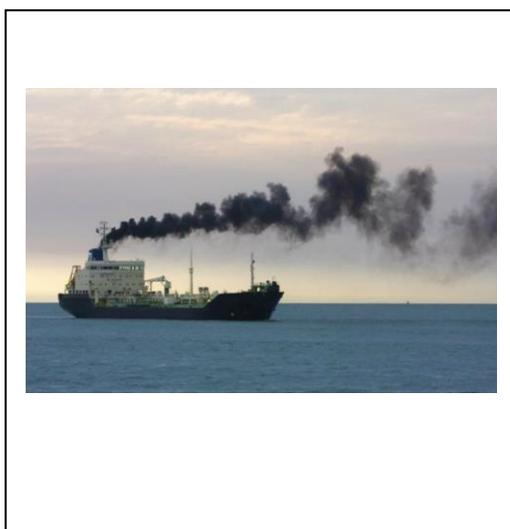**DTU**

DMF Project Ref. 2017-090 Sulfur Analysis of Fuels by Gasification (Svovlanalyse af brændstoffer ved forgasning)

1-10-2017/31-12-2019 – Final Report

Centre for Catalysis and Sustainable Chemistry

Foreword

The following report summarizes the main findings of the total project period between the 1st of October 2017 and the 15th of December 2019.

1. **Construction of Test-Rig**

Figure 1 shows a flow chart of the test-rig used to analyse the sulphur content in heavy fuel oil (HFO) and light fuel oil (LFO) samples by gasification.
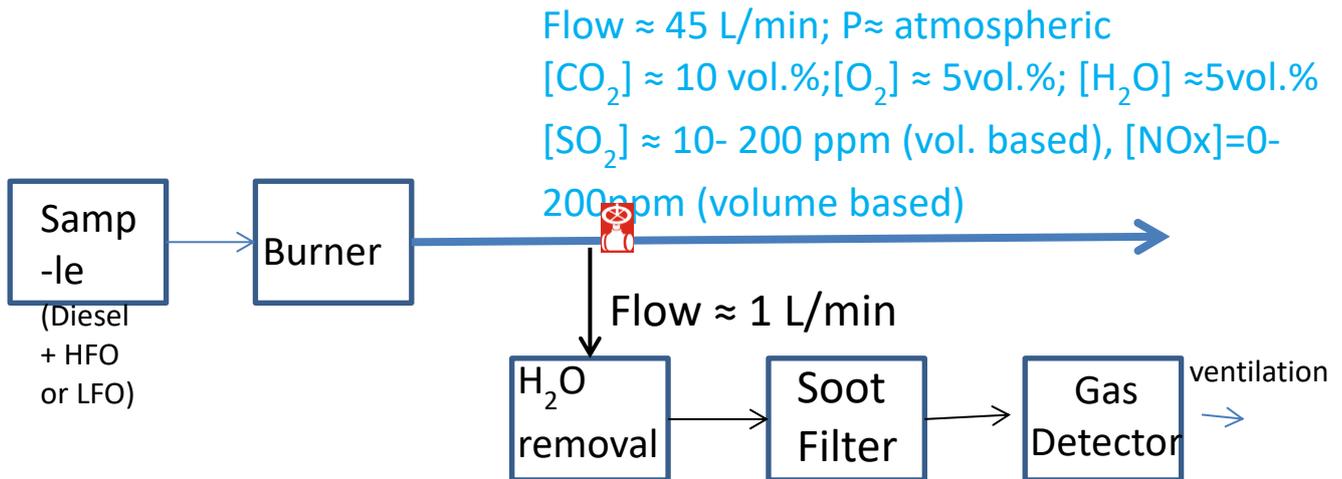
Flow ≈ 45 L/min; P≈ atmospheric
[CO_2] ≈ 10 vol.%;[O_2] ≈ 5vol.%; [H_2O] ≈5vol.%
[SO_2] ≈ 10- 200 ppm (vol. based), [NOx]=0-200ppm (volume based)

Samp-le	Burner			

(Diesel + HFO or LFO)

Flow ≈ 1 L/min

H_2O removal	Soot Filter	Gas Detector

ventilation

Figure 1: Flow Chart of Test-Rig

1.1 Sample Preparation & Burner

Since we have so far not been able to find a sufficiently small burner capable of burning pure HFO, we resorted to Diesel-HFO and Diesel-LFO blends, where the original samples of LFO and HFO were obtained from DFDS. The HFO concentration was varied between 1 and 5 wt.% with the lower limit being more practical due to a much lower rate of soot formation. The typical LFO content was 20 wt.%. Two burners sourced from the Eberspächer company were tested. The first one has a heat output of 2.2 kwh and relies on cooling by water, while the second one produces only 1.1 kwh of heat and relies on cooling by air. Most of the analyses were performed using the smaller burner because it is easier to use, mostly due to the air cooling mode but also because of lower rates of fuel consumption and heat disposal. Around 45 litre per minute (at STP conditions) of flue gas were generated with a composition as indicated in figure 1.

