incomplete reactions between ammonia and NO_X, a so-called slip can occur where ammonia is emitted with the exhaust into the surrounding air. This is strongly unwanted not least since ammonia has a strong smell. For the Swedish system of reduced fairway dues, NH_3 concentratons in the exhaust must be kept below 10 ppm. A slip of ammonia can occur if the reaction rate goes down, most commonly due to too low exhaust temperature. Further, if the urea dosing is not properly tuned slip may occur. This can be due to either that the spatial distribution of urea in the catalyst does not reflect the distribution of NO_X, or that the timing is not adjusted so that transients in NO_X formation (e.g. due to changes in load) cannot be followed. The design of

the system is also important. A too short mixing distance or a bend in the exhaust tube before the SCR catalyst may cause a slip.

2.3.2 Measurement needs

In order to study the mechanisms and operation of SCR systems, it is of interest to measure NH_3 with a high time resolution. This will give the opportunity to follow transients in, e.g., load and temperature. Further, a relatively high sensitivity is needed since the ammonia slip is frequently in the ppm range. A sensitive system with high time-resolution would open up for simplified tuning of SCR systems regarding mainly the urea injection strategy. Another issue related to certification is that the ammonia concentration in the exhaust may be unevenly distributed over the exhaust pipe. If a point measurement is performed this may lead to monitoring of unrepresentatively high or low concentrations of ammonia, depending on the exact position of the probe. A measurement technique that accounts for a larger geometrical area would eliminate this problem.

3. Measuring ammonia

3.1 Overview

Ammonia can be detected by a number of methods, like chemical and optical techniques. Ammonia has several absorption bands in the ultraviolet, infrared, near infrared and microwave region of the electromagnetic spectrum. Further, it easily forms ammonium ions in solutions that can be detected. Ammonia was the first polyatomic molecule to be detected in interstellar space, due to its strong absorption in the microwave region.
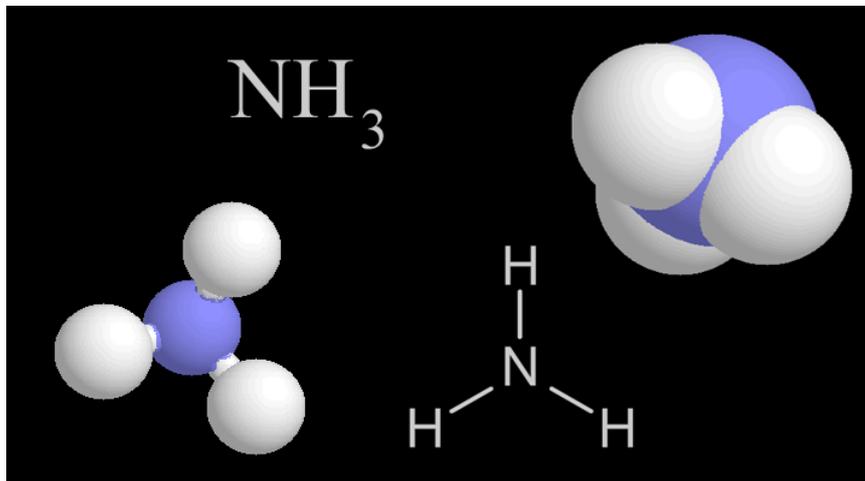

Figure 6.   The ammonia molecule.

Measurements of the amounts of a gas-phase species is often done by optical absorption. In this case there is a light source and a detector on mutual sides of the gas where the species to be measured is present. The amount of absorbers, i.e., the number of molecules, is then obtained from the Lambert-Beer equation:

$$\log (I_0 / I_1) = \alpha\, c\, l \qquad\qquad\qquad (3),$$

where I_0 and I_1 are the light intensities before and after the sample, α an absorption coefficient, c the concentration and l the path length in the sample (see Figure 7).
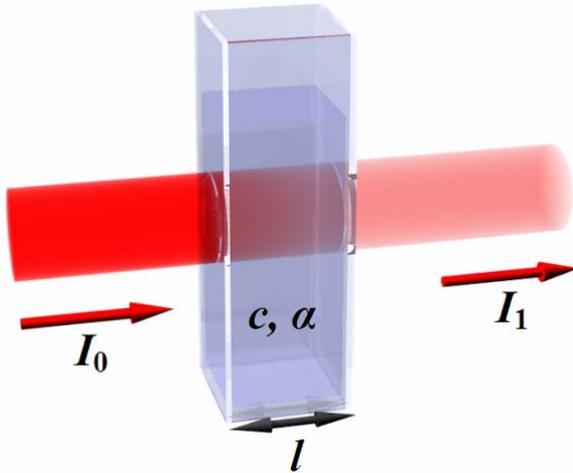

Figure 7.   Illustration of absorption measurement.

One way to divide different ammonia measurement techniques is as in-situ and ex-situ. The former is used to label a method where the ammonia concentration is measured at the desired location, e.g., an exhaust tube, with the sensors and light sources (for example) situated at this location. Thus, this will give the concentration that is wanted directly. A drawback with in-situ methods is that the environment may be harsh on the measurement equipment. For example, there may be soot present that will gradually decrease the transmission through windows, or high temperatures and water vapour may cause problems for electronics.

Ex-situ techniques imply that a probe of the gas is taken out from the location where the concentration is to be measured and let into a measurement device. This is often a practical method in the sense that probes that withstand harsh environments can be used. To obtain the wanted concentration, possible dilution needs to be accounted for. One drawback is that it may take some time for the sampled gas volume to reach the instrument and thus the response time may be long. A second disadvantage is that gases may condense or stick in tubing between the sampling site and the instrument. This is a concern for ammonia that easily sticks to various surfaces and may even react on these surfaces to form e.g., ammonium nitrate.

3.3 Absorption of visible/infrared light

Ammonia shows several absorption bands in the infrared region. Most notably at around 10.6, 1.5 and 0.8 μm. These bands are associated with different vibrational-rotational transitions within the molecule. This means that the absorption depends on the temperature in a significant way.

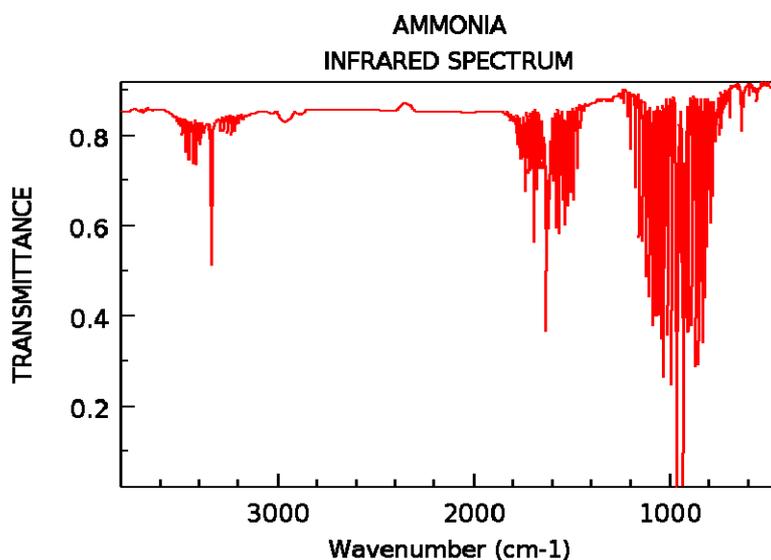Figure 8 shows an absorption spectrum for ammonia in the IR region.

Figure 8.   Infrared absorption spectrum for ammonia.

3.4 Wet chemistry

The method is an extractive technique which means that a gas sample is taken from the exhaust channel. The sample is collected in an absorbing solution during the sampling time. In a following analysis with a portable photometer on site, the average of the ammonia concentration during the sample time is obtained. This method is accredited to IVL by Swedac as a method to measure ammonia slip from marine diesel engines.

3.5 Chemical methods

Since ammonia easily adsorbs on different surfaces when using a probe, it is sometimes useful to make ammonia react to a more inert species that in turn can be detected. This can be done by oxidising ammonia into NO_X and using a NO_X-analyser for the detection. The oxidation can be accomplished with an oxidation catalyst and requires temperatures around 500°C. This method is described further below. Another possibility is to use the SCR reaction and have NO reacting with ammonia. Again, an NO_X-instrument can be used and the NH_3-concentration is in this case given as a decrease in the NO_X-signal.

