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# Remote sensing of sulphur and particle emission from ships

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Remote sensing of sulphur and particle emission from ships

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# Preface

This is the final report in the project with the official title "Surveillance of sulphur and particle pollution from ships", co-financed by the Danish Environmental Protection Agency (EPA) under the subsidy scheme MUDP 2012. The project lasted from July 2013 to December 2015 with the overall purpose of developing a fast method that could detect the sulphur content in fuel from ships by means of either remote sensing of emission or direct analysis of fuel.

The project is a partnership between ZenZors A/S, A/S Storebælt, Nordic Tankers Marine A/S, Danish Shipowners Association and Danish Technological Institute. In addition, Maersk Maritime Technology closely followed the project and results.

Danish Technological Institute

Aarhus, December 2015

# Summary and conclusion

In 2015, the maximum allowed sulphur content in fuel was reduced from 1% sulphur to 0.1% sulphur in Emission Control Areas (ECAs), referring to the International Maritime Organization (IMO).[1] Therefore, shipowners must either use low sulphur fuel or implement an emission abatement method, i.e. a scrubber system, which removes the sulphur oxides from the vessel exhaust gas. Either approach will result in a significant extra cost for the shipowners and opens up for possible violation. In order to create a level-playing-field for the shipowners and a credible risk of being observed when violating regulations, the ships have to be monitored. That calls for a simple and robust control method.

The overall project objective was to develop method(s) for fast determination of the sulphur content in fuel. The prime focus in the project was to estimate the sulphur content through plume measurements (remote sensing) when ships pass the eastern part of the Great Belt Bridge (Storebælt) (proof of concept). In parallel, two other potential fast methods that aim at fast analysis of the sulphur content directly in fuel were investigated, as they could be a supplement to remote sensing. During the project, the project objective was modified to aim at cost-effective monitoring technology for indicative classification due to awareness of similar international activities and already developed - but expensive - solutions.

In work package (WP) 1, the objective was to investigate and develop suitable methods for monitoring particulate matter (PM), $SO_2$ and $CO_2$ in vessel exhaust plumes from a distance of several hundred metres. In addition, initial $CO_2$ background measurements at the Great Belt Bridge were covered in order to determine whether background fluctuations were pronounced (due to, e.g., road traffic). In WP 2, the objective was to test the selected sensors and developed method at measurement locations at the Great Belt Bridge (proof of concept). The potential of the different possible measurement locations on the bridge, defined in WP 1, are to be investigated with respect to remote sensing of sulphur content in fuel. That will take place during different measurement campaigns aiming at a final measurement campaign of several weeks, and all of the campaigns will focus on cost-effective monitoring technology. The objective of WP 3 was to investigate the potential for developing a fast method for direct analysis of sulphur content in fuel within minutes. Such a method could allow the relevant authorities to check the sulphur content in fuel when the ships are at berth or at sea. That could be a strong supplement/alternative to the remote sensing approach. Finally, WP 4 will concentrate on the dissemination of project results. Due to the new regulations implemented in 2010 and 2015, the surveillance of sulphur pollution has been a burning topic in this decade. Because of the topicality, the dissemination of project results received its own work package.

Based on a comprehensive literature study, market survey and validation experiments in the lab, a basic sensor technology as well as a preliminary measurement location on the Great Belt Bridge were accomplished in WP 1, with the aim to implement cost-effective monitoring. Preliminary measurements from both Aarhus harbour and similar locations gave the project team strong confidence in the measurements from the Great Belt Bridge, due to unmistakable and significant $CO_2$ signals from a number of ships, when cost-effective $CO_2$ sensors were used. Based on the results, it was decided to continue measuring on the Great Belt Bridge and to carry out preliminary measure-

[1] http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-–-Regulation-14.aspx

ments from one of the pylon platforms on the bridge. There were many similarities between that location and other measurement positions used until that point in the project, but there were also similarities between what is being carried out at the port entrance of, e.g., Gothenburg. Preliminary $CO_2$ background measurements from the pylon platform did not show significantly higher background fluctuations than the ones observed at, e.g., Aarhus harbour and similar locations.

In WP 2, the sensors were brought to the Great Belt Bridge. It appeared that a number of locations at the Great Belt Bridge have potential with respect to remote sensing of sulphur content in fuel, based on cost-effective monitoring technology. These locations include measurements from the pylon platform but also from below the bridge. However, a number of improvements must be made on the sensor solution before such a solution can be commercialised. They depend on the permitted measurement uncertainty, and on whether an indicative classification of ships will be acceptable. They must be followed up by further inspection by the authorities, either when the ship is in port or at sea.

A final 2-week measurement campaign was carried out after a number of smaller, dedicated measurement campaigns at different strategic locations at the Great Belt Bridge using different sensor set-ups. In this context, it was very difficult to achieve a satisfactory high gas concentration for the chosen $CO_2$ sensor. That is to some extent surprising, as:

1) initial harbour measurements (WP 1) gave promising results from rather similar measuring conditions.
2) initial modelling suggests relatively high gas concentrations at some of the measurement locations. A possible explanation for this discrepancy could be that the ships in the Great Belt sail faster than at the other measurement locations, and therefore the plume is present for a shorter time span.

Preliminary calculations of sulphur fuel content, based on our measurements from the Great Belt, suggest that the present method can be used for a very rough estimate of sulphur content in fuel. This conclusion is based on measurements from both the pylon platform (measurement campaign during 1% sulphur conditions) and from a location right below the bridge at the lantern defining the outer boundary of the northbound lane (campaign during 0.1% sulphur conditions). However, it should be emphasized that the present method has a considerable uncertainty that is associated with the measurement, which is difficult to define at the moment. Currently, it is not advised to use the present method for routine monitoring. That is why a lot of work still exists in the attempt to make cost-effective monitoring best practice.

To achieve a reliable monitoring platform based on cost-effective sensor technology, further and more detailed modelling of exhaust gas plumes will be necessary in order to locate and define optimum measurement conditions. The initial modelling that was carried out suggests that it should be possible to locate higher gas concentrations at the Great Belt Bridge. In addition, it might be necessary with an improved sensor signal-to-noise ratio, if significantly higher gas concentrations are not located, together with an innovative concept regarding the measurement probe.

In this context, it should also be noted that Chalmers, Sweden, will be using their state-of-the-art sensor technology to carry out parallel measurements from the pylon platform during the period 2015-2016 (Danish EPA tender). To the best of our knowledge, they have so far obtained reliable measurement results. This is of course very satisfactory from an overall monitoring point of view, but in the long run it is not expected that this technology has the optimum potential to be broadened, due to the significant cost of such a monitoring platform.

In WP 3, the project team investigated two potential fast methods that aim at a fast analysis of the sulphur content directly in the fuel:

1. analysis of sulphur content in selected fuel samples using handheld X-ray fluorescence (XRF) and in this context XRF method optimization.
2. a theoretical survey of the potential for a laboratory technique that aims at a fast determination of the sulphur content by using a chemical detection “kit”.

A handheld XRF spectrometer was used for direct analysis of the sulphur content in 12 different fuel samples with varying sulphur contents from 0.1% to 3.3% sulphur. The results were very promising and all results were within 10% of the reference analyses carried out by DNV. Based on the results, the method seems to underestimate the sulphur content, which could likely be a question of calibration. However, with the present and described method it should be safe to conclude that the present method can distinguish 0.1% sulphur from 1% sulphur and from 2-3% sulphur and it can be used instantaneously.

In addition, several strategies for a fast determination of the sulphur content by a chemical detection “kit” have been investigated on a theoretical basis. Several plausible strategies have been found, and a strategy based on a two-step oxidative-precipitation method was considered and discussed in more detail. Further development of the proposed systems will require considerable experimental work involving development, selection of suitable oxidation agents, solvent systems, precipitation agents etc. with focus on simplicity, so inspectors could use the method as a routine in actual practice. Furthermore, a careful validation study would demonstrate the utility and compatibility of the proposed systems over a range of different marine oil products. The required development and validation is beyond the scope and resources of this project, but it could be pursued in a separate project.

In WP 4, the project results and ideas were disseminated in a number of different channels, including national and international seminars/workshops and national media. Based on the many dissemination activities it is concluded that the project activities and results have resulted in considerable exposure of the project, which is important in order to highlight the importance of cost-effective sulphur monitoring.

# Konklusion og sammenfatning

I 2015 blev den maksimalt tilladte svovlprocent i skibsbrændstof reduceret fra 1 % svovl til 0,1 % svovl i de såkaldte *Emisison Control Areas* (ECAs) med henvisning til den Internationale Maritime Organisation (IMO).[1] Skibsredere må således enten bruge lavsvovlsbrændstof eller implementere et emissionsbegrænsende system (et scrubber-system), som fjerner sovoloxider fra skibets udstødningsgas. Begge tilgange vil medføre betydelige ekstraomkostninger for skibsrederne og åbner op for mulig overtrædelse. For at sikre lige vilkår for rederne og en troværdig risiko for at blive fanget, hvis reglerne overtrædes, må skibene nødvendigvis overvåges. Det kræver en enkel og robust kontrolmetode.

Det overordnede mål med projektet var at udvikle en metode til hurtigbestemmelse af svovlindholdet i skibsbrændstof. Det primære fokus i projektet var at estimere svovlindholdet gennem røgfanemålinger (fjernovervågning), når skibene passerer den østlige del af Storebæltsbroen (højbroen) ved *proof-of-concept*. Sideløbende blev to andre potentielle hurtigmetoder for straksbestemmelse af svovl, der sigter på en hurtig analyse af svovlindholdet direkte i brændstof, undersøgt, som et muligt supplement til fjernovervågningen. I løbet af projektet blev projektmålet modificeret til at sigte mod omkostningseffektiv overvågningsteknologi til indikativ klassificering af skibene på grund af kendskab til lignende internationale aktiviteter og allerede udviklede, men dyre løsninger.

I arbejdspakke (WP) 1, var formålet at undersøge og udvikle egnede metoder til overvågning af partikler (PM), SO2 og $CO_2$ i udstødningen fra skibene fra en afstand på flere hundrede meter. Desuden blev de første $CO_2$-baggrundsmålinger på Storebæltsbroen udført for at fastslå, om der var væsentlige udsving i baggrundsniveauet (på grund af fx vejtrafik). I WP 2 var formålet at afprøve de valgte sensorer og udviklede metoder ved at måle forskellige steder på Storebæltsbroen (*proof of concept*). Potentialet i de forskellige målesteder på broen blev desuden defineret i WP 1, og de skal undersøges nærmere med hensyn til fjernovervågning af svovlindholdet i skibsbrændstof. Det vil ske gennem forskellige målekampagner med en afsluttende målekampagne, der varer flere uger. Alle målekampagnerne vil fokusere på omkostningseffektiv overvågningsteknologi. Formålet med WP 3 var at undersøge mulighederne for at udvikle en hurtigmetode til direkte analyse af svovlindholdet i brændstoffer inden for få minutter. En sådan fremgangsmåde vil gøre det muligt for de relevante myndigheder at kontrollere svovlindholdet i brændstof, når skibene er i havn eller på havet. Man kunne forestille sig, at dette var et stærkt supplement eller alternativ til fjernovervågningen. Endelig vil WP 4 fokusere på formidling af projektets resultater. På grund af de nye regler indført i 2010 og 2015 har overvågning af svovlforurening været et glødende emne i dette årti, og netop på grund af denne aktualitet har formidling fået sin egen arbejdspakke.