The majority of this gas stream was simply discharged to the ventilation system. A flow of around 1 litre per minute was diverted from the flue gas stream and sent to water and soot removal units before being introduced to a SO_2 detector. The diversion was achieved by increasing the pressure in the main stream using a manually controlled throttle. This could only been done to a minor extent due to the lowering effect on the

air to fuel ratio which resulted in increased soot formation. This problem can in principle be avoided by using a suction pump instead of the throttle.

1.2 H_2O Removal

A laboratory glass condenser as shown in figure 2 was used to lower the water content in the analysis gas stream. Water removal is necessary because H_2O interferes with the SO_2 analysis. Various cooling media (iced water, ice, dry ice, "no cooling") were tested. Keeping the condenser at a steady temperature turned out to be important for attaining a steady SO_2 signal. The most practical solution was to fully immerse the condenser into ice contained in an ice box.

Figure 2: Glass Condenser

1.3 Particulates Removal

Lowering of the concentration of particulates turned out to be of paramount importance for attaining a stable SO_2 signal. A SiC based automotive soot filter (length: 152.4 mm, diameter: 80 mm, 200 cpsi) was used and gave reasonable but not complete removal of particulates. In order to avoid soot build up in the filter and the need for regeneration, a platinum coated monolith located right after the burner should be installed. We have been in contact with a filter manufacturer (Liqtech A/S) to find out if oxidation of SO_2 to SO_3/H_2SO_4 is a problem. According to their test results no corrosion was observed downstream which is a clear indication that SO_2 is oxidized to a lesser extent.

Figure 3: Automotive soot filter

1.4 SO_2 Detection

In total, four SO_2 analyzers were tested, see table1.

Table1: Analyzers tested for SO_2 quantification.

Name/Company/Origin	Method	Cost	Issues	Picture
THE//China	Electrochemical	350-400€	Particulates, NOx, Sampling	
ESP/Aeroqual/New Zealand	Electrochemical	1000 €	Particulates, Sampling	
Evolution 220/Thermo Scientific/USA	UV-vis (general Purpose)	10-20,000 €	"Data Analysis", Size	
BINOS ULTRA.sens/Witech Sensorik/Germany	**UV-vis**	**3500 €**	Additional resistance to gas flow (membrane filter)	
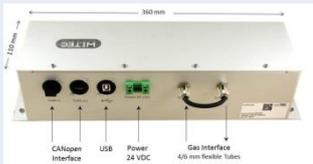
The two low-cost analyzers based on the electrochemical SO_2 detection/quantification method suffered from severe interference from particulates, especially when co-firing Diesel with HFO. Furthermore, both analyzers receive the gas mixture by means of a suction pump which prohibits simply passing a stream of analysis gas through the analyzers. Placing of these analyzers into a chamber being flushed with the off-gas seemed to be the only viable option and constituted a considerable source of error and experimental difficulty. NO_x gases had a signal lowering effect, especially on the instrument originating from China. Due to this host of issues we deemed analyzers based on the electrochemical method to be unfit for our task.

A general purpose UV-vis instrument was used to figure how applicable this analysis method is to our procedure. The main issues with this instrument are its high cost, large dimensions and the need to perform integrations on the raw absorption spectra. Possible interferences from NO_2 have not been observed. However, if using another burner operating at a higher temperature, this might become an issue. Burning of fuels rich in HFO probably necessitates higher temperatures and high oxygen contents, conditions favouring the formation of NO_x gases. Figure 4 shows a representative spectrum of a flue gas containing about 50 ppm of SO_2. Broadly speaking SO_2 generates two peaks, one at 190 to 240 nm and one at 240 to 320 nm. The former one gives higher absorbance, however, is incompletely measured and suffers more from interferences from particulates.
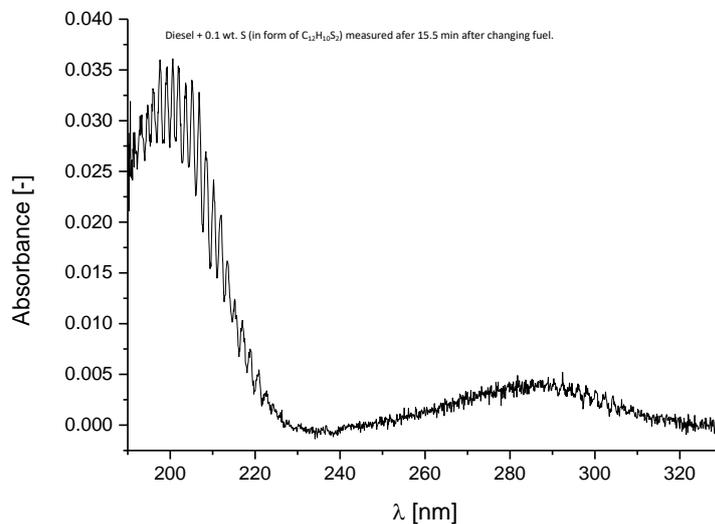