4. Methods used in the present study

4.1 Wet chemistry

The principle setup used for the wet chemistry measurements in this project are shown in Figure 9. The sampling is done with a pair of glass probes (Figure 10) that sample at two different locations

in the exhaust channel. The ammonia in the probe gas is absorbed in a 0.005 M H_2SO_4 solution. The formed ammonium ions are then measured with a portable photometer (Figure 11).
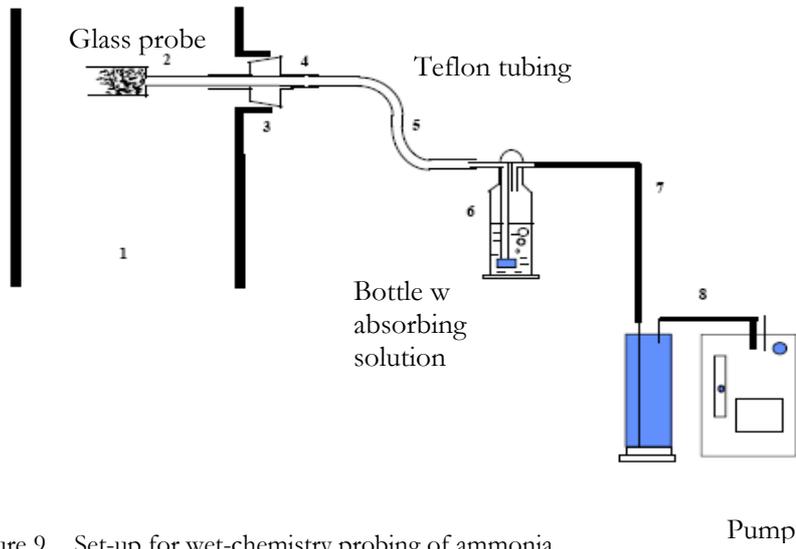

Figure 9.   Set-up for wet-chemistry probing of ammonia.

Figure 10. The probe used for wet chemistry sampling.

Figure 11. Photometer used for ammonium ion measurements.

4.2 Laser system

A laser system designed for ammonia measurements from Siemens Laser Analytics AB was used in this project[7,8,9]. The system is called LDS 6 and utilises a diode laser in the near-infrared region for single-line molecular absorption. The laser light is sent through the gas and detected by a receiver. The laser wavelength is scanned continuously over the ammonia absorption light and the signal from the receiver is analysed in terms of absorption strength. There is also an internal reference cell within the unit. An overview of the setup is shown in Figure 12. The sender and receiver are positioned on flanges on opposite sides of the exhaust channel. The laser is positioned inside the control unit and the light is transferred to the transmitter via an optical cable.
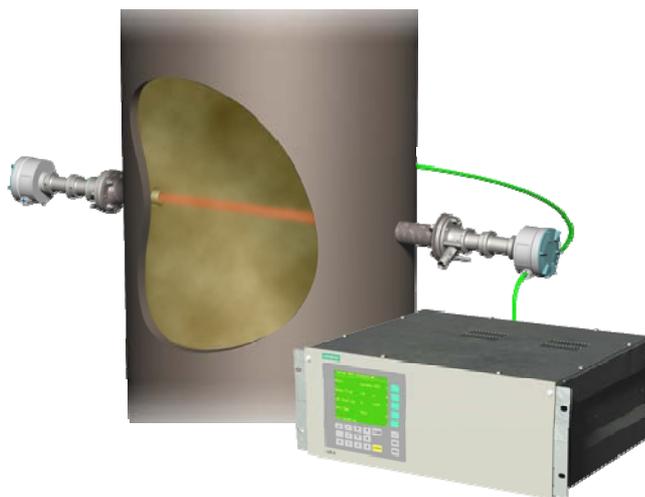

Figure 12. Overview of the LDS 6 system.

Within the transmitter and receiver units there are windows that need to be protected from soot and other impurities in the exhaust gas. This is done through purging with air using a set of fans. Figure 13 shows schematically how the purge-air is connected to the transmitter and receiver units. A photograph of the transmitter unit as mounted onboard a ship is given in Figure 14. The green cables are the optical ones and the tubing with purge air from the fan is the black welded tubing close to the flange.

For the measurements in this report, the LDS6 calculated the NH_3 concentration using a fixed input value of the temperature. This was sufficient for the purpose of following trends. For instance, the fixed value 290°C results in a maximum deviation of +-10% in the range of 250-330°C. The system is equipped with an input interface for the analogue signal of a temperature sensor, in case a more accurate absolute value is needed at varying temperatures.
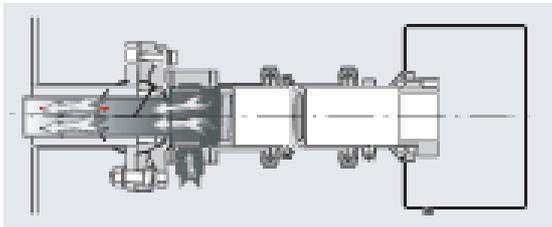

Figure 13. Illustration of the purging of the LDS 6 receiver/transmitter.

Figure 14. A picture of the LDS 6 transmitter mounted on the exhaust channel of a ship.

4.3 Infrared system

The infrared absorption measurements in this study where performed with a portable Fourier Transform Infrared (FTIR) spectrometer from Temet. The principle of this measurement is that an interferogram is generated in a Michelson interferometer. The interferogram is then sent through the sample and onto a detector. The signal is Fourier-transformed in a computer. FTIR spectrometers are known to give a good signal to noise ratio. The frequency of measurement is decided by the needed resolution in the spectra. A schematic setup of a FTIR system is given in Figure 15.
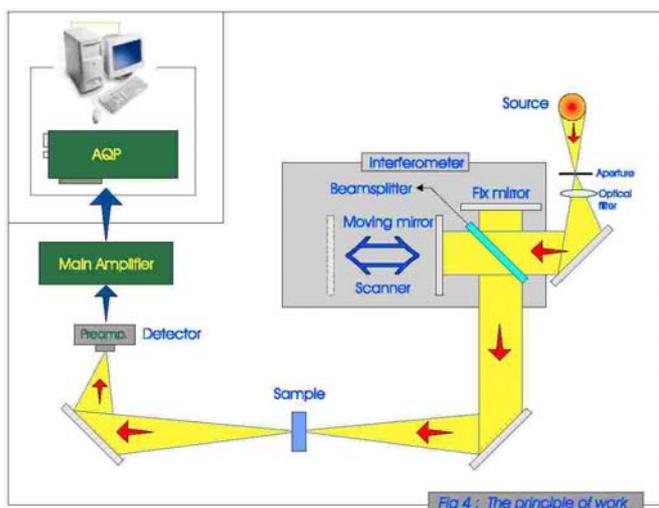

Figure 15. Schematic view of a FTIR system.

The FTIR setup used onboard the ships is outlined in Figure 16. A stainless steel probe (Figure 17) is used for gas sampling and the probed gas volume is transferred to the FTIR system through heated tubing and a gas mixing system, providing constant volume flow. Since the FTIR measurement is non-destructive, the same probe gas is also used to measure other components with a Horiba system (see below). It is thus an extractive measurement where the exhaust is sent to the FTIR via a heated tube (PTFE teflon) and a pumping unit. The GASMET system is designed for field measurements and contains a heated cell where the gas is flown through and the absorption measurement takes place. A number of spectra were taken and averaged to get stable values. This gives the time-resolution of the system. Further, the time resolution of the setup is also decided by the gas flow through the FTIR and the length of the tubing. For gases that may adsorb on walls there can be a significant induction period before stable values are obtained.
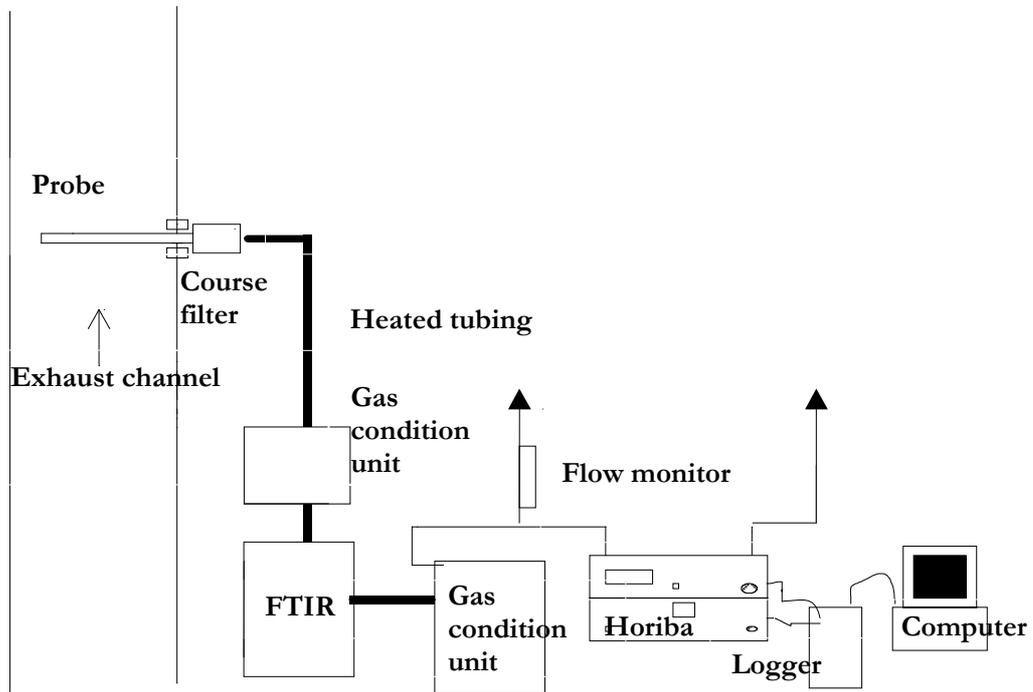
Figure 16. The setup for FTIR measurements onboard the ships.