Baseret på en omfattende litteraturundersøgelse, markedsundersøgelse og valideringseksperimenter i laboratoriet blev en grundlæggende sensorteknologi samt en indledende sensorplacering på Storebæltsbroen valgt i WP 1. Formålet var at gennemføre omkostningseffektiv overvågning. Foreløbige målinger fra både Aarhus havn og lignende steder gav projektgruppen stærk tiltro til de kommende målinger fra Storebæltsbroen, ikke mindst på grund af umiskendelige og betydelige $CO_2$-signaler fra en række skibe, når omkostningseffektive $CO_2$-sensorer blev brugt. På baggrund af resultaterne blev det besluttet at fortsætte målinger på Storebæltsbroen og foretage foreløbige målinger fra en af pylonplatformene på broen. Der var mange ligheder mellem denne placering og de andre målepositioner, der hidtil var blevet anvendt i projektet, og også ligheder med hvad der bliver udført ved indsejlingen til fx Göteborg. Foreløbige $CO_2$-baggrundsmålinger fra pylonplatformen viste ikke signifikant højere baggrundsudsving end dem observeret ved fx Aarhus havn og lignende steder.

I WP 2 blev sensorerne anvendt på Storebæltsbroen. Baseret på omkostningseffektiv overvågningsteknologi har det vist sig, at en række steder på Storebæltsbroen har potentiale for fjernovervågning af svovlindhold i brændstof. Disse placeringer omfatter målinger fra pylonplatformen men også fra under broen. Dog skal en række forbedringer foretages på sensorløsningen, før en sådan løsning kan kommercialiseres, hvilket også afhænger af den tilladte måleusikkerhed, og hvorvidt en vejledende klassificering af skibe vil være tilstrækkelig. Myndighederne skal følges op på dette med mere inspektion, enten når skibet er i havn eller til havs.

En afsluttende 2-ugers målekampagne blev udført efter en række mindre, dedikerede målekampagner på forskellige strategiske steder på Storebæltsbroen ved brug af forskellige sensoropstillinger. I denne sammenhæng var det meget vanskeligt at opnå en tilfredsstillende høj gaskoncentration for den valgte $CO_2$-sensorteknologi. Det er i et vist omfang overraskende, eftersom:

1. de indledende havnemålinger (WP 1) gav lovende resultater under sammenlignelige målebetingelser.
2. indledende modellering antyder, at der er relativt høje gaskoncentrationer på udvalgte målesteder. En mulig forklaring på denne uoverensstemmelse kunne være, at skibene sejler hurtigere, når de passerer Storebælt, end ved de øvrige målesteder, og derfor eksisterer røgfanen i en kortere periode.

Foreløbige beregninger på brændstoffets svovlindhold, baseret på vores målinger fra Storebælt, tyder på, at den nuværende metode kan bruges til et meget groft estimat over svovlindhold i brændstof. Denne konklusion er baseret på målinger fra både pylonplatformen (målekampagne ved 1 % svovlkrav) og fra en placering lige under broen ved et lanterneudtag, som definerer den ydre grænse af det nordgående spor (kampagne ved 0,1% svovlkrav). Imidlertid bør det understreges, at den foreliggende fremgangsmåde har en betydelig usikkerhed tilknyttet målingen, som er vanskelig at definere i øjeblikket. Det kan således i øjeblikket ikke anbefales at bruge den nuværende metode til rutinemæssig overvågning, og der eksisterer stadig et stort stykke arbejde i forsøget på at gøre omkostningseffektiv overvågning til bedste praksis.

For at opnå en pålidelig overvågningsplatform baseret på omkostningseffektiv sensorteknologi vil yderligere og mere detaljeret modellering af røgfaner være nødvendig for at lokalisere og definere de optimale målebetingelser. Den indledende modellering, der blev gennemført, antyder, at det bør være muligt at lokalisere højere gaskoncentrationer på Storebæltsbroen, end hvad der blev fundet. Herudover kan det være nødvendigt med et forbedret sensor signal-/støjforhold, hvis signifikant højere gaskoncentrationer ikke lokaliseres, sammen med et innovativt koncept vedrørende måleprobe.

I denne forbindelse skal det også bemærkes, at Chalmers, Sverige, i perioden 2015-2016 vil benytte deres avancerede sensorteknologi til at udføre parallelle målinger fra pylonplatformen (opgave for Miljøstyrelsen). Så vidt vi ved, har de hidtil opnået pålidelige målinger fra Storebælt. Dette er naturligvis meget tilfredsstillende ud fra et overordnet overvågningssynspunkt, men i det lange løb er det ikke forventeligt, at denne teknologi har det optimale potentiale til at kunne udbredes på grund af de betydelige omkostninger en sådan overvågningsplatform medfører.

I WP 3 har projektgruppen undersøgt to mulige hurtigmetoder, der sigter mod en hurtig analyse af svovlindholdet direkte i brændstof:

1. Analyse af svovlindholdet i udvalgte brændstofprøver under anvendelse af håndholdt røntgenfluorescens (XRF) og i denne sammenhæng XRF-metodeoptimering.
2. en teoretisk undersøgelse af mulighederne for udvikling af en laboratorieteknik, der sigter mod en hurtigbestemmelse af svovlindholdet ved hjælp af udstyr til kemisk detektion.

Et håndholdt XRF-spektrometer blev anvendt til direkte analyse af svovlindholdet i 12 forskellige brændstofprøver med svovlindhold varierende fra 0,1 % til 3,3 % svovl. Resultaterne var meget lovende og alle var inden for 10 % af referenceanalyseværdierne foretaget af DNV. Baseret på resultaterne lader det til, at metoden konsekvent undervurderer svovlindholdet en smule, hvilket dog sandsynligvis er et spørgsmål om kalibrering. Med den foreliggende beskrevne fremgangsmåde kan det konkluderes, at metoden kan skelne 0,1 % svovl fra 1 % svovl og fra 2-3 % svovl, og vil med det samme kunne implementeres i overvågningen.

Desuden er adskillige strategier til hurtigbestemmelse af svovlindholdet ved udvikling af et udstyr til kemisk detektion blevet undersøgt på et teoretisk grundlag. Der er flere plausible strategier, hvoraf en strategi baseret på en totrins-oxidativ udfældningsmetode er blevet behandlet og diskuteret i flere detaljer. Videreudvikling af de foreslåede systemer vil kræve et betydeligt eksperimentelt arbejde, der involverer udvikling, udvælgelse af egnede oxidationsmidler, solventsystemer, fældningsmidler osv. med fokus på enkelhed, så inspektørerne i praksis vil kunne bruge metoden rutinemæssigt. Desuden ville en omhyggelig valideringsundersøgelse kunne demonstrere anvendeligheden og foreneligheden af de foreslåede systemer over en række forskellige marine olieprodukter. Den nødvendige udvikling og validering ligger dog uden for dette projekts rammer og ressourcer.

I WP 4 blev projektets resultater og ideer formidlet gennem forskellige kanaler, herunder nationale og internationale seminarer / workshops og nationale medier. Baseret på de mange formidlingsaktiviteter konkluderes det, at projektets aktiviteter og resultater har resulteret i en betydelig eksponering af projektet, hvilket er vigtigt for at understrege betydningen af omkostningseffektiv svovlovervågning.

# 1. Introduction

Shipowners are faced with strict requirements regarding fuel sulphur content in Emission Control Areas (ECAs). In 2010, the maximum allowed sulphur content in fuel was reduced to 1%, and in 2015 the limit was reduced further by 0.1% sulphur, according to the International Maritime Organization (IMO).[2] As such, shipowners are required to either use low sulphur fuel or implement an emission abatement method, i.e. a scrubber system, which removes the sulphur oxides from the vessel exhaust gas. The latter makes it possible to continue using heavy fuel oil (HFO) with high sulphur content if the vessel has a continuous emission monitoring system installed in order to document the sulphur equivalent emissions.

The North European $SO_x$-ECA, covering the Baltic and the North Sea area, including the English Channel, can be seen in Figure 1. The $SO_x$ regulations are visualized in Figure 2. In addition to the North European $SO_x$-ECA, there is also the North American ECA, which comprises most of the US and Canadian coast and the US Caribbean ECA.[2] In addition to $SO_x$ regulations, the North American ECA also regulates $NO_x$ emissions from new ships built on or after 1 January 2016. Other ECAs may very likely be added at a later stage.

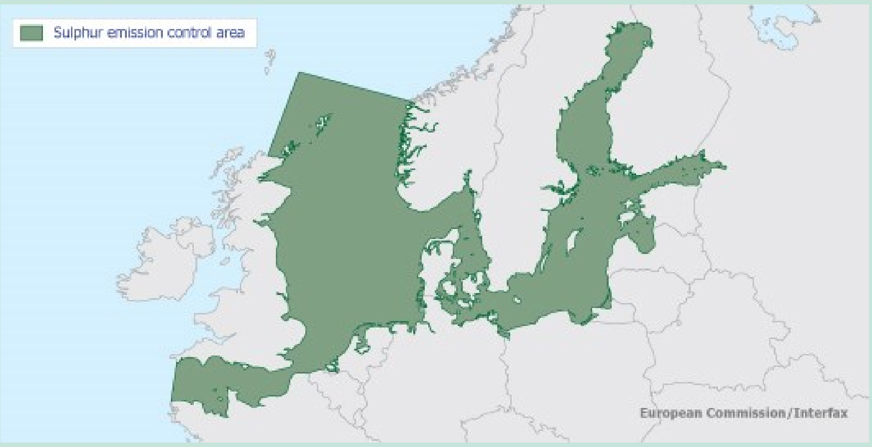


**FIGURE 1**
NORTH EUROPEAN EMISSION CONTROL AREAS (ECAS), COVERING THE BALTIC AND THE NORTH SEA AREA, INCLUDING THE ENGLISH CHANNEL

Investment in compliant fuel or $SO_x$ scrubber systems will result in a significant extra cost for the shipowners and open up for possible violation. In order to create a level-playing-field for the shipowners and a credible risk of being observed when violating regulations (especially the emission control requirements) the ships have to be monitored. So far, the relevant authorities primarily control the fuel sulphur content by random checks of bunker delivery notes, fuel logs and occasional fuel sample analyses when ships are in port. Those enforcement methods should not stand alone. Effective enforcement and equal conditions for the shipowners call for a simple and robust control

[2] http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Sulphur-oxides-(SOx)-–-Regulation-14.aspx

method that has the potential to be used worldwide. Today, that only exists in the form of a rather expensive solution using state-of-the-art sensors.