Figure 4: UV-vis spectrum obtained on general purpose instrument. Diesel + 0.1wt. % sulphur (in the form of C$_{12}$H$_{10}$S$_2$)

Because of the generally encouraging results and the more practical issues related to the general purpose UV-vis instrument a dedicated SO_2 meter based on this method of analysis was purchased from Witech Sensorik (Germany). The main advantages of this instrument over the general purpose UV-vis meter are:

(1) a longer sample cell (250 mm) leading to a stronger absorbance/ higher sensitivity; (2) correction for possible NO_2 interference; (3) automated signal integration greatly facilitating data analysis. Furthermore, this instrument was equipped with a membrane filter to further reduce the amount of particulates interfering with the analysis.

2. Materials & Experimental Procedure

Diesel ("D miles") was purchased from a "Circle K" petrol station in Kgs. Lyngby. Diphenyl disulphide ($C_{12}H_{10}S_2$; CAS: 882-33-7) was purchased from Alfa Aesar and used as received. HFO was received from DFDS and the sulphur content was stated to be between 2.1 and 2.7 wt.%. Diesel – $C_{12}H_{10}S_2$ blends were prepared and stored in 500 mL borosilicate bottles and will hereafter be referred to as "standards" and abbreviated by "D-S-x" with x being the weight percentage of sulphur. Blends of HFO (1-2.5 wt.%) and Diesel were prepared by thoroughly mixing the two fuels and are denoted as D-HFO-y. In many cases, ternary mixtures of Diesel, HFO and $C_{12}H_{10}S_2$ were prepared in order to measure at higher SO_2 concentrations. These are abbreviated by D-S-x-HFO-z with x and z being the concentrations of added sulphur and HFO, respectively. Small amounts of HFO would typically settle at the bottom of the bottle after about 30 minutes. Therefore, thorough mixing just before using the blend was imperative. Diesel-LFO blends were prepared in the same way.

The Eberspacher burner was started using pure Diesel as fuel. The UV-vis based analyzers were flushed with the resulting flue gas, which had passed the water and dust removal units, for about 30 minutes. The signal of this gas was used as the baseline. In the case of the BINOS ULTRA.sens instrument this was done by setting the SO_2 concentration to 0 ppm. Then the pure Diesel was typically replaced by a D-x standard. After attaining a steady state SO_2 signal, another standard was used. This typically took around 30 minutes. Values were saved every 30 seconds. In order to shorten the time it takes to saturate all lines with SO_2, short (few minutes), interim burning of a D-x blend with high sulphur concentration was sometimes performed. After a calibration line was constructed, the D-HFO-y or D-S-x-HFO-z sample was fed to the burner. After this, the test-rig was again flushed with flue gas originating from pure Diesel. Sometimes, this was followed by a second round of calibration and measurement. For each measurement, a separate calibration line was constructed.

Experiments using the standard addition method where various sulphur loadings are added to D-HFO-y (fixed y) were rarely performed. This is because the amount of burned HFO and the duration of its burning increase significantly compared to the calibration method. This might increase the total amount of soot being formed with all the ensuing problems.

The condenser was emptied at the end of each day and always had substantial spare capacity. The soot filter was taken out of its containment after about 50-100 working hours and treated with compressed air in order to remove the trapped particulates. Complete regeneration was attained by calcination at 500 C for several hours.

3. Results

3.1 HFO Analysis with General Purpose UV-vis

 The HFO concentration of all the D-HFO-y and D-S-x-HFO-z blends presented in this section was 2.5 wt.%.