Figure 17. Probe used for gas sampling to the FTIR system and the Horiba instrument.

4.3 Oxidation catalyst

The idea with using an oxidation catalyst in combination with a NO_X-instrument, was to find a simple way to probe the ammonia content in an exhaust gas with high time-resolution. The setup for the lab experiments is outlined in Figure 18. An oxidation catalyst of the kind that is used in diesel cars to oxidise hydrocarbons and CO, was situated in a heatable quartz tube, containing mainly platinum on alumina. The gases were mixed in front of the tube and a NO_X-instrument was used to probe the product gas. For the ship measurements, a similar setup was used (Figure 19). The catalyst was situated in heated stainless steel tubing with a quartz tube inside. The NO_X level was at the same time measured with another instrument.

Figure 18. Setup for lab experiments with catalyst.

Figure 19. Setup for trials with catalyst onboard.

4.4 Other measurements

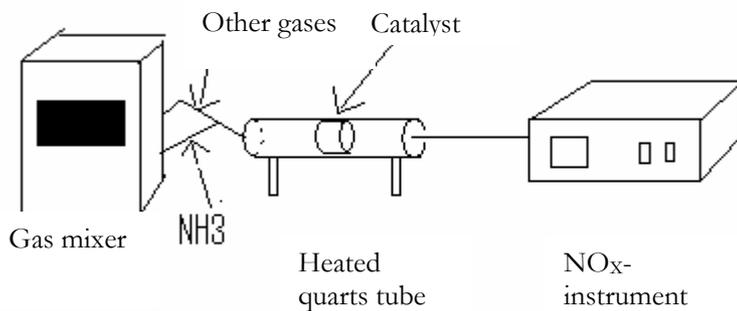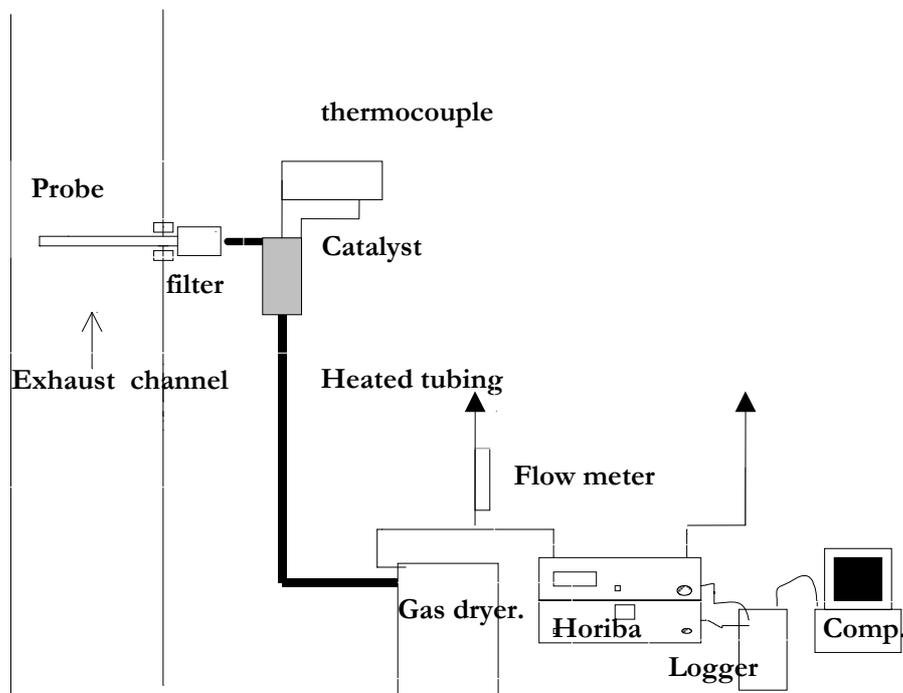During the sampling of ammonia a number of other gases in the exhaust were measured. Nitrogen oxides (Horiba PG-250 chemiluminescence instrument), carbon monoxide and carbon dioxide (Horiba PG-250 NDIR), oxygen (Horiba PG-250 galvanic cell), total hydrocarbon (Bernath Atomic BA 3006 FID), and in some cases sulphur dioxide (Horiba PG-250 NDIR) were measured. The temperature and humidity were monitored and the measurements corrected according to international standards. Engine data were obtained from the ships' instrumentation. Further details on the measurement methodology can be found in Cooper[10]. In the case that the fuel consumption is not known, the gas flow is calculated from the CO_2 measurement and the carbon content in the fuel. In this case, the obtained CO_2 emission factor will originate directly from the carbon content in the fuel. Fuel samples were taken from the ships and analysed after the campaigns.

5 Measurements and results

5.1 Campaign A

The first campaign took place in April 2006 onboard a ferry in connection with certification measurements for an SCR system. This SCR system was equipped with ammonia slip catalysts. However, on one of the main engines the slip catalyst was not put in place until later in order to make it possible to investigate ammonia measurement techniques in this study. The ammonia slip was in this campaign studied using three methods: wet chemistry, FTIR, and laser absorption.

The ferry makes short journeys between Sweden and Denmark. The trip only takes around 20 minutes and the period with cruise load is only around 12 minutes. Thus this ferry is a good object to study transients in NH_3 emission since the urea injection is turned off while manoeuvring and in port.

Sampling was done through holes in the exhaust channel close to the funnel. One 2" hole was used for continuous monitoring of gases (NO_X, CO, CO_2, HC and O_2) and one was used for sampling of ammonia using the wet chemistry method. Two other holes were taken opposite to each other and used for the transmitter and receiver of the diode laser system, respectively.

Wet chemistry sampling was done several times during this campaign. The results obtained are shown as average concentrations in the exhaust during the measurement periods. The results can be seen in Table 2.

Table 2.   Results from wet chemistry NH_3 measurements on Hamlet.

Sampling time (min)	Comment	NH_3 concentration (ppm)
60	One full round trip	7.0
10	One cruise	14.5
7	One cruise	26.2