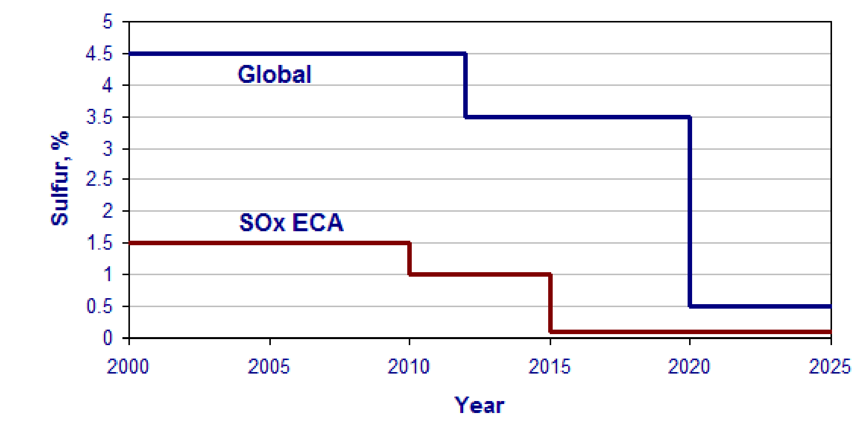


FIGURE 2
DEVELOPMENT IN $SO_X$ REGULATIONS, IN THE PAST, PRESENT AND EXPECTED FUTURE REGULATIONS AS DEFINED BY THE INTERNATIONAL MARITIME ORGANIZATION (IMO), MARPOL ANNEX VI.

Different projects are initiated both nationally and internationally. During the past decade, Chalmers University of Technology in Gothenburg, Sweden, has developed a monitoring platform that makes it possible to measure sulphur concentration both from the air and from fixed installations by using state-of-the-art measuring equipment.[3] That results in the ability to make very precise measurements of sulphur concentration, and the equipment has been positioned outside Gothenburg for some years. The Finnish Meteorological Institute (FMI) has also used a similar platform for monitoring, in cooperation with Chalmers. In addition, similar equipment will from 2015-2016 be used to measure from the Great Belt Bridge, supervised by Chalmers (tender from the Danish EPA). In Denmark, a parallel initiative has had some success with emission measurements from drones, and it was also co-financed by the Danish EPA in the same way as this project.[4] In combination with our approach, this latter initiative opens for potential for making a combined and cost-effective monitoring platform from both fixed locations and from drones.

## 1.1 Project objective

The objective of the project was to develop method(s) for fast determination of sulphur content in fuel. If such a suitable monitoring platform is developed, it will provide the shipowners with the assurance that their investments in low-emission technologies and/or low-sulphur fuels will not give shortcomings compared to their competitors. In addition, a successful implementation of the sulphur directive will lead to a 90% reduction of SO2 as compared to before 2015 as well as a significant reduction of particulate matter (PM). Oxidation of $SO_2$ is commonly regarded as a major driver for new particle formation.

The prime focus in the project is estimation of sulphur content by plume measurements (remote sensing) when ships pass the Great Belt Bridge (proof of concept). In total, 20-25,000 vessels passes the Great Belt each year corresponding to about three vessels per hour.[5] In Denmark, the majority of the vessel traffic passes either the Great Belt Bridge or the Oresund Bridge so by monitoring these strategic locations, a large part of the fleet can quickly be screened.

[3] J. Mellqvist and N. Berg, *Identification of gross polluting ships*, Chalmers University of Technology, 2010
[4] J. Knudsen *et al.*, *Surveillance of SO2 emission by drones*, Explicit
[5] http://www.statistikbanken.dk/statbank5a/SelectVarVal/Define.asp?MainTable=SKIB25&PLanguage=0&PXSID=0&wsid=cftree

In parallel, we also investigated two other potentially fast methods that aim at a fast analysis of the sulphur content directly in fuel, which could be a supplement to remote sensing: 1) analysis of sulphur content in selected fuel samples using handheld X-ray fluorescence (XRF) instrumentation, and 2) a small survey on potential for a laboratory technique. The latter aims at a fast determination of the sulphur content by using a chemical detection “kit” that can be brought on board the ship. These two methods could have potential for being used during inspection by relevant authorities, either when the ship is in port or at sea.

During the project, the project objective was modified to aim at cost-effective monitoring technology for indicative classification due to awareness of similar international activities and already developed solutions.[3] Therefore, the project team found it inappropriate to develop basic ideas for such a system once again and, and in agreement with the Danish EPA, decided to focus on cost-effective monitoring technology in the latter part of the project. The team was aware that this result in higher risk of not obtaining the goals of the project, but this instead has greater potential and perspective in the coming years as a cost-effective alternative to state-of-the-art sensor technology.

## 1.2 Project execution

The project was initiated 1 July 2012 and terminated 31 December 2015. Compared with the original time schedule, the project was extended with 6 months in order to thoroughly complete the project milestones and activities.

The work carried out in the four individual work packages is described in the following sections.

# 2. Work package 1: Development of methods for measuring ship emissions from bridges

## 2.1 Objective

In this work package, the objective was to investigate suitable methods for monitoring PM, $SO_2$ and $CO_2$ in vessel exhaust plumes from a distance of several hundred metres. Our initial considerations and preliminary measurements in the laboratory, near Aarhus harbour and similar locations will be discussed, as well as initial considerations regarding the optimum location for measurements on the Great Belt Bridge.

In addition, initial $CO_2$ background measurements on the Great Belt Bridge were carried out to determine whether the background fluctuations were pronounced (e.g., due to road traffic), and a safety course was completed in order to be allowed to work on the bridge.

## 2.2 Sniffer systems and state-of-the-art

The basic idea when measuring sulphur emissions from a bridge is to monitor $SO_2$ and $CO_2$ in the plume and to use the ratio multiplied by a constant to determine the sulphur content. This is an accepted method for calculating sulphur equivalents in exhaust gas, e.g., using $SO_x$ scrubbers.

Sniffer equipment requires relatively close proximity to the vessel and is restricted by wind conditions. However, the wind conditions can be dealt with by placing measuring equipment on both sides of the shipping lane concerned. One system has been in operation in Gothenburg, Sweden, for some years and is based on standardized state-of-the-art equipment for air quality monitoring and for measuring gases ($SO_2$, $NO_x$, $CO_2$) with a relatively high precision. The sulphur content is then determined from the ratio of $SO_2$ to $CO_2$ using the following calculation, which is an accepted method and equation for calculating sulphur equivalents in exhaust gas.[6]

$$\%\mathrm{S\ in\ fuel} = \frac{[\mathrm{SO2}]\ (\mathrm{ppb})}{[\mathrm{CO2}\}\ (\mathrm{ppm})} \cdot 0.232$$

The formula assumes that all sulphur is oxidized into $SO_2$ and carbon into $CO_2$. This is of course an assumption, in particular for $SO_2$, since sulphur can also be emitted as particulates (e.g., $SO_3$ and $SO_4$), but according to the literature the error is quite small and within a few percent.[3] In all cases, the sulphur content is likely underestimated, in favour to the shipowners. Experience from the Chalmers project suggests that the overall error is approximately 10-15%, considering all losses in their set-up.

[6] IMO's guidelines for scrubbers, MEPC.259(68)

Also other scientific equipment, like particle analysers, can be added to the sniffer system. The Swedish equipment is fully automatic, including calibrations, and contains software packages for ship tracking and identification. The equipment has to be built into a weatherproof box and weighs about 100 kg. The total cost for one installation is estimated to 100 k€ in pure instrumental hardware plus installation and running costs.

In the first part of the present project, a great deal of effort was put into gaining knowledge and learning from other projects. That gave considerable knowledge on existing solutions and expected $CO_2$ and $SO_2$ gas concentrations that can be measured from a distance. In addition, relevant actors in Sweden (Chalmers) and Finland (FMI) were contacted.

In this context, the project manager visited Chalmers in Gothenburg where the University and the actual sniffer prototype installation in the port entry were inspected. This visit provided key knowledge on existing solutions and issues that need to be addressed. The visit made it even more clear that $CO_2$ monitoring is one of the major challenges, especially as the background level is quite high (~400 pm). Therefore, Chalmers uses cavity ring down spectroscopy (CRDS) for $CO_2$ measurements, which is a very expensive technology (about half a million DKK for hardware alone). The expected measured concentration at a distance of a few hundred metres is typically 5-15 ppm above background level, depending on wind conditions, and therefore it can be compared to the analogue of "weighing a mosquito on top of a moving elephant".

Another important learning made after visiting Chalmers was that particle sensors respond very quickly to the appearance of an exhaust gas plume. The measured particle concentrations typically have a much higher signal-to-noise level than $CO_2$ and $SO_2$ sensors and can be used as a first indicator of the presence of a plume.

## 2.3 Measurement equipment

This section provides a short overview of the most important instruments that were chosen and used for particle and gas measurements during the project. The remaining part of this report will refer to these instruments.

### 2.3.1 DiSCmini particle counter

A DiSCmini particle counter (Matter Aerosol) is a simple, handheld device used for particle counting in the size range of 10-700 nm. Particles from combustion-generated processes typically have sizes in the nanoparticle size range, meaning below 100 nanometres, and they typically peak around 30-40 nm. In addition to particle counting, the instrument provides a mean particle diameter (mode diameter) in the size range of 10-300 nm and therefore provides some size information. The instrument was acquired in the early part of the project. Important for the project, it is now possible to carry out measurements over several days with the instrument in contrast to other handheld counters such as, e.g., the P-Trak described below.

### 2.3.2 P-Trak particle counter

Compared to the DiSCmini, the P-Trak (TSI) is able to count particles in the size range of 20-1,000 nm and it is necessary to saturate a wick with alcohol 2-3 times per day in order to enlarge the particles for optical detection. Therefore, the instrument can be used for shorter measurement campaigns, is not as sensitive to contamination as the DiSCmini, and is also suitable for identifying the plume.

### 2.3.3 $SO_2$ monitor

For a shorter period of time, the $SO_2$ monitor from Thermo Scientific (model 43*i*) was rented from Air Monitors Ltd. and used throughout the project. The instrument uses pulsed fluorescence technology and UV excitation with a detection limit of a few ppb of $SO_2$ in the air with exact detection limit and response time depending on averaging time. The instrument and principle is similar to what has been used for state-of-the-art sensor monitoring platforms in other projects (Chalmers and FMI), however, with an inferior detection limit of this particular instrument, and therefore a cheaper solution. The detection limit is still within the expected $SO_2$ concentrations (ppb range). It should also be mentioned that in other studies, the VOC filter (kicker) in the instrument was removed in order to shorten the response time. We did not bypass the kicker in this project due to possible interference of VOCs on the $SO_2$ signal. Consequently, we have a higher response time but eliminate the possible error caused by VOCs that in ship exhaust gas can be in the range of 50% of the $SO_2$ concentration.[7]

#### 2.3.4 CozIR $CO_2$ sensor

The CozIR ($CO_2$ Meter) was the final choice of $CO_2$ sensor technology for the project. The communication is USB based and can be carried out directly from a PC. CozIR uses non-dispersive infrared sensor (NDIR) technology and contains an infrared source, a sample chamber, an optical filter and an infrared detector. The CozIR sensor has, in this project, been isolated within a box to minimize the interaction from outside. In addition, stacking of several individual sensors has been attempted to improve the signal-to-noise-ratio.

### 2.4 Initial experiments

#### 2.4.1 Lab experiments

In the laboratory, the main initial focus was on suitable $CO_2$ sensor monitoring equipment for some rough, initial measurements to get an impression of the expected $CO_2$ concentrations, measured from several hundred metres distance (as will be the case at the Great Belt). The project team decided to make preliminary measurements with a simple and cheap $CO_2$ sensor (NDIR $CO_2$ sensor from Thermo), already available at DTI prior to the project.