3.1.1 Calibration of General Purpose UV-vis

Figure 5 shows a calibration curve based on the peak area in the region 190-240nm. A perfectly straight trend line was established.
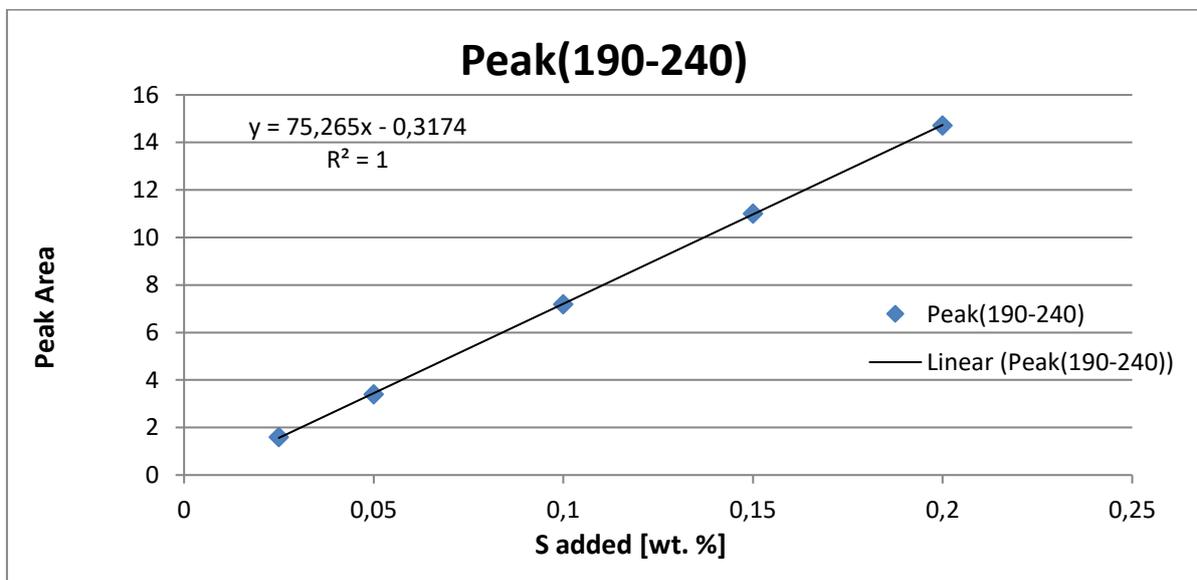

Figure 5: Calibration curve (D-S-x) using the general purpose UV-vis instrument. Peak area derived in the region 190-240 nm. Sulphur added in form of $C_{12}H_{10}S_2$.

Figure 6 shows the corresponding calibration curve based on the peak at 240-320 nm with and without an outlier at 0.025 wt.% of added sulphur. The values shown in figure 5 and 6 were derived from the same experiments. A highly linear correlation was again established, demonstrating that the test-rig can deliver satisfactory results at least when firing Diesel without HFO.
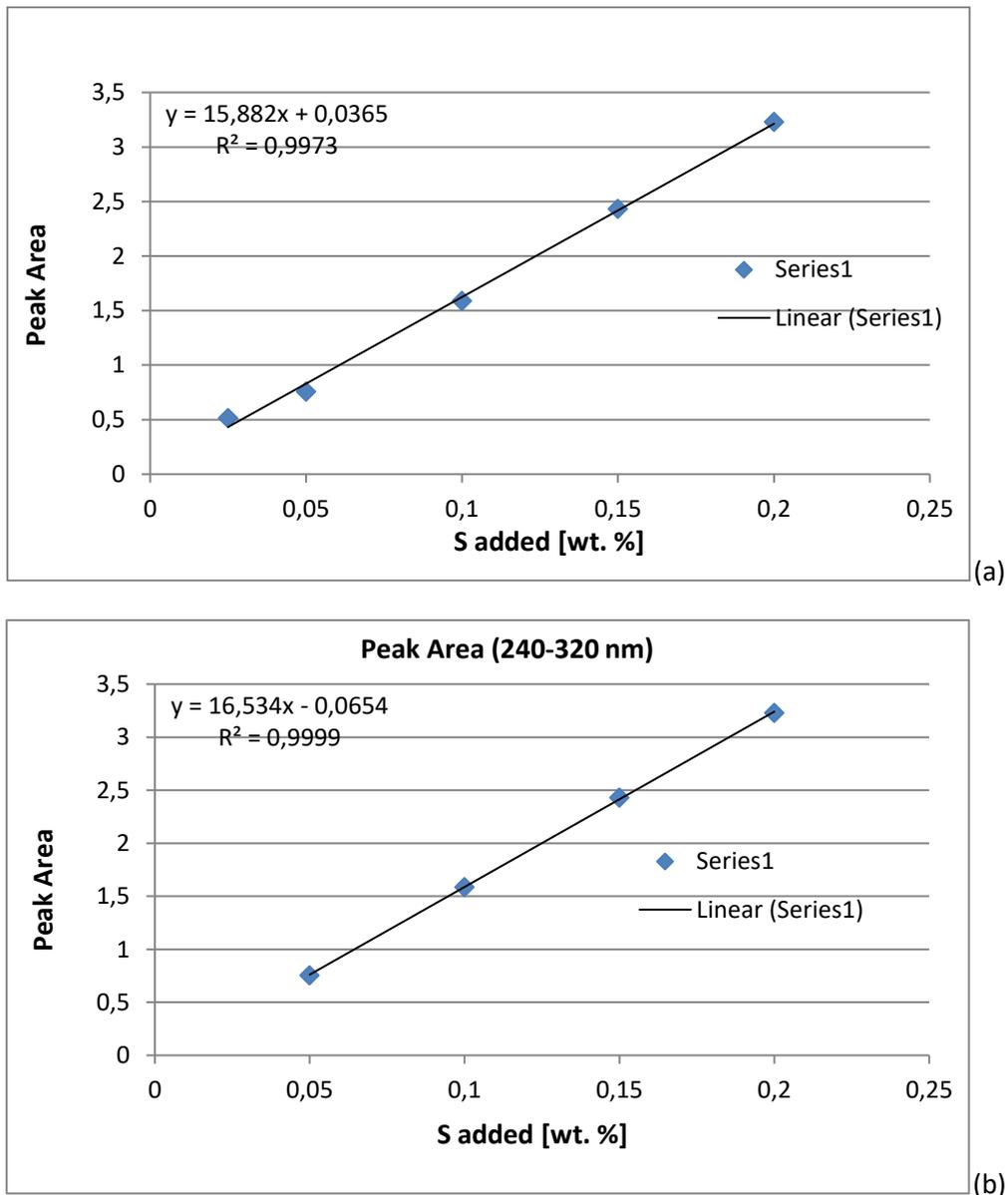
Figure 6: Calibration curve (D-S-x) using the general purpose UV-vis instrument. Peak area derived in the region 240-320 nm. Sulphur added in form of $C_{12}H_{10}S_2$. Versions (a) and (b) are including and excluding an outlier, respectively.