The FTIR measurements generally showed no or very weak signals of NH_3. This is probably related to the low concentrations in combination with the ex-situ measurements making ammonia stick to surfaces in tubing etc and therefore not detected in the FTIR (se further below). Figure 20 shows the ammonia signal (A) and some other components (B) measured with the FTIR during one round trip of about one hour. The NO_X concentrations as measured with the chemiluminescence instrument are also shown.
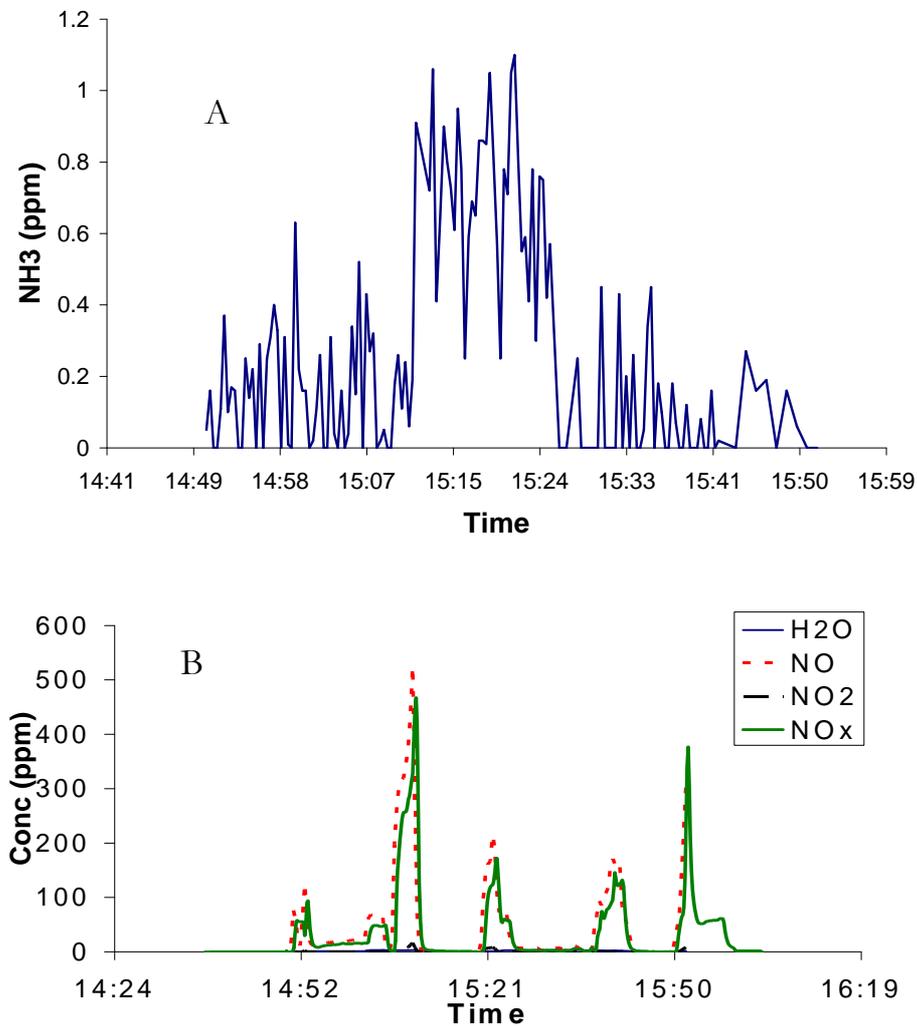

Figure 20. Concentration of some gases measured with FTIR: NH_3 (A), H_2O, NO, NO_2 and NO_X from Chemiluminescence instrument (B).

The NO$_X$ signals from the two measurements show very good agreement. Note that the fraction of NO$_X$ that is present as NO$_2$ is very low. Further, the more "sticky" components, water and ammonia, are hard to measure ex-situ.

The ammonia signal from the laser system is shown in Figure 21 together with the NO$_X$ measurement from the chemiluminescence instrument. The NO$_X$ emission shows clear peaks during stopping and starting of the ship. Soon after the start, the urea injection into the SCR system is initiated. This can be seen as an increase in the ammonia slip during the cruise. The ammonia slip and the NO$_X$ emission differ between the two cruises. This is related to the operation of the ship, where the engine pulls one way and pushes the other way. It should be noted that this data is collected for a system that was in the process of being optimised and, further, that the slip catalyst was mounted after these measurements.
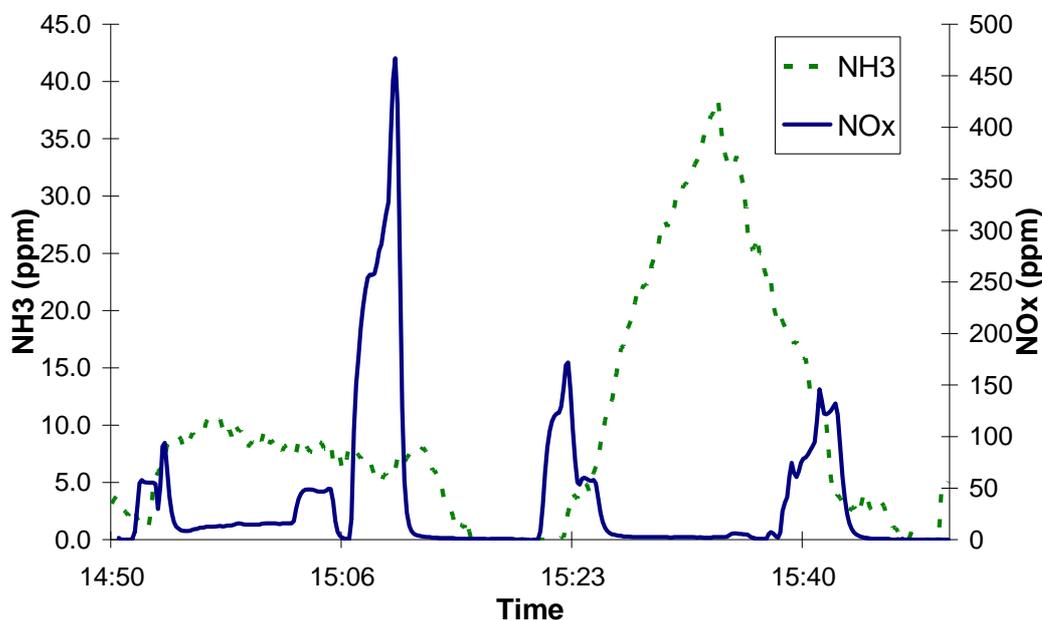
Figure 21 Ammonia signal from laser measurement and NO$_X$ signal from chemiluminescence instrument during one round trip for Hamlet.

A comparison between the different ammonia measurement techniques applied during this campaign can be seen in Figure 22. The result from wet chemistry measurement is given as a line with the obtained value during the period sampling was done. The laser measurement shows the time evolution of the ammonia emission with levels up to 38 ppm during the crossing. The average value resulting from the laser measurement, for the period corresponding to the wet chemistry sampling, was 10 ppm. The signal from the FTIR measurement was very weak as mentioned above.
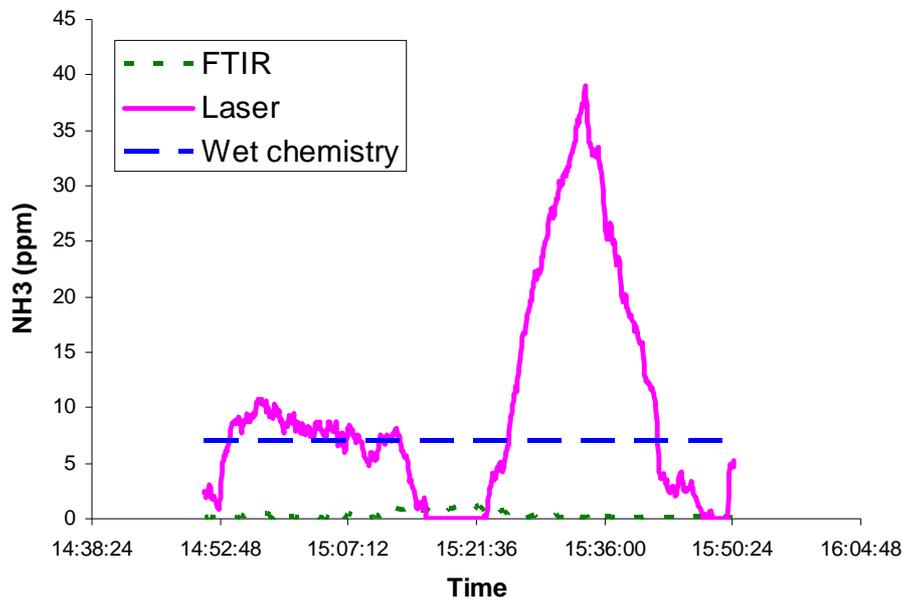
Figure 22. A comparison of the ammonia measurement results using different techniques.

The ammonia slip and the NO_X emission can be related to the engine load (Figure 23). The turquoise line represents the load of the engine. As can be seen there is a significant NO_X emission as the engine power is increased rapidly. After about a minute the NO_X signal goes down as the SCR system starts to operate and the NO_X is reduced by ammonia. After this a slip of ammonia can be seen as double peaks during one journey, giving between 5 and 10 ppm NH_3. The urea injection is set up as a function of the engine power (and exhaust temperature) in order to maximise NO_X conversion and minimise ammonia slip.

Figure 23. NO_X emission and ammonia slip related to the engine power. The NO_X signal is divided by 20 and the power is in arbitrary units.