Stability in time as well as response on $CO_2$ addition was evaluated before bringing the sensor to preliminary test areas (Aarhus harbour). The sensor did achieve a satisfactory response on $CO_2$ with an acceptable signal-to-noise ratio but the software and data communication platform was not optimal. More importantly, the instrument was not able to reach a constant background level following $CO_2$ spiking and is very sensitive to noise as well.

Therefore, efforts were put into finding another cost-effective sensor, and after a thorough market survey by DTI and Zenzors, the partners agreed to choose the CozIR sensor technology (section 2.3.4) as it has a much better communication platform and modification options.

#### 2.4.2 Experiments at harbour areas

The CozIR sensor in combination with a pump, able to draw a very constant flow across the sensor membrane, was brought to the Aarhus harbour area, close to DTI, for a test day. Measurements were conducted in the proximity of departure and arrival of different ships within a few hundred metres distance.

It was possible to detect a $CO_2$ signal from almost all departures and arrivals on the specific day with a signal height of about 10-20 ppm. The sensor was located outside the car with pump and PC inside the car (no car engine on), see example in Figure 3. A relatively poor signal-to-noise ratio is observed but the $CO_2$ peak is evident.

[7] H. O. Kristensen, DTU, 2012, *Energy demand and exhaust gas emissions of marine engines*

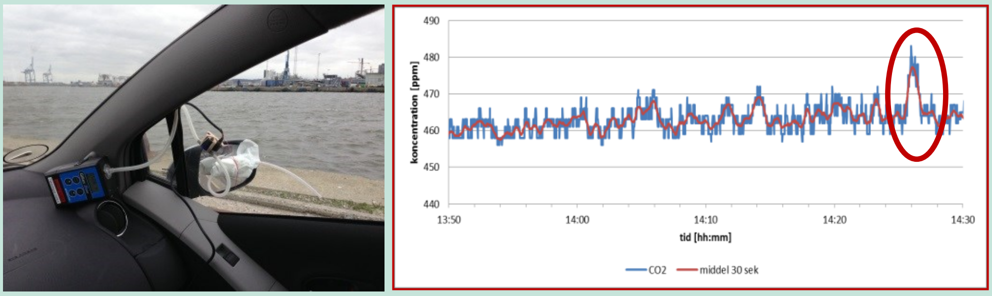


**FIGURE 3**
MEASUREMENT AT AARHUS HARBOR WITH A COZIR SENSOR. ARRIVAL OF A SHIP IS MARKED. A RUNNING AVERAGE (30 SECONDS AVERAGING) IS SHOWN TOGETHER WITH RAW DATA.

A set-up similar to what was tested at Aarhus harbour was used at another, similar location. The results obtained were similar to what was observed at Aarhus harbour. It was possible to detect a significant $CO_2$ signal from five out of eight departures/arrivals on the specific day with concentrations ranging from 10-30 ppm, which was very promising.

## 2.5 Initial considerations regarding the optimum measurement location on the Great Belt Bridge

At the Great Belt Bridge, the vessels pass in a southbound and northbound channel. For example, in August 2013 there were 1,700 passages corresponding to approximately 3 vessels per hour (northbound and southbound), which is a typical amount of passages. See Figure 4. As can be observed, the majority of the vessels pass the bridge at a distance of approximately 400 metres from each of the two pylons. The distance between the two pylons is 1624 metres and the clearance height is 65 m.

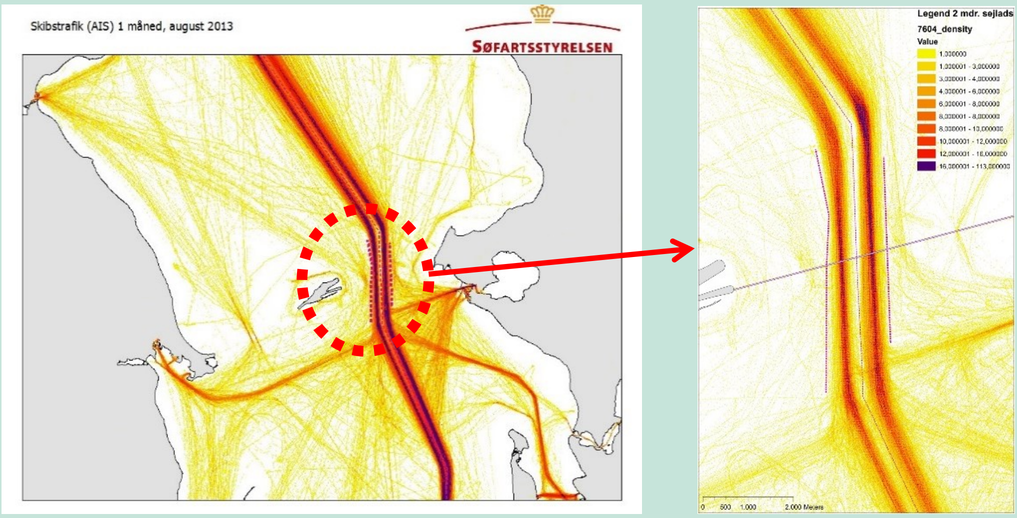


**FIGURE 4**
TRAFFIC DENSITY PLOT FROM AUGUST 2013 WITH ZOOM OF THE AREA NEAR THE ELEVATED BRIDGE TO THE RIGHT. THE NORTHBOUND LANE IS LOCATED TO THE EAST AND SOUTHBOUND TO THE WEST. THE MARKS DEFINING THE OUTER BOUNDARY OF THE CHANNELS APPEAR AS LINES IN THE PLOT.

The potential measurement locations on the Great Belt Bridge were also inspected in the initial part of the project.

In addition to the original idea with instruments positioned in a box right next to the road traffic and directly above the northbound channel, A/S Storebaelt suggested to also carry out measurements from below the bridge through a lantern outlet. This lantern marks the outer boundary of the northbound channel (65 m above sea level). Measurement equipment can be located inside the bridge and in that way be shielded from the environment, which is highly preferable. Another option is to measure from one of the pylon platforms at a height of ~25 m above sea level. See Figure 5. These new opportunities are very interesting, since

1) $CO_2$ background interference from road traffic will probably be minimized.

2) accessibility for inspection will be much easier. Therefore, especially these two options were pursued in the remaining part of the project.

**FIGURE 5**
POTENTIAL MEASUREMENT POSITIONS AT THE GREAT BELT BRIDGE INDICATED BY ARROWS.

In addition to evaluating and inspecting potential measurement positions, a safety course was completed in November 2013 in order to be allowed to work on the bridge. This clearance has to be renewed every second year.

## 2.6 Background measurement on the Great Belt Bridge

Short measurement campaigns were accomplished in the early part of 2014 at the pylon platform with proper wind conditions, ranging from SW-NW. These campaigns will be discussed in detail in the next section.

The $CO_2$ background level fluctuations at the pylon platform (background noise), important for the choice of sensors and method, were not observed to be higher than what was seen at Aarhus harbour and similar locations. In addition, $CO_2$ interference from road traffic did not seem to appear.

## 2.7 Conclusion

Based on a comprehensive literature study, market survey and validation experiments in the lab, basic sensor technology as well as preliminary measurement locations on the Great Belt Bridge were selected in WP 1, with the aim of cost-effective monitoring. Preliminary measurements from Aarhus harbour and similar locations gave the project team strong confidence in the measurements from the Great Belt Bridge, due to significant $CO_2$ signals that unmistakably came from a number of ships.

Based on the results, it was decided to continue with measurements on the Great Belt Bridge and to carry out preliminary measurements from the pylon platform at the Great Belt Bridge. That location has many similarities with the measurement locations so far, but also with what Chalmers has accomplished in the port entrance of Gothenburg. Preliminary $CO_2$ background measurements from the pylon platform do not show significantly higher fluctuations than observed at, e.g., Aarhus harbour and similar locations.

# 3. Work package 2: Proof of concept by measuring from the Great Belt Bridge

## 3.1 Objective

In this work package, the picked sensors are tested at measurement locations on the Great Belt Bridge. The potential of the different measurement positions, defined in WP1, will be further investigated with respect to remote sensing of sulphur content in fuel. This will take place during different measurement campaigns aiming at a final measurement campaign of several weeks. All with focus on cost-effective monitoring technology.

All measurements are correlated with information from Vessel Traffic Service (VTS) Storebaelt in order to unambiguously identify the individual ships.

As part of WP2, it will also be concluded whether or not reliable monitoring can be carried out from the Great Belt Bridge.

## 3.2 Initial measurement campaigns from pylon platform

Due to the very promising results in WP1 on $CO_2$ signals from ships it was decided to bring equipment to the Great Belt Bridge and carry out measurements. Initially, measurements were accomplished from the eastern pylon platform of the suspension bridge, approximately 400 metres from the centre of the northbound channel, see Figure 6.

**FIGURE 6**
VIEW FROM THE MEASUREMENT POSITION AT THE EASTERN PYLON PLATFORM OF THE GREAT BELT BRIDGE (LEFT) WITH A NORTHBOUND SHIP SHOWN. THE GAS INTAKE TO THE SENSORS IS SHOWN TO THE RIGHT.

When measuring from the pylon platform it is important to position the gas intake at least five metres from the two pylon legs in order to minimize turbulence. Some turbulence from the platform wall (0-20 m. above sea level) was also evident, but particle signals from the ships were very clear. The smell from the exhaust gas plumes was also evident and often lasted several minutes.

Several short measurement campaigns were initially accomplished in order to cover different meteorological conditions and measurement strategies from the platform. The campaigns and learnings are summarized in Table 1.

**TABLE 1**
SUMMARY OF INITIAL MEASUREMENT CAMPAIGNS FROM THE PYLON PLATFORM. ALL CAMPAIGNS WERE CARRIED OUT IN ONE DAY.

| Time | Weather | Wind speed [m/s] and direction | Purpose | Measurements | Conclusion |
|---|---|---|---|---|---|
| Feb. 2014 | Partly rainy, very foggy | 3.5-4 (SW-W) | Preliminary measurements and inspection of options | Particles, $CO_2$ | Position located at the platform and preliminary measurements accomplished |
| March 2014 | Sunny | 1-4 (SW-W) | The first "true" measurement campaign | Particles, $CO_2$ | $CO_2$ signals visible for 6/13 ships but <10 ppm increase. Very clear particle signals |
| April 2014 | Cloudy and windy | 15-18 (W-NW) | Measurements with high wind speeds | Particles, $CO_2$ | Particle signals OK but no visible response on $CO_2$ sensor under these wind conditions |
| June 2014 | Few clouds | 1-3,5 (SW-S) | Air drawn from 6 metres above pylon platform – better signals? | Particles, $CO_2$ | Small indication of higher signals. $CO_2$ signals still low. |

An example of a measurement from the campaign in March 2014 is shown in Figure 7, showing a very clear particle signal when the ship is present. The rise in $CO_2$ signal can also be observed for this ship, however, with a short delay as compared to the particle signal. This delay is likely due to a different response time and the not fully calibrated clocks on the different sensors, even though alignment of clocks was in focus. For the March campaign the rise in $CO_2$ signal, as compared to the background level, was visible in 6/13 ships.