3.1.2 Standard Addition Method using D-S-x-HFO-z

These experiments were carried out directly following those presented in section 3.1.1 (calibration). The calibration curves presented in section 3.1.1 can therefore be applied to the data generated in section 3.1.2.

Figure 7 shows the peak area (190-240nm) as a function of sulphur added to a Diesel-HFO blend. The regression of the trendline is obviously not satisfactory. Extrapolation of the trend line gives a sulphur content of 1.59 wt.%. Using the value of the intercept in conjunction with the calibration curve shown in figure 5

yields a sulphur concentration of 2.05 wt.%. The slope is significantly larger than in the absence of HFO, see figure 5.
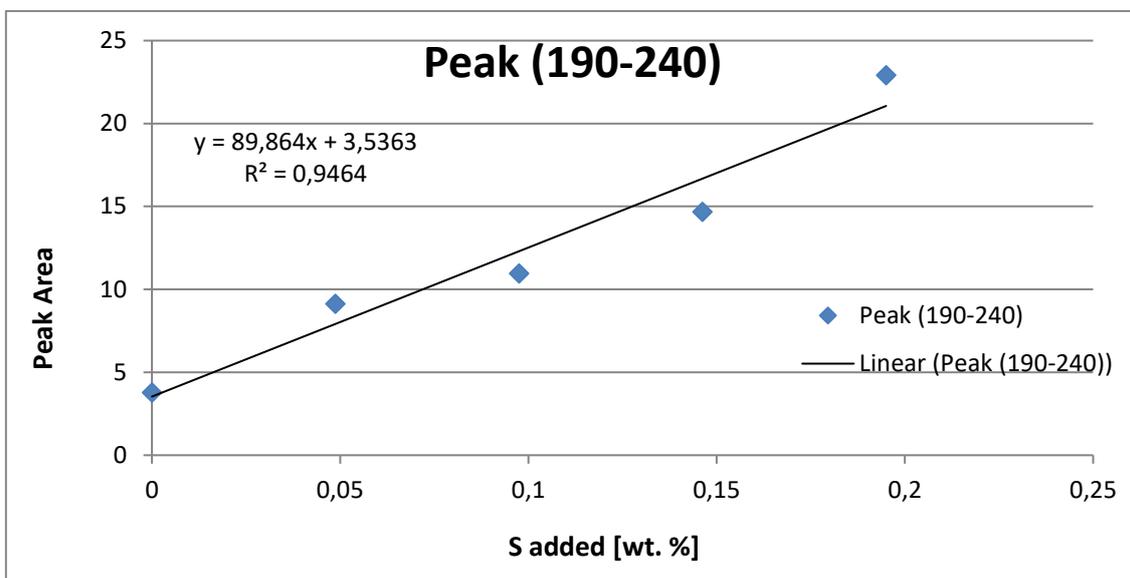

Figure 7: Standard addition method using D-S-x-HFO-2.5. Peak area derived in the region 190-240 nm. Sulphur added in form of $C_{12}H_{10}S_2$.

Figure 8 shows the scattering of the individual measurements leading to the average values presented in figure 7. The relative scattering of the points at added sulphur concentrations of about 0.05 and 0.2 wt.% were deemed to be too high and hence excluded for further analysis. One possible reason for the scattering could be fluctuations in the combustion process leading to unstable soot formation and excess air, another one changing temperatures in the water trap.
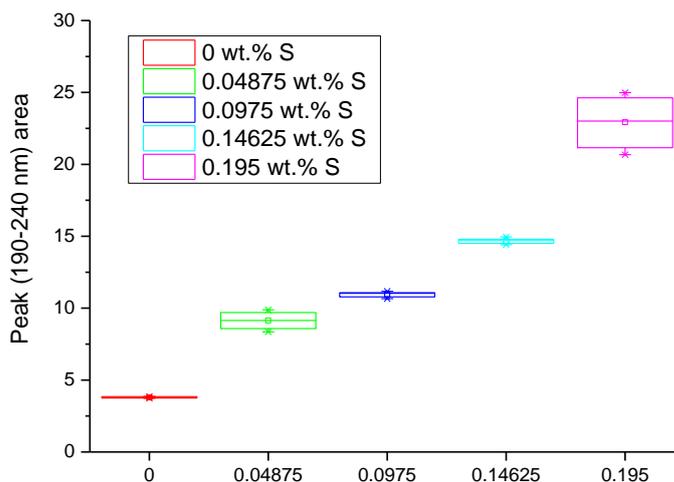

Figure 8: Scattering of data presented in figure 7.