5.2 Campaign B

The second measurement campaign took place in December 2006 on a ferry in the Baltic Sea. Measurements were done on one main engine which was equipped with a SCR system without an ammonia slip catalyst. Ammonia measurements were performed using wet chemistry, FTIR, the laser system and an oxidation catalyst in combination with a NO_X instrument.
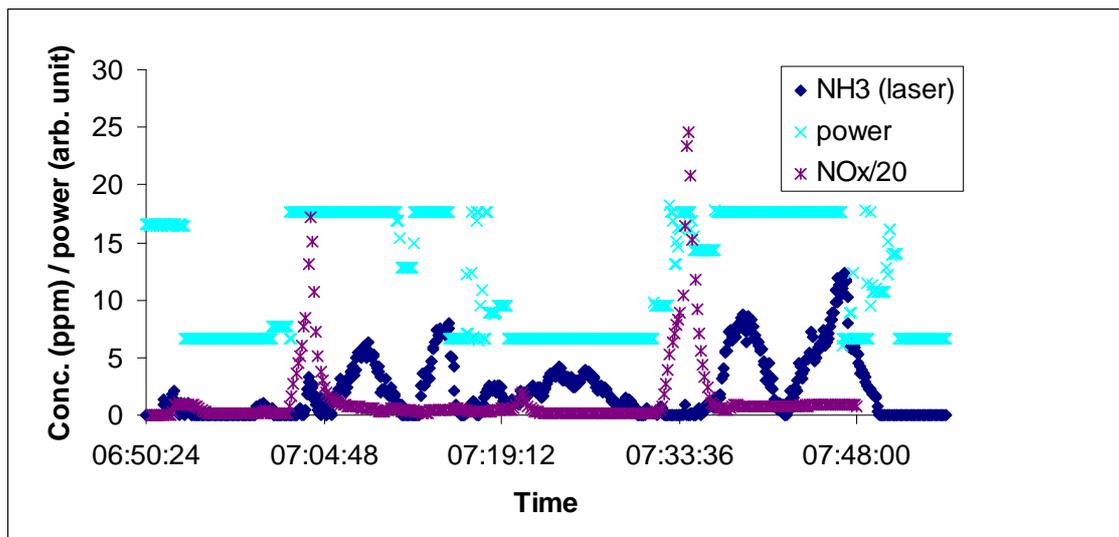
The ferry makes journeys of about five hours with stops in harbour for several hours. The ammonia slip was monitored continuously during several journeys. Measurement holes for the instrumentation was placed in the funnel about ten metres after the SCR catalyst. Two holes opposite each other were used for the laser system, one hole was used to sample gas for the FTIR or the system with oxidation catalyst combined with a NO_X instrument. Another hole was used for the continuous monitoring of NO_X, CO, CO_2, HC, SO_2 and O_2. There was also a hole for the wet chemistry sampling.

Wet chemistry sampling was done at several occasions during the campaign. The samples were in this campaign analysed in two ways. First the standard in field analysis was done using the portable photometer as described above. Secondly, the samples were re-analysed in the IVL laboratory after the campaign. The results from the wet chemistry measurements are given in Appendix 2. There is good correspondence between the two analysis methods. Table 3 give the resulting ammonia concentrations during the Campaign.

Table 3.   Results from wet chemistry ammonia sampling in the second campaign.

Sampling time (min)	NH_3 concentration (ppm)
13	158
14	205

During this campaign the ex-situ FTIR measurements worked well. Figure 24 shows the ammonia signal from the FTIR instrument during one round trip. Note that the instrument was disconnected from the exhaust system at 18.50 (in order to give room for other measurements). Also shown are the results from two wet chemistry samples. The FTIR shows a continuously increasing signal during the trips. The oscillations observed in the second trip are believed to be real fluctuations in the ammonia slip (see further below).
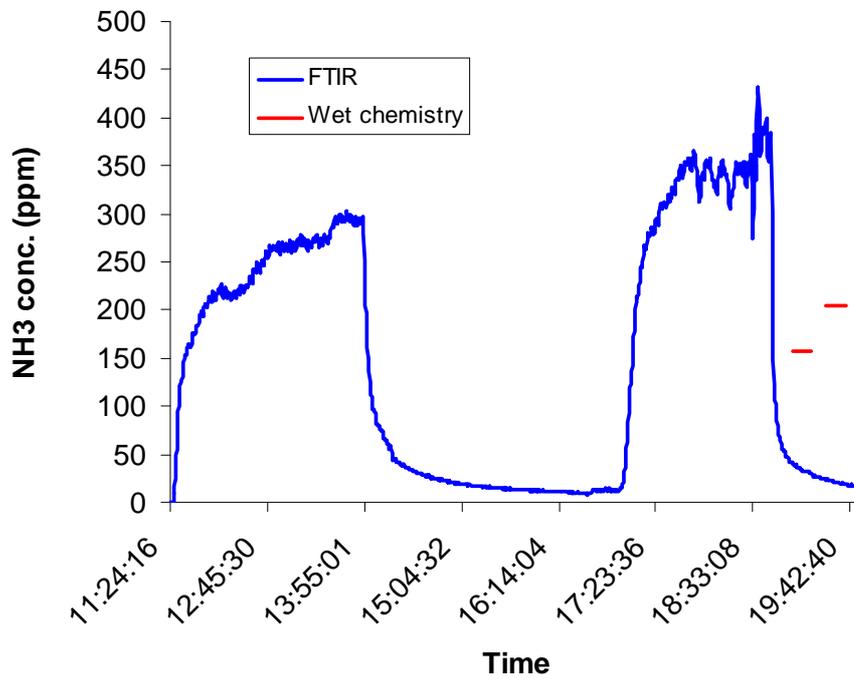
Figure 24. FTIR measurement of the ammonia slip in the second campaign. Also shown are the results from two wet chemistry measurements.

The laser was used continuously in this campaign. As is described above, the setup comprises fans to generate purge air in order to protect the windows from getting covered rapidly by soot and other particulate matter in the exhaust gas. Figure 25 shows the resulting laser signal. The shape of the signal shows the same general trends as the FTIR measurement. One can observe the oscillations in the ammonia slip during the second journey. During the first journey there are two spikes in the curve. These are due to that the fans were turned off in order to investigate the influence on the measurement.

Figure 25. Ammonia as measured with the laser system during the second campaign.

Turning off the fans resulted in an increase in the apparent NH_3 concentration by 28 ppm (from 83 to 111 ppm) or by 31%. This is due to an increased optical path length with ammonia present. With the fans off, ammonia is present not only in the exha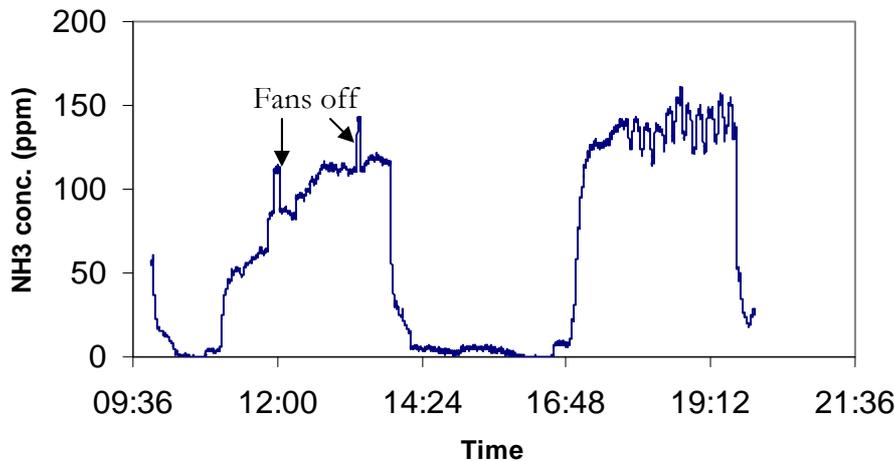ust channel but also in the tubes leading to the windows in front of the laser transmitter and receiver, respectively. This corresponds to an increased length of about 50 cm (from 130 to 180 cm) or 38%. Thus the observed increase in the signal corresponds well to the increased distance where ammonia is present with the fans off.