In conclusion, the $CO_2$ signal was evident from about half of the ships during optimum wind conditions (SW-NW). Signals were observed during wind speeds of up to 4 m/s for the present measurements. The best data were acquired for signals >1 minute and all signal increases were below ~10 ppm, which was a bit surprising taking the rather high concentrations observed in WP1 from harbour measurements into consideration. The particle sensors provide a very clear and safe indication of the presence of the exhaust plume. This is important for the identification part.

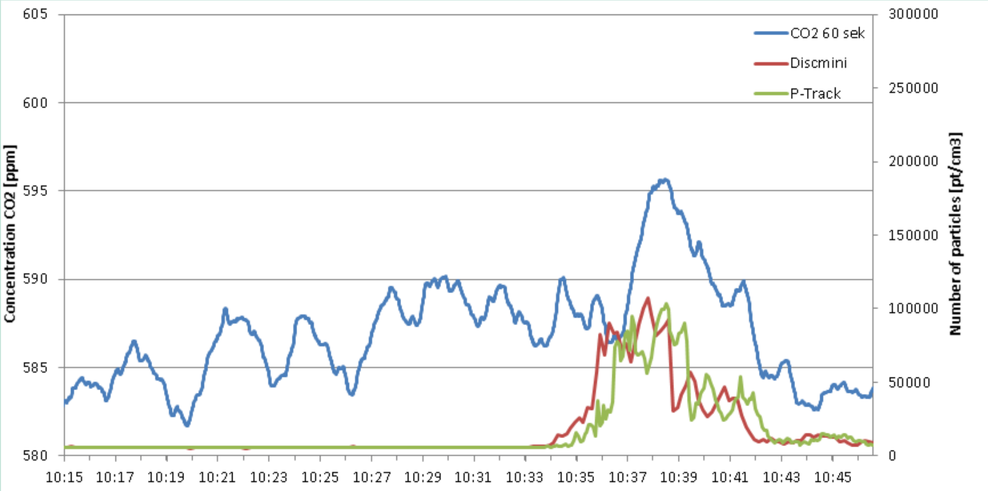


**FIGURE 7**
AN EXAMPLE OF A SHIP PASSING THE GREAT BELT BRIDGE WITH PLUME MEASURABLE FROM 10:35. PARTICLE SIGNALS FROM TWO DIFFERENT PARTICLE COUNTERS (GREEN AND RED CURVE) SHOW CLEAR INDICATIONS OF THE PRESENCE OF A SHIP AND THE CO2 SIGNAL INCREASE CAN ALSO BE OBSERVED FOR THIS PARTICULAR SHIP (BLUE CURVE). THE CO2 SIGNAL IS CALCULATED AS A RUNNING AVERAGE OF 60 SECONDS.

Due to the challenges observed with respect to measuring $CO_2$ it would be preferable to measure closer to the exhaust plume or to improve the sensor signal-to-noise ratio. Therefore, more effort was put into this and it was also decided to carry out short measurement campaigns from below the bridge close to the lantern outlet, as discussed in section 2.5.

An attempt was also made to measure 6 m above the pylon platform in order to get further away from the platform “wall” in front of the platform. That did not result in any significant signal increases, as mentioned in Table 1, during the June 2014 campaign. However, the signals were definitely not worse as compared to the position at the platform. Pictures from measurements 6 m above the pylon platform can be observed in Figure 8.

**FIGURE 8**
MEASUREMENT POSITION 6 M ABOVE THE PYLON PLATFORM AS WELL AS 2 M ABOVE THE PLATFORM (PICTURES FROM CAMPAIGN IN JUNE 2014).

## 3.3 Initial modelling and sensor optimization

### 3.3.1 Modelling

Due to the relatively weak $CO_2$ signal from the pylon platform (low and short signals), some rough, initial modelling (CFD calculations) was carried out in order to get an indication of potential higher gas concentrations elsewhere, e.g., at an elevated position. Since this was not part of the original application, only very limited, steady-state calculations were carried out with the ship fixed in one location defined as 500 m orthogonal to the pylon platform and just below the suspension bridge. 500 m was chosen to have a worst-case scenario regarding the distance to the ship. Focus was at $CO_2$ broadening in the plume.

The modelling indicated that a larger portion of the exhaust gas plume would be measurable further above the pylon platform, relatively close to the road.

### 3.3.2 Sensor optimization

In addition to the modelling, it was decided to use several $CO_2$ sensors in order to improve the signal-to-noise ratio (stacking). These sensors were built into a protective housing, minimizing the interference from the surroundings. The sensors are inexpensive compared to other state-of-the-art $CO_2$ sensors, used for remote sensing.

In the laboratory it appeared that the sensor stacking method could distinguish ambient $CO_2$ concentrations from ambient plus 5 ppm, see Figure 9. Therefore, signals at least >5 ppm above the background level should be measurable. We expect this will work on the Great Belt Bridge for $CO_2$ increases higher than 5 ppm and with a reasonable signal length.

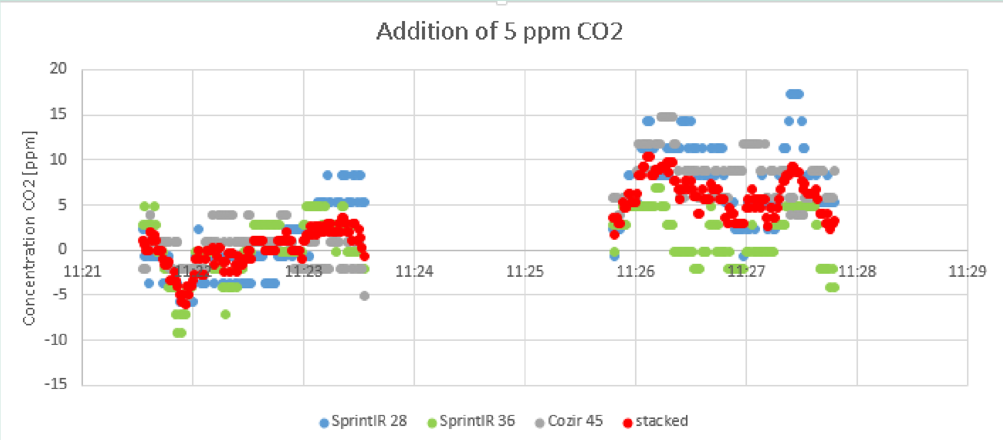


**FIGURE 9**
BACKGROUND SUBTRACTED $CO_2$ SIGNAL FROM EACH INDIVIDUAL $CO_2$ SENSOR AND THE STACKED SIGNAL OF THE THREE SENSORS (SHOWN LEFT). THE RESULTING SIGNALS FOLLOWING ADDITION OF 5 PPM $CO_2$ ARE SHOWN TO THE RIGHT.

## 3.4 Measurement campaigns from elevated locations

### 3.4.1 Measurements through lantern outlet below the suspension bridge

Based on the results given in the previous sections as well as motivations for measuring in the height, just below the bridge, measurement campaigns were accomplished with the probe positioned next to the lantern outlet below the suspension bridge. For comparison, parallel measurements from the pylon platform were attempted, now also including $SO_2$ measurements. As compared to previous campaigns, three individual $CO_2$ sensors were now used for 1) stacking purposes and 2) for having the possibility to measure in parallel at different strategic positions. The measurement set-up is shown in Figure 10 and Figure 11, and the results from these measurements are summarized in Table 2.

**FIGURE 10**
MEASUREMENT LOCATION AT THE PYLON PLATFORM, NOW INCLUDING SO2 MEASUREMENTS.

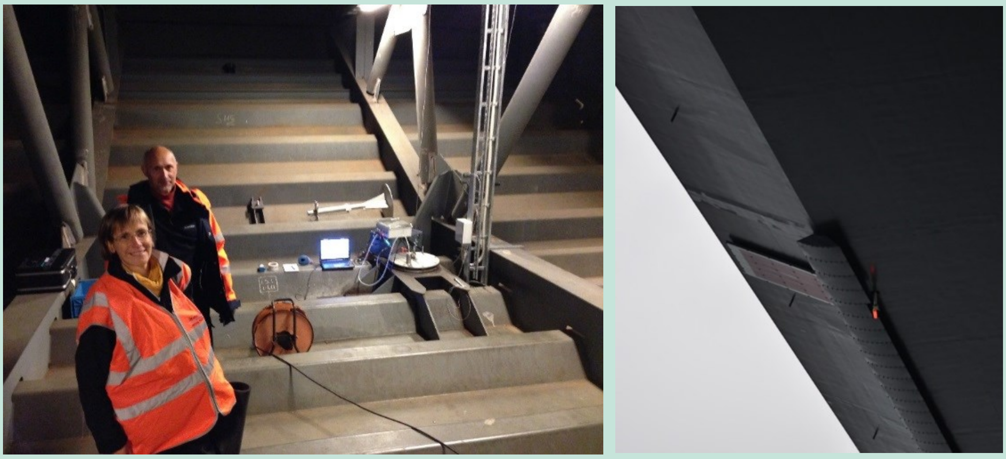

**FIGURE 11**
MEASUREMENT SET-UP LOCATED INSIDE THE SUSPENSION BRIDGE (LEFT). THE MEASUREMENT PROBE WAS POSITIONED THROUGH THE LANTERN OUTLET, MARKING THE OUTER BOUNDARY OF THE NORTHBOUND CHANNEL (RIGHT PICTURE).

**TABLE 2**
SUMMARY OF MEASUREMENT CAMPAIGNS FROM THE LANTERN OUTLET AND FROM THE PYLON PLATFORM. ALL CAMPAIGNS WERE CARRIED OUT IN ONE DAY.

| Time | Weather | Wind speed [m/s] and direction | Purpose | Measurements | Conclusions |
|---|---|---|---|---|---|
| Sept. 2014 (1) | Cloudy | 11-14 (NW) | Measurements in parallel from lantern outlet and pylon platform (6m above platform) at high wind speeds | Particles, $CO_2$ | 2 $CO_2$ sensors at the lantern and one at the platform. Particle sensors at both positions. Too windy to achieve reasonable results |
| Sept. 2014 (2) | Very foggy (at the bridge) | 0.5-2 (NW) | Same as above, but at low wind speeds | Particles, $CO_2$ | Unfortunately no clear signals due to the very foggy weather |
| Nov. 2014 | Sunny | ~4 (NW) | Same as above, but now including $SO_2$ measurements from the platform | Particles, $CO_2$, $SO_2$ | Ideal conditions, but unfortunately only 2 ships passed in 7 hours! Relatively low signals and no clear indication of higher concentrations below the lantern. Fair $SO_2$ signals from the platform |
| Dec. 2014 | Cloudy | 11-12 (W) | Platform (6 m) with $SO_2$ sensor and stacking of 3 CO2 sensors during expected low wind conditions | Particles, $CO_2$, $SO_2$ | Too windy for reliable measurements. Same morning 3-4 m/s predicted by DMI/YR.no! |

In summary, the results from the measurement campaigns listed above did unfortunately not allow us to conclude on the optimum measurement position, due to parameters listed in Table 2. However, some important learnings were drawn. In conclusion:

- Higher $CO_2$ concentrations were not observed at the lantern outlet compared to the pylon platform, under the conditions stated in Table 2 (based on very few passages).
- During high wind speed conditions better signals were achieved at the pylon platform as compared to the lantern outlet.
- During low wind speed conditions similar results were achieved with indication of better signals at the lantern outlet.
- Reasonable $SO_2$ measurements were achieved from the pylon platform and signals up to ~35 ppb were measured.