Figure 9 shows the results of the standard addition method as presented in figure 7 excluding the two outliers as identified in figure 8. The resulting trendline is perfectly straight and extrapolation yields a sulphur concentration of 2.20 wt.% in HFO. Using the value of the intercept in conjunction with the calibration curve shown in figure 5 yields a sulphur concentration of 2.34 wt.%. The slope of the trendline is almost identical to the one in the absence of HFO, see figure 5. This finding is important because it shows that relying on a HFO free calibration curve is probably possible and thus reduces the total amount of HFO burning and in turn reduces the risk of soot plugging.
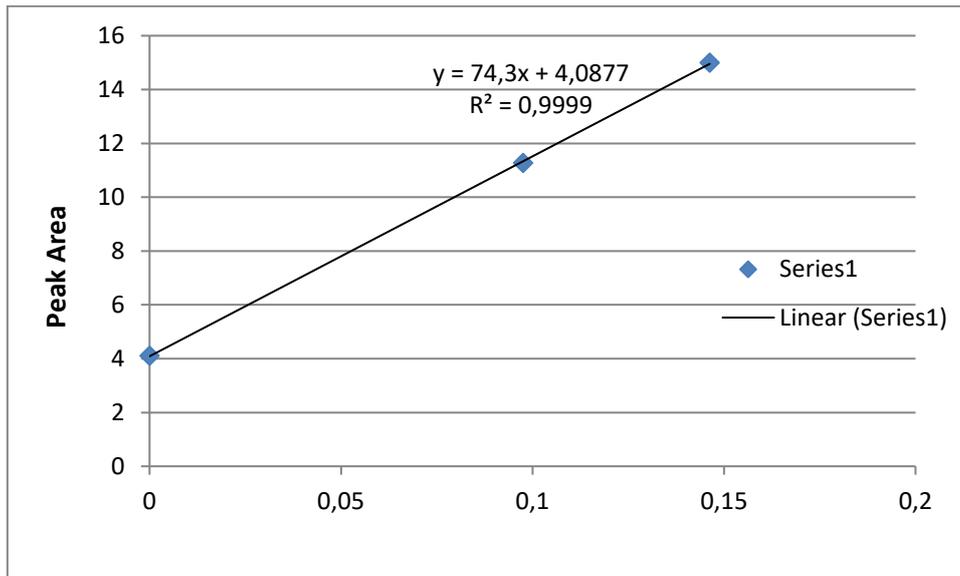

Figure 9: Standard addition method using D-S-x-HFO-2.5. Peak area derived in the region 190-240 nm. Sulphur added in form of $C_{12}H_{10}S_2$. Data as presented in figure 7 excluding two outliers.

Figure 10 shows the peak area (240-320nm) as a function of sulphur added to a Diesel-HFO blend. Extrapolation of the curve yields a sulphur concentration of 3.42 wt.% and using the intercept in conjunction with the trend line shown in figure 6 a concentration of 3.28 wt.%. These values are reasonably close to each other, suggesting again that using the standard addition method is not necessary. However, the values are above the range given by DFDS and significantly higher than those based on the analysis of the peak at 240 to 320 nm. Possible reasons for these discrepancies could be faulty peak integration and a strong influence of particulates on the 190-320 nm peak.
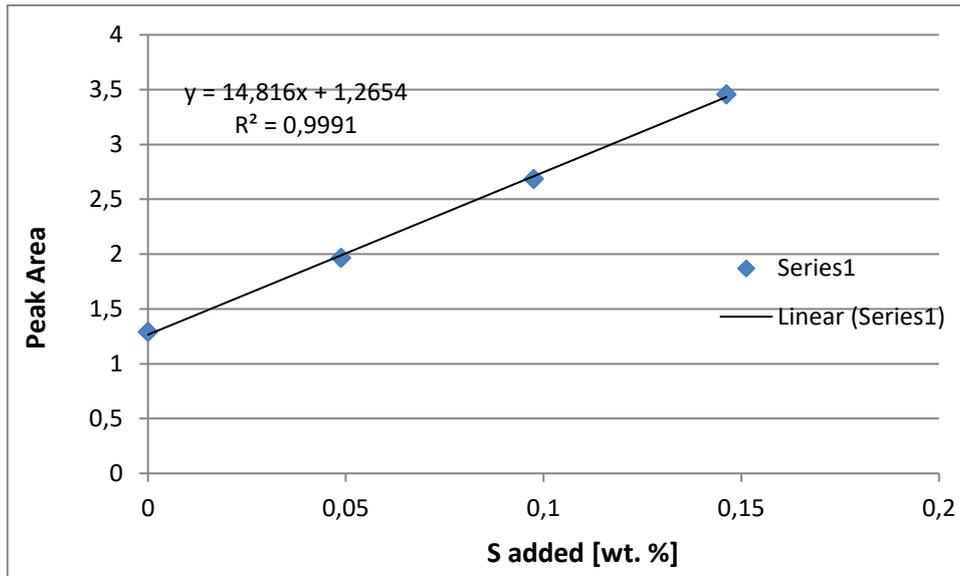
Figure 10: Standard addition method using D-S-x-HFO-2.5. Peak area derived in the region 240-320 nm. Sulphur added in form of $C_{12}H_{10}S_2$.