In Figure 26 the ammonia measurements using wet chemistry, FTIR and laser absorption, are compared. Note that the scale for the FTIR values are on the right-hand axis while the laser and wet chemistry values are according to the scale on the left. Thus the observed signal from the FTIR is much higher than what was measured with the laser. Part of the data is expanded in Figure 27. Here it can be seen that there is a phase difference in the oscillations in the ammonia signal as measured with the FTIR and laser, respectively. This reflects the time-delay in the FTIR measurement caused by the technique being ex-situ and thus the sample gas is pumped via heated tubing into the FTIR cell. Some tests were made with applying the probe for the FTIR at different positions in the exhaust tube. Large variations (ca a factor of two) in the ammonia signal were then observed indicating an unevenly distributed ammonia concentration through the channel.
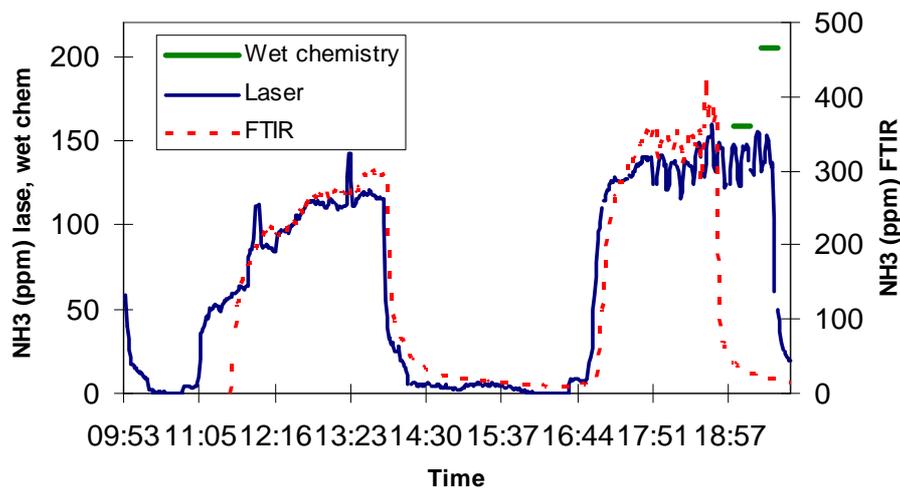

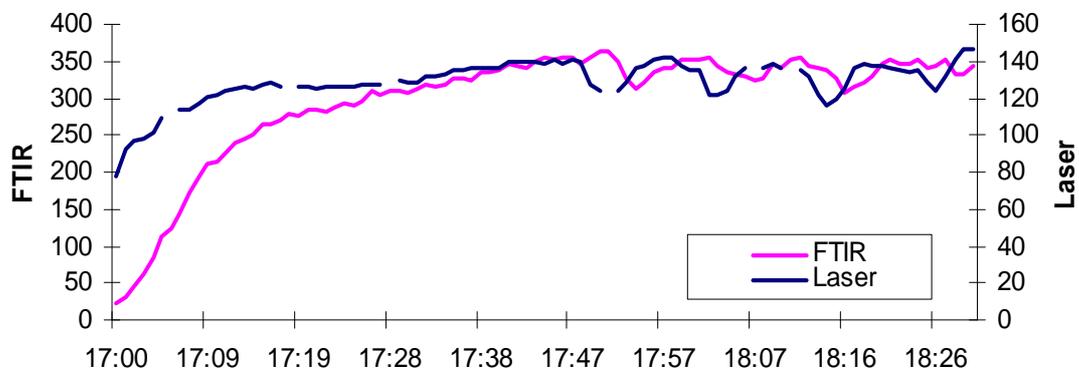Figure 26. Comparison of the different ammonia measurements during campaign B.

Figure 27. Expansion of the data from Figure 26.

The technique of measuring ammonia with an oxidation catalyst in combination with a NO_X instrument was tested in field during this campaign. The catalyst was positioned in a heatable cell as described in section 4.3, and gas was pumped through this cell and into the Horiba instrument where NO_X, SO_2 and CO were measured. At the same time, the NO signal was monitored with the FTIR system using a different hole in the exhaust channel for probing. The idea is thus that the catalyst will oxidise the ammonia with the surplus oxygen in the exhaust. The ammonia signal can then be obtained as the difference between the NO_X signal from the Horiba instrument and the NO signal from the FTIR. These two signals for the trial with the oxidation catalyst are shown in Figure 28.
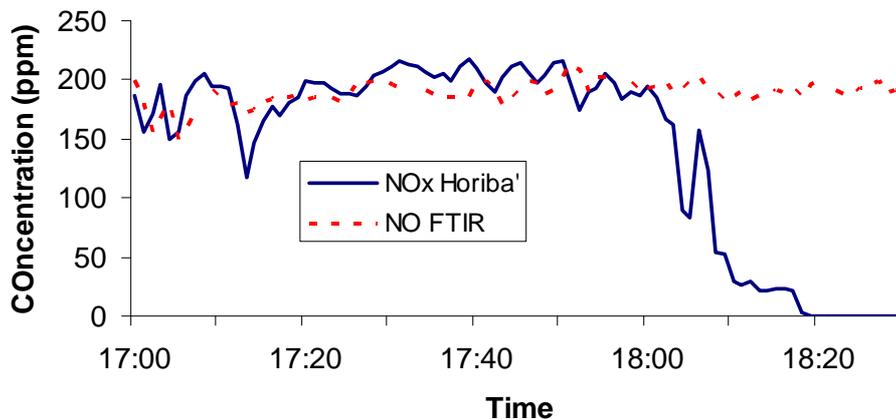

Figure 28. NO_X signal from the Horiba after the oxidation catalyst and the NO signal from the FTIR recorded while testing the oxidation catalyst for ammonia detection.

The heating of the oxidation catalyst was started at 17:12. There is a decrease in the NO_X signal soon after this. This is due to ammonia reacting with NO_X to from N_2, according to the SCR reaction, over the oxidation catalyst. As the temperature in the oxidation catalyst increases, the SCR reaction stops to be important and the oxidation of ammonia becomes apparent as an increase in the NO_X signal. The NO_X signal then stays at 10 - 20 ppm above the FTIR-NO signal with the catalyst at around 550°C. The heating of the oxidation catalyst was turned off at 17:45 where after the catalyst cooled down to ambient temperature. The heating was turned on again at 17:59. A decrease in the NO_X signal was then observed followed by an increase. This is due to the SCR reaction followed by the ammonia oxidation as described earlier. However, at around 18:08 there was again a decrease in the NO_X signal which went down to zero. The CO signal and the SO_2 signal as measured during the same period are shown in Figure 29 and Figure 30, respectively. The CO signals can be seen to decrease as the catalyst is heated due to oxidation of CO into CO_2. It then increases again as the catalyst is cooled down and decreases at the end of the sequence. A similar pattern is observed for SO_2 which is oxidised into SO_3 as the catalyst is heated.

At the end of the sequence it was observed that the tubing after the catalyst had become blocked. Most likely this was due to the formation of compounds like ammonium sulphate. Further the activity in ammonia oxidation observed was low. Considering that there was around 120 ppm ammonia present according to the laser measurements, the NO_X signal would have been expected to increase more than what was observed in Figure 28. This is likely due to the deactivation of the catalyst by e.g., sulphur.
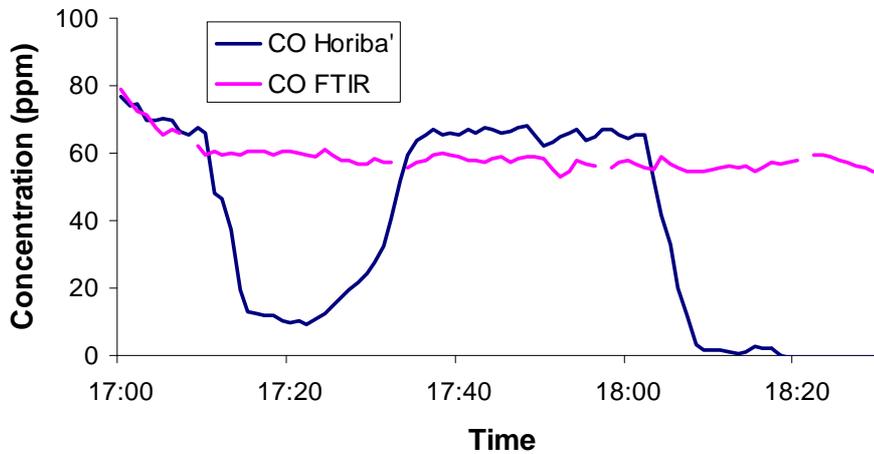
Figure 29. The CO signal during the test of the oxidation catalyst.
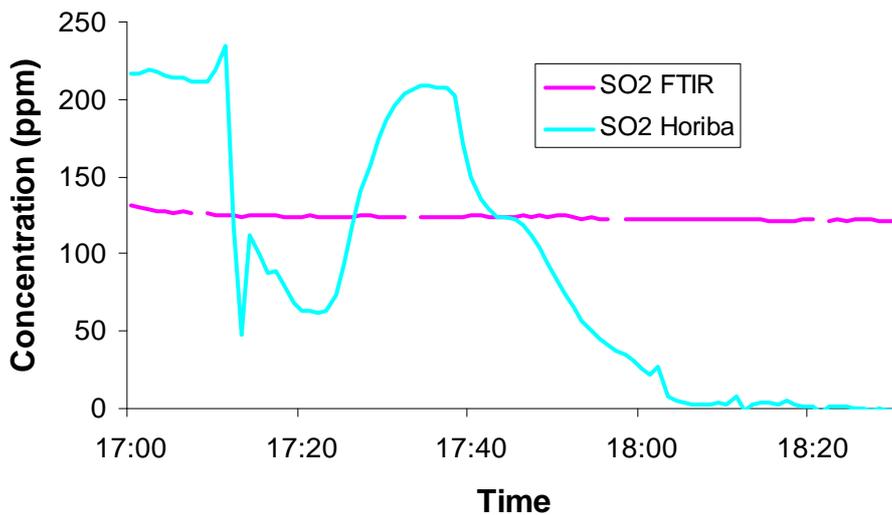
Figure 30. The SO_2 signal during the test of the oxidation catalyst.