As parallel measurements with $SO_2$ and $CO_2$ are present, it became possible to estimate the sulphur content for particular ships. For one particular ship a $SO_2$ content of about 20 ppb was measured, and assuming a $CO_2$ content in the plume of 5 ppm (definitely not much higher judged from our results), and using the formula given in section 2.2 for calculating the sulphur content that gives a sulphur content just below 1%. That corresponds very well with the expected fuel sulphur content of a particular ship of 1% (info from the Danish Shipowners Association). This shows that we are within the correct prediction range. Using the present method, measurements from the pylon platform can probably be used for a very rough estimate of the sulphur content. However, it should be emphasized that the present method has a considerable uncertainty associated with the measurement, which at the moment is difficult to estimate, and it is definitely too high to recommend using the method at the moment.

Due to the resource-demanding task of preparing and carrying out these short measurement campaigns, it was decided not to define the optimum location to be either at the platform or at the lantern, as no clear indication of significantly higher gas concentrations were observed at the lantern. Instead, the project team decided to perform measurements high above the pylon platform, since modelling as described in section 3.3.1 suggests that this is where the highest concentrations are.

### 3.4.2 Measurements from high above the pylon platform

The objective of measuring high above the platform was to achieve higher measurable gas concentrations as predicted by initial CFD calculations. Two shorter measurement campaigns were accomplished, approximately 23 m and 32 m above the platform, respectively. A diagonal wire across the two pylon legs made it possible to reach these measurement locations.

In total, 25 ships passed the bridge during these two days. Of them, 12 northbound ships had clear particle signals. The wind speed ranged from 3-10 m/s; that gave good measuring conditions as there was no rain or fog.

No visual $CO_2$ increase was evident when looking at the resulting data from the campaigns. Instead, we attempted some pure mathematical treatment of the stacked $CO_2$ data from the three sensors, using no visual judgment of data. See example and description in Figure 12.

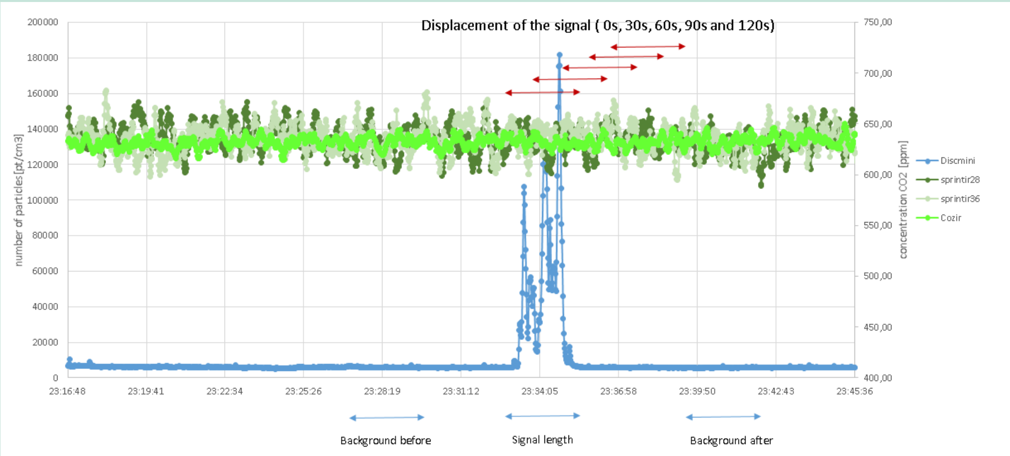


**FIGURE 12**
EXAMPLE OF A SHIP PASSING THE GREAT BELT BRIDGE WITH A CLEAR PARTICLE SIGNAL (BLUE CURVE) BUT WITH NO EVIDENT INCREASE IN $CO_2$ (GREEN CURVES). WIND SPEED WAS 6 M/S, DIRECTION WNW.

IN ORDER TO QUANTIFY THE $CO_2$ SIGNAL IN THE PLUME, THE SAME SIGNAL LENGTH AS FOR THE PARTICLE SIGNAL IS USED TOGETHER WITH DIFFERENT TIME DELAYS AS COMPARED TO THE PARTICLE SIGNAL. THE DIFFERENT TIME DELAYS (DISPLACEMENTS) SHOWN IN THE FIGURE WERE USED TO TRY TO ACCOUNT FOR THE DIFFERENT SENSOR RESPONSE TIMES AND POTENTIAL SLIGHTLY MISALIGNED CLOCKS. AFTERWARDS, AN AVERAGE OF THE BACKGROUND SIGNAL MEASURED BEFORE/AFTER THE PASSAGE WAS SUBTRACTED FROM THE RESULTING $CO_2$ SIGNAL.

IF NO $CO_2$ CAN BE MEASURED WITH THE $CO_2$ SENSOR, THE ACTIVITY SHOULD RESULT IN PURE NOISE AVERAGING TO A $CO_2$ CONCENTRATION OF ZERO PPM.

When the data treatment, described in Figure 12, had been carried out on each passage, it was clear that the overall positive $CO_2$ signals were evident, measuring from above the platform, with very few negative $CO_2$ signals (mostly during high wind speed conditions). Therefore, based on statistics, it is clear that:

- A $CO_2$ signal increase is registered by the sensors, also when the signal cannot be seen by the naked eye.
- The $CO_2$ signal is measured to be max. 4-5 ppm, and often less (the average over the entire plume duration).

In conclusion, these two campaigns, high above the platform, did not result in a significantly greater signal than previously observed 6 m above the pylon platform. However, there were indications of slightly higher gas concentrations in the height above the platform.

Due to the non-conclusive results on the optimum measurement location at the Great Belt Bridge, the project team returned to the modelling in order to conclude from where it would make most sense to carry out a final measurement campaign of two weeks duration in the final part of the project. Further initial modelling shows that it is reasonable to measure far above the ship and just below the bridge. Since the measurements from the lantern outlet, described in section 3.4.1, did not result in much statistics, primarily due to unfortunate conditions, it was decided to carry out the final measurement campaign from this location, judging that this set-up would provide the most useful information in the final part of the project.

## 3.5 Final measurement campaign

The objective of this campaign was primarily to investigate whether the findings of significantly higher gas concentrations from the ship plumes directly below the road (from CFD calculations) could be measured in practice at the lantern outlet. A longer measurement period (from 25 September to 5 October 2015) was executed to obtain more data than so far. The physical properties in the closed room below the road constituted a good measurement location as it provided instrument shelter. The chosen measurement location was directly under the road.

### 3.5.1 Instrumentation

The $SO_2$ analyser and $CO_2$ sensors were set up so both types of equipment were supplied with the same air, using a T-piece. A filtering flask ensured that the instruments were prevented from being flooded with water that might be sucked through the sample line during wet conditions. For all gas connections, Teflon tubing was used. See Figure 13.

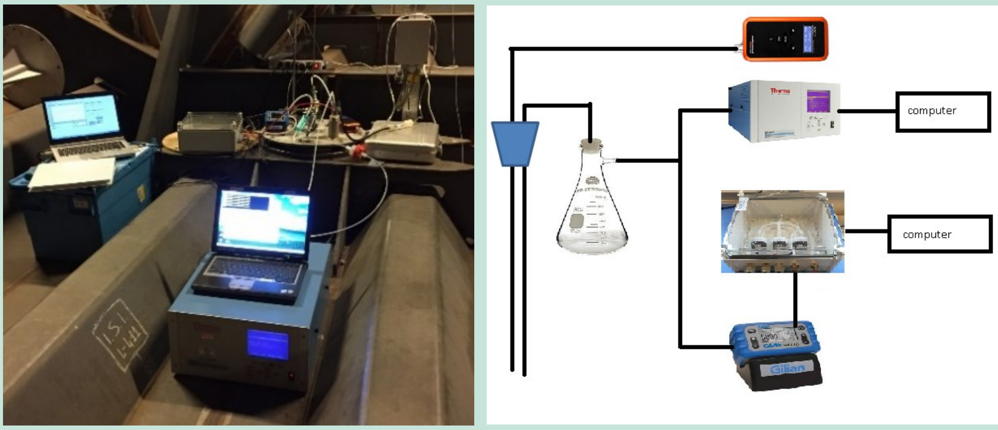


**FIGURE 13**
SET-UP OF INSTRUMENTS. TO THE LEFT INSTRUMENTS INSIDE THE BRIDGE AND TO THE RIGHT SCHEMATIC OF THE SET-UP WITH DISCMINI PARTICLE COUNTER, $SO_2$ ANALYZER AND THREE $CO_2$ SENSORS IN A PROTECTIVE HOUSING. THE MEASURED GAS WAS LED BACK TO THE OUTSIDE THROUGH THE PLUG IN ORDER TO PREVENT INSTRUMENT INTERFERENCE FROM A SLIGHT OVERPRESSURE INSIDE THE BRIDGE.

The $SO_2$ analyser, $CO_2$ sensors, and DISCmini logged data every second. A RealTerm: Serial capture program 2.0.0.70, which is a data-logging program, was used for the $SO_2$ analyser. A program was programmed in LabView at DTI to log data every second from the $CO_2$ sensors. Particle data logging was internal instrument logging that was stored on a SD card.

The campaign lasted for 12 days, and since remote surveillance of the equipment was not established, the set-up was checked twice during the campaign, resulting in 3 measuring periods. As the equipment could not monitor the number of ships that passed under the bridge on a daily basis, such information was provided by VTS Storebaelt. VTS monitors all traffic below the bridge. Information on wind speed and wind direction came from Sund & Baelt A/S.

### 3.5.2 Data analysis and results

In conclusion, the set-up at the bridge ran well, taking into consideration that this was the first time the set-up was implemented for a longer period of time. Some loss of data on the particle counter and the $CO_2$ sensors occurred due to malfunction of the $CO_2$ pump and error on the particle counter. The measuring campaign still provided a significant number of ships for the analysis and more statistics than the previous short campaigns described in previous sections. The wind conditions were good with wind velocities ranging between 1 to 7 m/s with short periods having up to 10 m/s, except for the last two days with alternating wind directions and a wind velocity of around 0 m/s.

Whenever the DiSCmini showed a peak that indicated a ship passage, VTS data was used to achieve the ship information and to judge whether the timestamp between VTS and the particle counter matched. Based on this, Figure 14 shows an overview of the ships that passed the bridge during the campaign, excluding the period from 29 September to 2 October (due to an error on the particle counter) and from the morning of 3 October onwards (due to wrong wind directions and/or lack of wind). Signals from two ships that were not very far apart or from two ships (northbound and southbound) that met each other around the bridge are included in the number referring to "northbound ships without clear particle signal". Other reasons for lack of particle signal could be wrong wind direction, but in a couple of cases the particle signal is missing although the right wind directions/conditions are available.