3.2 Operational Difficulties with D-HFO-2.5

Burning blends containing 2.5 wt.% of HFO proved to be unviable in the long run. After about 100-150 hours of operation, including calibration, the burner would no longer start because it was completely plugged with soot. The combustion chamber alone contained about 25 g of soot, see figure 11. The strong soot formation can probably be ascribed to the burning of heavy oil in a burner designed to burn Diesel. The fact that a throttle was used which increased the pressure in the combustion chamber (lowering of air/fuel ratio) probably exacerbated the problem, but to an unknown extent. Towards the end of 2019 we also found out that some of the soot formation can probably be ascribed to flame disturbances caused by the suction system which removes the major share of the flue gas. This fact might be very relevant when installing a burner system on-board of a ship.
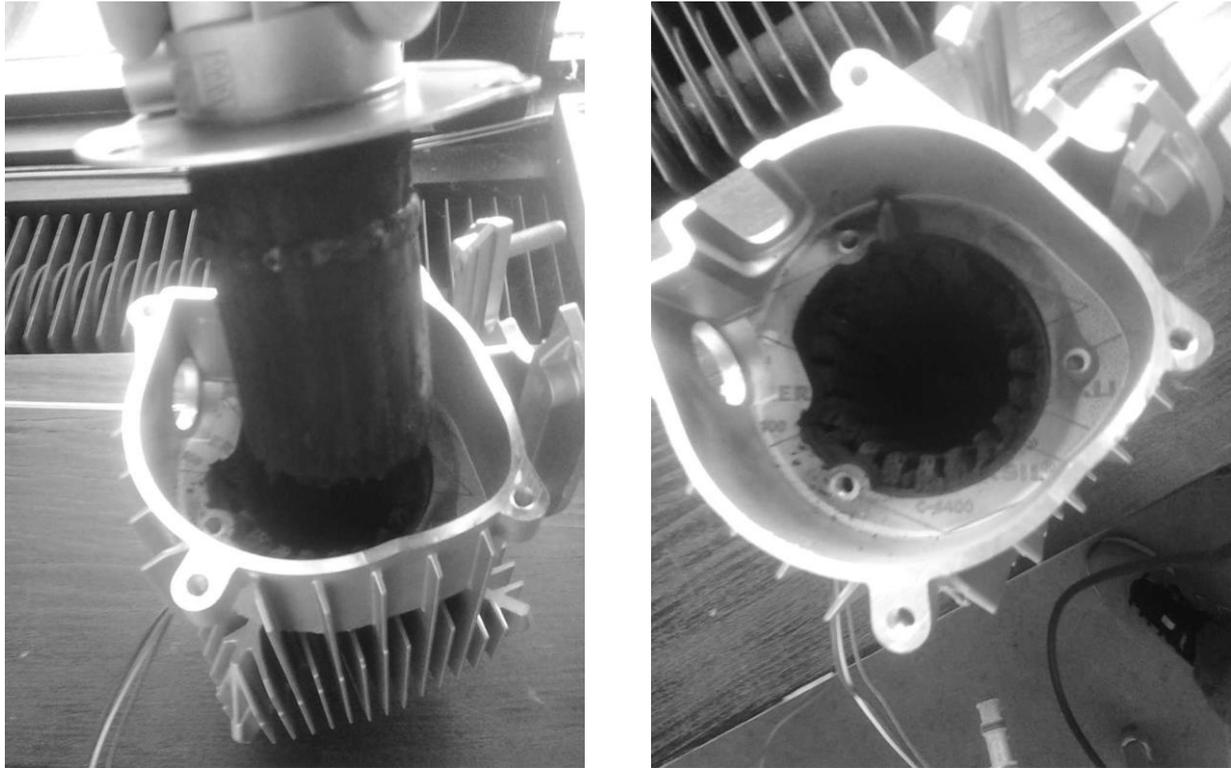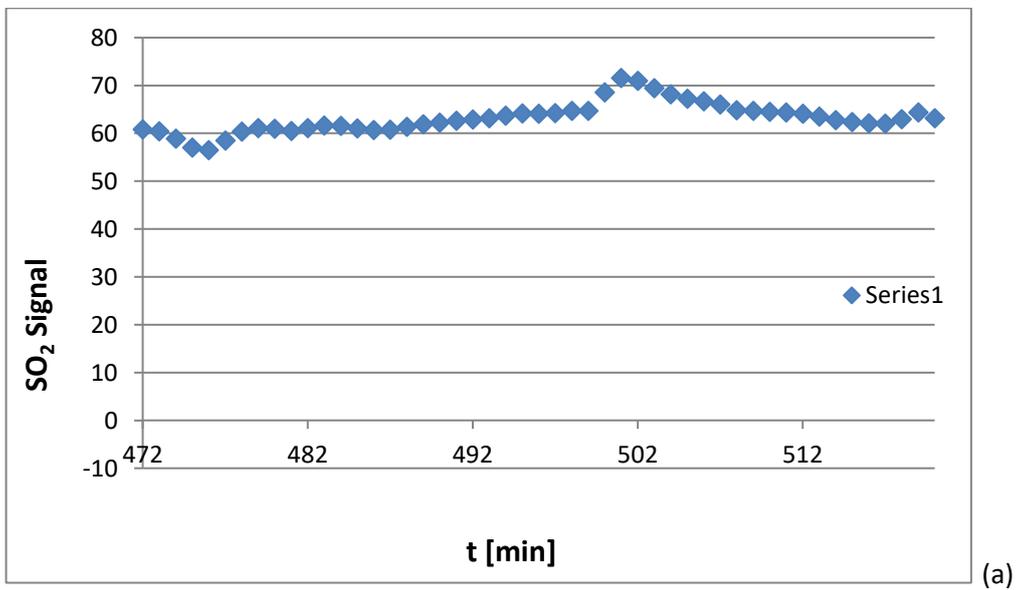
Figure 11: Soot deposits in combustion chamber of Eberspacher Airtronic.