5.3 Lab experiments

Some experiments where conducted in a lab in order to test the ammonia measurement techniques. The methods tested here were FTIR, wet chemistry, laser absorption and the oxidation catalyst. A specific gas mixture was obtained from a gas mixing system with mass flow controllers. The gas contained argon as carrier gas and a mixture of one or several of NO, NO_2, O_2, H_2O, NH_3 and CO_2. The mixed gas was heated in a quartz tube to a temperature of 350°C or as indicated. The wet chemistry method was tested by analysing diluted NH_3 from a bottle used for calibration.

The principle of the setup for the FTIR and laser measurements can be seen in Figure 31. The gases were mixed in the gas mixing system with the exception for ammonia and water which were added just in front of the heated quartz tube. Ammonia was obtained from a bottle with 500 ppm

NH₃ in argon. The water injection was obtained from a system where water is heated in an external oven.
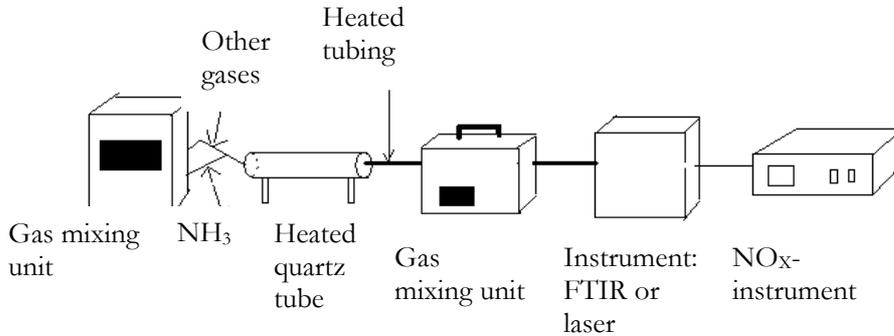
Figure 31. The setup used in the lab experiments fro testing the laser system and the FTIR.

The response from the FTIR upon introducing 100 ppm NH₃ can be seen in Figure 32. After this introduction the gas composition was changed in a certain sequence. The composition and the corresponding ammonia signal from the FTIR system is presented in Table 4. It can be seen that for these measurements the presence of oxygen makes the ammonia signal go down. Also the addition of NO has an influence on the ammonia signal. Water and CO_2 did not influence the signal. In general, too low values are given by the FTIR.
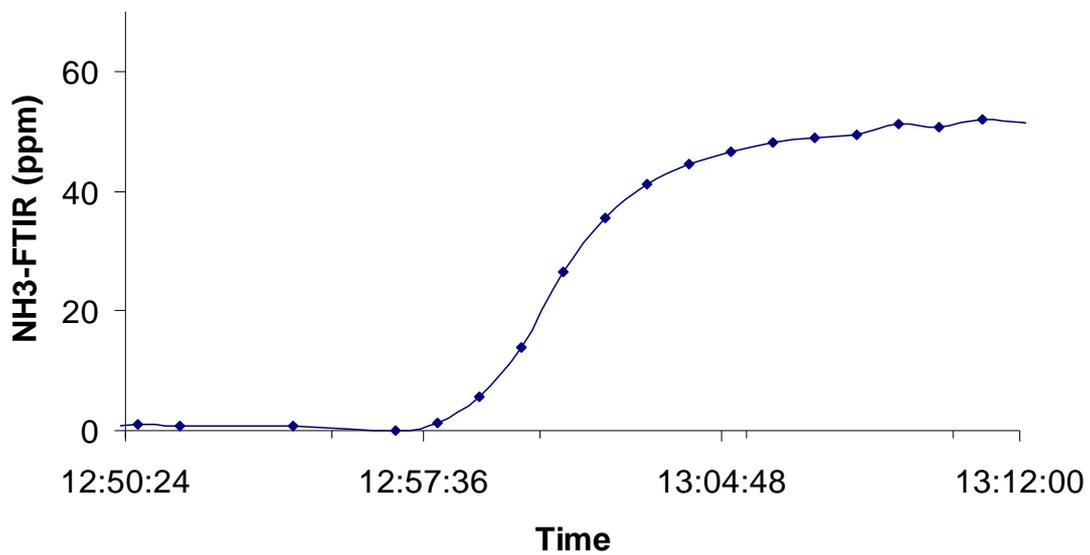
Figure 32. The response of the FTIR-NH₃ signal upon changing the gas mixture from 0 to 100 ppm NH₃ in Ar.

Table 4.   The response of the FTIR to different gas compositions.

Gas composition (Ar as carrier gas)	NH$_3$ response from FTIR
100 ppm NH$_3$	51
100 ppm NH$_3$ + 8% O$_2$	12
100 ppm NH$_3$ + 100 ppm NO	41
100 ppm NH$_3$ + 100 ppm NO + 8% O$_2$	14
100 ppm NH$_3$+ 100 ppm 5% H$_2$O	51
100 ppm NH3 + 1000 ppm CO$_2$	58

Also the laser system was tested in the lab. The main purpose was to check for interference with other gases. The transmitter and receiver were placed on opposite ends of a stainless steel tube (see Figure 33). The heated gas mixture was flown through the tube. Thus, the laser system was in the lab tests arranged to measure ex-situ which was not the case for the field measurements onboard the ships. This arrangement gave a relatively slow response time since the gas in the tube had to be replaced after each change in the gas composition before a stable signal was obtained. A decrease in the measured signal was found when 8% O$_2$ was added to 100 ppm NH$_3$. No change was observed from the addition of NO.

Figure 33. The stainless tube used for the ex-situ tests with the laser system in the lab.

The method to detect ammonia by oxidising it to NO was also tested in the lab. The setup used is depicted in Figure 18. Basically, the oxidation catalyst is placed in a heated quartz tube and the gas mixture is analysed by a NO$_X$ analyser. It should be noted that this is a preliminary test to determine if the method is feasible.

Figure 34 shows the response from the NO$_X$ instrument as the catalyst is heated. Two different gas compositions were used; the first with 50 ppm NH$_3$ and 8% O$_2$, and a second one where 100 ppm NO was added. The total NO$_X$ was thus 50 ppm and 150 ppm respectively. The response in ammonia and oxygen shows an increased yield of NO with increasing temperature. It is required to reach a temperature of about 500°C to get full oxidation of NH$_3$ into NO$_X$.
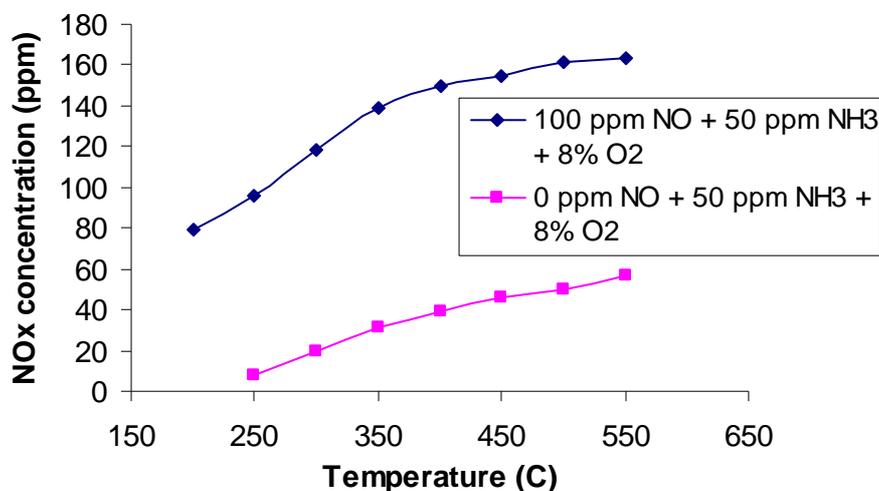
Figure 34. The response of the NO_X-instrument as a function of temperature with 50 ppm NH_3 and 8% O_2 plus either 0 or 100 ppm NO.