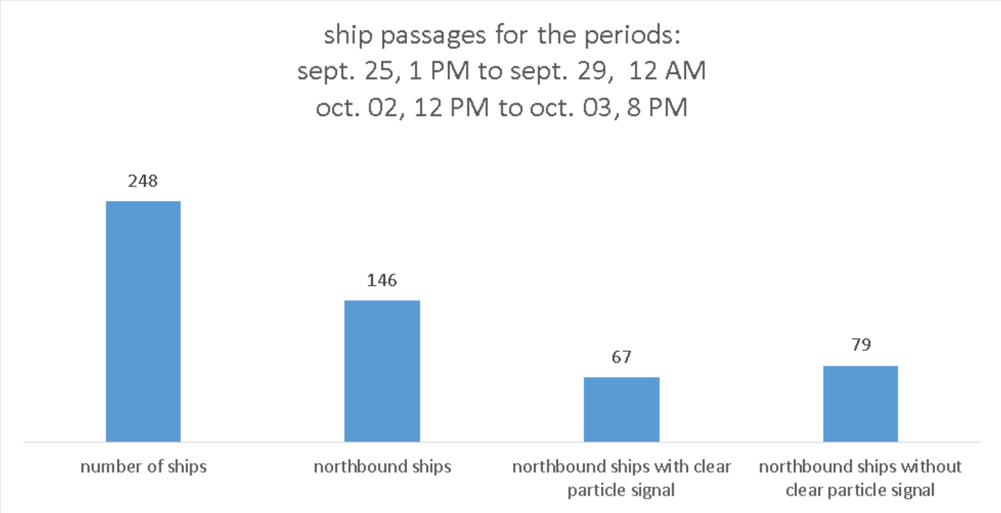


**FIGURE 14**
OVERVIEW OF NUMBER OF SHIPS THAT PASSED THE BRIDGE DURING THE CAMPAIGN, EXCLUDING THE PERIOD FROM 29 SEPTEMBER TO 2 OCTOBER (DUE TO AN ERROR ON THE PARTICLE COUNTER) AND FROM 3 OCTOBER MORNING ONWARDS DUE TO ERRONEOUS WIND DIRECTION AND LACK OF WIND.

Based on an initial rough data inspection, it was again very hard to visually evaluate, whether there are $CO_2$ peaks from plumes. None of the data from the 12 measuring days showed a significantly larger $CO_2$ signal than previously observed. The signals were close to the detection limit of the sensors. To analyse the $CO_2$ data, the mathematical approach, described in section 3.4.2, has been used, since that approach provided some reasonable results on the pylon platform data analysed earlier. This mathematical approach on the $CO_2$ data analysis again showed a clear indication of positive $CO_2$ signals, but most often they were far below 10 ppm, as previously found during platform measurements. However, the signal intensities showed a slightly higher value in average than at the measurement point 23 and 32 m over the platform.

Previously, the particle signal was very reliable, when a plume from a ship was at the measurement location. In about 60% of the cases of observed distinct particle signals from passages, a clear $SO_2$ signal could be observed. The $SO_2$ signals that were measured (up to ~7 ppb) are known to be maximum 50% of the true signal due to an unfortunate loss in a leaky filter in front of the $SO_2$ analyser, identified during and after the campaign. Keeping in mind that the $SO_2$ signals were too low due to the leaky filter, the hit rate for $SO_2$ signals should be even higher than 60%. Comparing this campaign to previous pylon platform measurements in 2014, where the limit was still 1% sulphur, all $SO_2$ measurements from 2014 were significantly higher than this 2015 campaign, making very good sense from a legislation-measurement comparative point of view.

## 3.6 Conclusion

In conclusion, we have shown that a number of locations at the Great Belt Bridge have some potential with respect to remote sensing of sulphur content in fuel, based on cost-effective monitoring technology. However, a number of improvements must be made on the sensor solution before such a solution can be commercialised. The improvements depend on the permitted measurement uncertainty, and on whether an indicative classification of ships will be acceptable. The measurements must be followed up by further inspection by the authorities.

A final measurement campaign of 12 days was carried out together with smaller, dedicated measurement campaigns at different strategic positions on the Great Belt Bridge. In this context, it has proven difficult to achieve a satisfactory high gas concentration for the particular $CO_2$ sensor. This is to some extent surprising since 1) our initial harbour measurements (WP1) gave very promising results from similar measuring conditions, and 2) initial modelling suggests relatively high gas concentrations at some of the measurement positions. A possible explanation for this discrepancy could be that the ships at the Great Belt move faster than at the other measurement locations, with the plume in a shorter time span. It should still be possible to locate higher gas concentrations, and further CFD modelling will be necessary in this context.

Preliminary calculations of sulphur fuel content suggest that the present method can be used for a very rough estimate of sulphur content in fuel. This conclusion is based on measurements from both the pylon platform (measurement campaign during 1% sulphur conditions) or from a position just below the bridge at the lantern defining the outer boundary of the northbound lane (carried out during 0.1% sulphur conditions). However, it should be emphasized that the present method has a high associated measurement uncertainty, which is difficult to define at the moment, and as such, it is not advised to use the present method for routine monitoring. As such, there still exists a significant portion of work to make cost-effective monitoring the best practice.

In this context, it should be noted that Chalmers, Sweden, will be carrying out parallel measurements from the pylon platform during the period 2015-2016 (Danish EPA tender), using their state-of-the-art sensor technology. To our best knowledge they have accomplished reliable measurements so far. This is of course very satisfactory from an overall monitoring point of view, but in the long run it is not expected that this technology has the optimum potential for further broadening, due to the significant costs of such a monitoring platform.

To achieve a reliable monitoring platform based on cost-effective sensor technology, further and more detailed modelling of exhaust gas plumes will be necessary in order to locate and define optimum measurement conditions. In addition, it might be necessary to improve the sensor signal-to-noise ratio, if no higher gas concentrations are located, together with an innovative concept regarding the measurement probe.

# 4. Work package 3: Development of fast methods for direct analysis of sulphur in fuel

## 4.1 Objective

The objective of this work package was to investigate potential for developing a fast method for direct analysis of the sulphur content in fuel within minutes. Such a method would allow the relevant authorities to check the sulphur content in fuel when the ships are at berth or at sea. This could be a strong supplement/alternative to the remote sensing approach, described in the previous chapters. It should be noted that this approach requires the physical presence of personnel on board the ship in question.

Two potential fast methods that aim at fast analysis of sulphur content directly in fuel were investigated in this project:

1. analysis of sulphur content in selected fuel samples using handheld X-ray fluorescence (XRF) and in this context XRF method optimization.
2. a theoretical survey on potential for a laboratory technique aiming at fast determination of the sulphur content by using a chemical detection “kit”.

This work is described in the following two sections.

## 4.2 Analysis of sulphur content in selected fuel samples using handheld X-ray fluorescence (XRF)

For XRF measurements, a handheld Delta analyser from Olympus was used. Such an instrument costs approximately 30,000 Euros (the cheapest) and it allows quantification of elements higher than sodium in the periodic table, also sulphur. The instrument was borrowed from another department at DTI where it is typically used to identify and quantify heavy metals in building waste, paint, etc.

Maersk Maritime Technology collected 12 different fuel samples for the project with known sulphur content, already analysed by DNV. The sulphur content ranged from 0.1 to 3.3% sulphur in order to have a representative span of concentrations for the XRF test.

Different options for analysis were investigated and it was concluded that having the oil sample in a petri dish covered by a thin film could be a proper way for sample preparation. The XRF interface must not have direct contact with the oil sample.

Para film was initially used to cover the oil samples in the petri dishes, but the signal was damped significantly through para film, likely due to the film thickness. Instead, ordinary plastic wrapping was found appropriate for this application, due to the thin matrix. Therefore, plastic wrapping was used for the measurements.

Each sample was analysed three times (triplicates). The results are summarized in Figure 15.

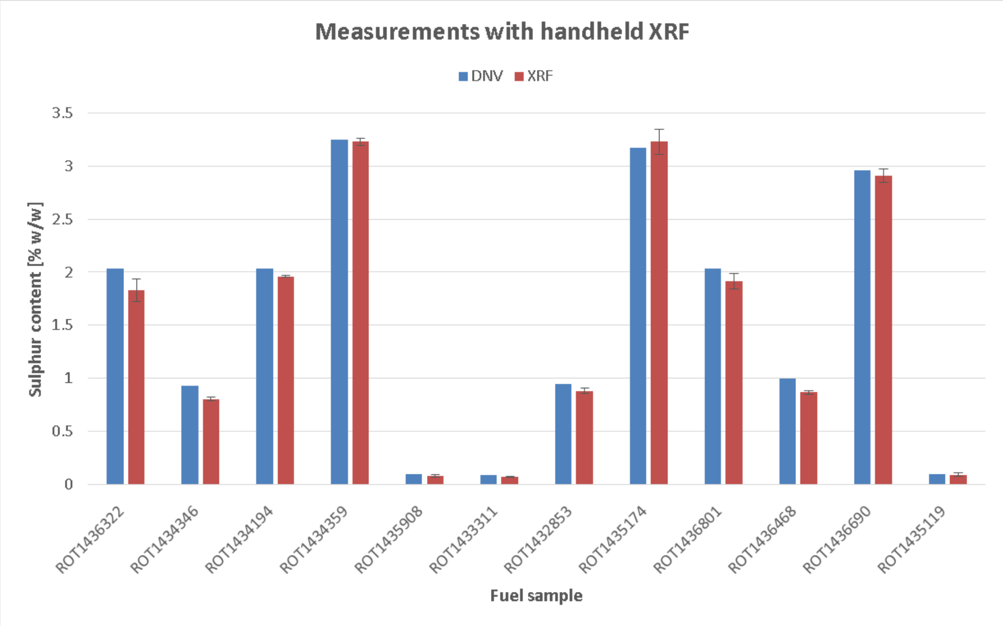


**FIGURE 15**
COMPARISON OF DNV REFERENCE ANALYSIS FOR SULPHUR CONTENT WITH HANDHELD XRF MEASUREMENTS ON THE SAME 12 SAMPLES.

The results were very promising and all results (average of 3 individual measurements) are within 10% of the reference analyses carried out by DNV. Based on the results the method seems to underestimate the sulphur content, which could likely be a matter of calibration.

By calibrating the instrument against film thickness and perhaps using adequate cuvettes for liquid analysis, the results could be further optimized and the precision could be increased. This is of course a matter of desired measurement uncertainty – with the present and described method it should be safe to conclude that the method can distinguish 0.1% sulphur from 1% sulphur and from 2-3% sulphur.

### 4.3 Fast determination of sulphur content by development of a chemical detection "kit"

This section discusses the initial theoretical considerations that aim at a laboratory technique suitable for a fast determination of sulphur content by a chemical "kit".

In heavy oil, sulphur is the third most abundant element after carbon and hydrogen. The sulphur content and the nature of the organic sulphur compounds vary to a great degree in different fractions obtained through the refining of crude oil, see Table 3.