The results from the wet chemistry measurements in the lab proved to give accurate results when tested on a calibration bottle of NH_3. The value of the routine to rinse the tubes was also tested and proven to be important. In general, there seems to be high accuracy in this method.

6. Discussion and conclusions

This study examines how different methods for analysing ammonia emissions can be used in field measurements. The methods were then used in a way that is similar to a standard test situation and the instruments were applied without any modification.

The FTIR was in this study applied as an ex-situ method where a stainless steel probe and a heated tube were used to sample the gas to be measured. The measurements with FTIR during Campaign A did not give a reliable response for ammonia. Most likely this is related to the low concentration of ammonia in combination with reactions between ammonia and oxygen or NO over the surfaces in the probe system. During Campaign B the FTIR system worked well. The time resolution was fairly good although there was a noticeable delay due to the tubing. The signal was higher than for the other measurements. This is likely due to the uneven concentration of ammonia through the exhaust channel. In the lab experiments it was observed that the presence of oxygen in the gas mixture influence the measured values. This is likely due to oxidation reactions taking place over metal surfaces and in the gas phase. This is thus a consequence of the method being ex-situ and may lead to erroneous values in field measurements.

The laser system was used onboard a ship for the first time during Campaign A. The mounting requires two holes opposite each other on the exhaust channel. The setup of the system was simple and there were no problems in aligning the laser beam. An accurate measurement of the probe distance is needed to obtain a reliable result. Purge air was provided from two fans that were brought specially for this measurement. One can also use compressed air but this was not tested. Cleaning of the windows was required on one occasion when it was observed that the laser signal had decreased too much. The response from the system was good, both a high sensitivity and a

good time resolution. In general, the setup worked without interference during the campaign. In Campaign B the laser set up was similar. This setup was put up without assistance from Siemens. By turning on and off the fans supplying purge gas, it was deduced that the effective probe distance is the diameter of the exhaust channel, i.e., the smaller tubes leading to the optical windows will be filled with clean purge-air. The system worked continuously without problems during the campaign, gave good time resolution and high sensitivity. Since the probing volume is a cylinder across the exhaust tube, the obtained concentration will be an average over a line across the exhaust channel. This minimises the potential influence of uneven concentration distributions of ammonia on the response and thus give a good representation of the actual emission out of the funnel. One could set up more flanges and thus probe alternative lines across the exhaust channel in order to further minimise the influence of local, unrepresentative ammonia concentrations. The time resolution obtained allows for on-line adjustment of the parameters for urea injection. This opens up for a much more rapid and effective adjustment in order to minimise both NO_X emissions and NH_3 slip and to assess the status of the catalyst. Further, it also opens up the possibility to design the urea injection so that the SCR system can operate during e.g., manoeuvring, starts and stops. There is also the possibility to use the system for continuous monitoring of the ammonia slip. However, the long-term use was not tested in this project. The possibility of a drop in signal due to covering of the optical windows by soot etc should be investigated if a long-time monitoring use is requested.

The wet chemistry method to sample gas in a sulphuric acid and analysing for amine content with a photometer works well. The method proved reliable in the lab studies, however, it was found to be of importance to make sure that the material that stick to the tubing are collected as well. The drawbacks of the method are several. The time response is low, although we found in this study that the field analysis with the portable photometer well matches the analysis made in the laboratory. The sampling is made of a small volume within the exhaust channel which makes the method sensitive to uneven distribution of ammonia.

The method where an oxidation catalyst was used in combination with a NO_X instrument showed some promise in the lab studies with synthetic gas mixtures. The method gave the possibility to measure ammonia in the presence of a large oxygen surplus and in the presence of NO. Further, a good time response to changes in the gas-mixture was obtained. However, in the field test the method was found not to be applicable. The main reason was a deactivation of the catalyst due to the presence of high amounts of sulphur in the exhaust gas.

Some general conclusions from this study are:

- This study has examined a number of ammonia measurement techniques applied to ammonia slip measurements for SCR systems onboard ships.

- Ex-situ methods for ammonia measurements are problematic when the concentrations are low.

- Other gases (oxygen, water) may influence the result when ex-situ measurements are used.

- The use of probes that sample a small volume within the exhaust channel may give unrepresentative results if the ammonia distribution within the exhaust channel is uneven.

- FTIR requires careful calibration and when used ex-situ, surfaces within the system must be saturated with ammonia before reliable results are obtained.

- The laser absorption method worked well onboard the ships. High accuracy and good time-resolution was obtained. The system was easily handled and mounted. The setup requires purge-gas and two flanges opposite each other on the exhaust tube.

- The wet-chemistry sampling gave accurate results but is time-demanding and does not in full account for uneven distributions of ammonia.

- The method with an oxidation catalyst and a NO_X instrument proven not to work for marine exhausts.

7. Outlook

The results from this study open up some suggestions for future monitoring of ammonia slip from SCR systems onboard ships.

There is a clear opportunity to apply continuous monitoring. This could be done with the laser system or ex-situ with FTIR. It remains to prove the long term function of the systems considering the harsh environment in ships' exhaust systems.

A good time-resolution was obtained with the laser system but also with the FTIR (provided the concentration of ammonia is not too low). This opens up for tuning the SCR systems, i.e., the urea injection in order to maximise NO_X conversion and minimise ammonia slip during e.g., transients in engine power. It may also open up for extended operation time of the SCR systems, e. g., in ports.

Considering the results in this study it appears feasible to use the laser method as an accredited method in certification measurements.

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Appendix 1 Ships and fuel

Ship A

Property	ME and AE Fuel
Viscosity at 50 °C, mm²/s	2.39
Density at 15 °C , g/cm³	0.8409
Carbon, C wt-%	85.5
Hydrogen, H wt-%	13.3
Nitrogen, N wt-%	0.06
Sulphur, S wt-%	0.03
Oxygen, O wt-%	1.1
Effective heating value, MJ/kg	42.89

	MEs	AEs
Manufacturer / Engine Type	Wärtsilä	Mitsubshi
Rated Speed, rpm	1000	1500
Rated Power, kW	1530	490
No. / config. of cylinders	9L20	S6R-MPTA
Bore, mm	200	170
Stroke, mm	280	180
Combustion cycle	4 stroke	4 stroke
Cooling medium	HT and LT	HT
Fuel type used	GO E10	GO E10
Exhaust channel diameter, m	ca 0.7	ca 0.3
Exhaust sampling ports	2 x 2"	2x 2"

Ship B

Property	ME Fuel
Viscosity cSt, at 50 ^oC	417
Density kg/lit, at 15 ^oC	0.9898
Carbon, C wt-%	88.0
Hydrogen, H wt-%	10.6
Nitrogen, N wt-%	0.45
Sulphur, S wt-%	0.51
Oxygen, O wt-%	0.4
Effective heating value, MJ/kg	40.75

	MEs
Manufacturer / Engine Type	Wärtsilä 12V 46C
Rated Speed, rpm	500
Rated Power, kW	12 600
No. / config. of cylinders	12 Vee
Bore, mm	460
Stroke, mm	580
Combustion cycle	4 stroke
Cooling medium	Water
Fuel type used	Heavy Fuel Oil
Ref. temp of intercool. air, ^oC	50

Appendix 2. Results from ammonia analysis in lab

Sample no.	NH$_4^+$ content field analysis (mg)	NH$_4^+$ content lab analysis (mg)
1	4.5	4.370
2	4.0	4.236
3	3.7	3.896
4	2.7	2.988
5	>10	11.479
6	3.5	3.629
7	3.0	2.916
8	2.3	2.368
9	1.8	1.823
10	6.8	7.117