**TABLE 3**
VARIOUS OIL FRACTIONS OF SULPHUR CONTENT AND SULPHUR COMPOUND DISTRIBUTIONS. ADAPTED FROM JAVADLI *ET AL.* "DESULFURIZATION OF HEAVY OIL" APPL PETROCHEM RES (2012), 1, 3–19

| Oil fraction (distillation range) | Sulphur content (in %) | Sulphur compound distribution (in %) | | | |
|---|---|---|---|---|---|
| | | Thiols | Sul-phides | Thiophenes | Benzothio-phenes & heavy sulphides |
| **Distillate (220-350 °C)** | 0.9 | 15 | 15 | 35 | 35 |
| **Vacuum gas oil (350-550 °C)** | 1.8 | 5 | 5 | 30 | 60 |
| **Vacuum residue (>550 °C)** | 2.9 | trace | trace | 10 | 90 |

Marine fuel is typically a mixture of the heavier fractions from crude oil refining. Often the distillate, vacuum gas oil and for some heavier fuels the vacuum residue fractions are the main component.

The distribution of sulphur containing compounds ranges from reactive thiols, disulphides to stable benzothiophenes containing multiple sulphur-atoms. Therefore, chemical detection of the total sulphur content in marine oil is not a trivial task.

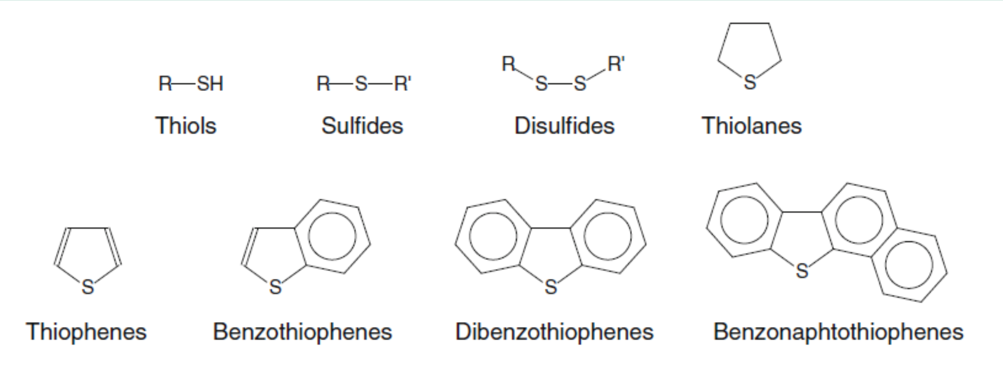


**FIGURE 16**
VARIOUS TYPES OF ORGANIC SULPHUR COMPOUNDS TYPICALLY FOUND IN CRUDE OIL. (R= ALKYL)

To obtain low-sulphur (LS) or ultra low sulphur (ULS) marine fuels, subsequent desulphurization was performed. Typically, hydrodesulphurization (HDS) and in some cases oxidative desulphurization (ODS) is performed to bring the total sulphur content below the limits of 1% for LS or 0.001% for ULS. HDS and ODS will result in the removal of the most reactive organo-sulphur compounds, leaving only the most stable benzothiophenes behind.

In order to perform a chemical detection of the sulphur content in marine fuel it is possible to adapt some of the techniques from the above-described desulphurization methods. HDS methods involve the use of hydrogen gas under high pressure and elevated temperatures typically employing a heterogeneous catalyst making this method an unsuitable part of a chemical detection kit. ODS, however, typically utilizes hydrogenperoxide as the oxidation agent in combination with an organic acid, e.g., acidic acid or formic acid, or phosphotungstic acid making this method very attractive for a chemical detection kit.

It is envisioned that a two-step process consisting of an oxidation step followed by a detection step would yield a system capable of detecting sulphur in marine fuel at a concentration that is above 1% total sulphur. This is relevant in the context of monitoring in ECAs.

A schematic representation of the envisioned detection strategy is depicted in Figure 17. A fixed volume (1-5 mL) of marine oil is withdrawn from the ship-bunker and added to a glass vial. Subsequently, a mixture containing an oxidation agent (e.g., fixed amount of $H_2O_2$ in presence of acidic acid) and the vial containing the combined liquids are shaken for a few minutes. A precipitation agent (e.g., a barium or silver salt) is added to the resulting oxidized mixture, which will result in the precipitation of oxidized sulphur compounds such as sulphates, sulphites, etc.[8]

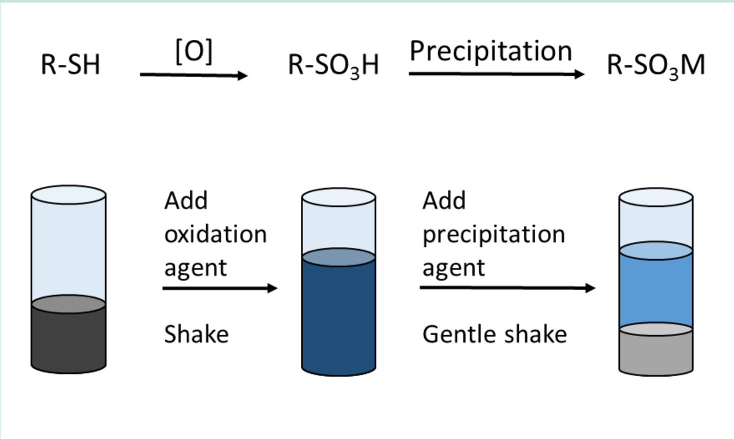


**FIGURE 17**
SCHEMATIC REPRESENTATION OF A CHEMICAL DETECTION SYSTEM BASED ON AN OXIDATION-PRECIPITATION STRATEGY

The precipitate enables visual confirmation of the presence of sulphur. The sensitivity of the method can be adjusted by varying both of the amount of oxidation agent as well as the precipitation agent. It is estimated that a sensitivity enabling the differentiation of 3% sulphur versus 0.1% sulphur is likely to be achievable. However, validation through iterative series of experiments is required to demonstrate this and is beyond the scope of this project.

### 4.3.1 Alternative strategies

In addition to the above-described method, several other approaches may provide a rapid evaluation of sulphur content in marine oil.

1. *Total oxidation by controlled combustion* would enable a similar approach as the above-described method. However, the precipitation step of the method would in this case require capture and oxidation of the produced $SO_2$.

2. *Detection and quantification by "sulphur-markers" in analogy to pregnancy test.* Identification of a sulphur-containing compound and correlation of this compound's relation to the total sulphur content would allow for the development of a colorimetric detection scheme in which a fixed amount of coloured oxidation agent, e.g., KMnO4, results in colour loss as the oxidation takes place.

[8] C. Alewell, Plant and soil, 1993, 149, 141-144

3. *Electrochemical detection of sulphur by electrochemical oxidation.* Sulphur containing compounds are electrochemically active due the many oxidation steps of sulphur. The electrochemical potential required for oxidation is correlated to the chemical structure of the sulphur containing compound, and a "sulphur-marker" strategy can be envisioned for the electrochemical detection of sulphur content.

## 4.4 Conclusion

A handheld XRF spectrometer has been used for direct analysis of sulphur content in 12 different fuel samples with different sulphur content ranging from 0.1% to 3.3% sulphur. The results are very promising and all results are within 10% of the reference analyses carried out by DNV. Based on the results, the method seems to underestimate the sulphur content, which could be a question of calibration. However, with the present and described method it should be safe to conclude that the present method definitely can distinguish 0.1% sulphur from 1% sulphur and from 2-3% sulphur.

In addition, several strategies for a fast determination of sulphur content by a chemical detection "kit" have been investigated on a theoretical basis. Several plausible strategies have been found, and a strategy based on a two-step oxidative-precipitation method was considered and discussed in more detail. Further development of the proposed systems will require significant experimental work involving selection of suitable oxidation agents, solvent systems, precipitation agents, etc. Furthermore, a careful validation study will demonstrate the utility and compatibility of the proposed systems over a range of different marine oil products. Finally, proper handling of chemicals must be addressed. The required development and validation for such a method is beyond the scope and resources of this project but could be pursued in a separate project.

# 5. Work package 4: Dissemination of project results

## 5.1 Objective

Due to the new regulations implemented in 2010 and 2015, surveillance of sulphur pollution has been a burning issue in the present decade. Due to the actuality of the topic, dissemination of project results received its own work package.

## 5.2 Dissemination of project results – activities

Some of the most important dissemination activities performed throughout the project are listed below:

- At "Seminar on clean shipping", Dec. 2013, held at the Danish Shipowners Association, the project manager presented the project. The talk focussed on the basic project ideas, the concept of "sniffing", but also on which mechanisms should be initiated if a non-compliant ship is detected. Maersk Maritime Technology was also present and held a talk on the importance of a level-playing field between the shipowners, and mentioned the project as part of their supported initiatives.

- "DR Nyheder" interviewed the project manager in September 2014, resulting in an article focussing on cost-effective sulphur surveillance from the Great Belt Bridge.[9] A number of other media followed with similar web-articles.

- At "Danish Maritime Days", Oct. 2014, Maersk Maritime Technology held a talk on the importance of a level-playing field between the shipowners, and again mentioned the project as part of their supported initiatives. Danish Technological Institute and the Danish Shipowners Association were also present at this seminar.

- During the third meeting of the international Steering Committee of the Priority Area on Clean Shipping in the EU Strategy of the Baltic Sea Region, October 2014, the project manager presented the project and preliminary results. At this meeting, Explicit I/S also presented their parallel project regarding sulphur surveillance with drones and helicopters also using cost-effective technology.

- Danish Technological Institute was inspired to carry out new project activities and further international activities and collaboration during the annual "ETH Conference on combustion-generated nanoparticles", in 2013, 2014 and 2015.

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[9] http://www.dr.dk/nyheder/viden/miljoe/storebaeltsbroen-tester-kunstig-naese

In addition to the above-listed activities, the Danish Shipowners' Association mentioned and discussed the project and the importance of sulphur surveillance at numerous national/international meetings/seminars. Within forums such as ECSA (The European Community Shipowners' Associations) or ICS (International Chamber of Shipping), many know about the project and in this context believe that a monitoring system is actually up and running in relation to the project. This in itself has a preventive effect for shipowners who consider violating the regulation.

## 5.3 Conclusion

Based on the activities listed in section 5.2 we conclude that there has been considerable exposure of the project activities and results, including national and international seminars/workshops and national media. These initiatives are important for highlighting the importance of cost-effective sulphur monitoring.

**Remote sensing of sulphur and particle emission from ships**

The prime focus of the project was estimation of sulphur content of marine fuels by plume measurements (remote sensing) on ships passing the Great Belt Bridge, using cost effective sensors. In parallel, two other potential fast methods aiming for fast analysis of sulphur content directly in fuel were investigated. The project results indicate, that the investigated methods can give a rough indication of the sulphur content. Further work is, however, needed in order to make cost-effective monitoring best practice.

Det primære fokus i projektet var bestemmelse af svovlindholdet i skibsbrændstoffer ved måling på skibenes røgfane (remote sensing) ved brug af omkostningseffektive sensorer, når skibe passerer Storebæltsbroen. Desuden er to andre, potentielle metoder til hurtig bestemmelse af svovlindholdet direkte i brændstoffet undersøgt. Projektets resultater tyder på, at de undersøgte metoder kan give et estimat af svovlindholdet, men at de er behov for yderligere udvikling for at gøre omkostningseffektiv overvågning til bedste praksis.

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