Burning of blends containing 2.5 wt.% HFO also lead to relatively unstable SO_2 signals, see figure 12. Burning of blends only containing 1 wt.% HFO typically gave a more stable signal. Therefore, further testing was conducted using fuel blends only 1 wt.% of HFO.
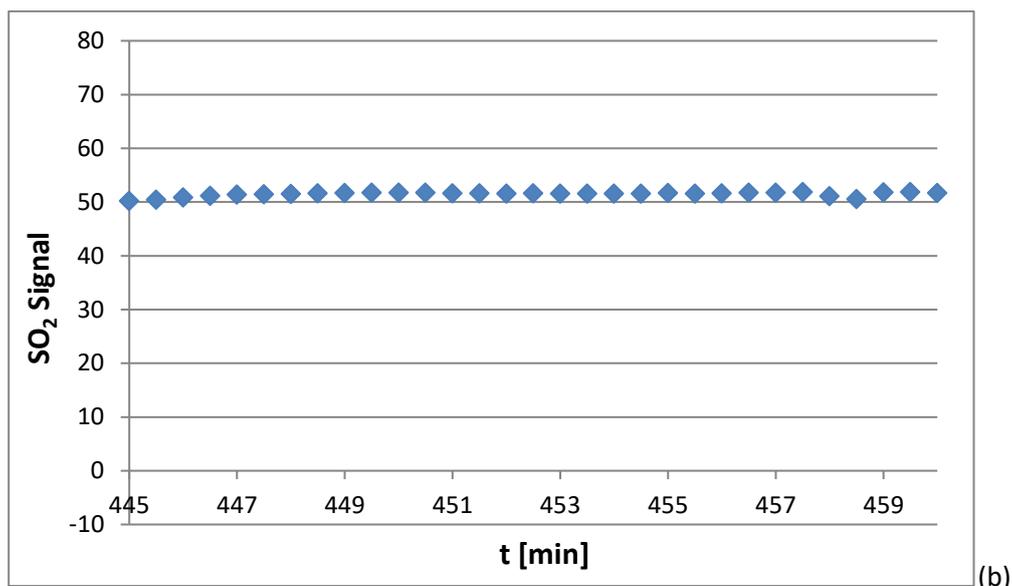

(a)

(b)

Figure 12: SO$_2$ signal as function over time as measured by the BINOS ULTRA.sens UV-vis based instrument. (a): Burning of D-S-0.075-HFO-2.5. (b): Burning of D-S-0.100-HFO-1

3.3 HFO Analysis with BINOS ULTRA.sens

All data presented here was generated with blends containing 1 wt.% HFO. Different calibration strategies were tried out. Experiments with three and five calibration points were conducted, the former having the advantage of shorter measurement time but also having a higher margin of error/uncertainty. Often 0.1 wt.% sulphur were added to D-HFO-1 in order to achieve a more stable signal and to shorten the time it takes to saturate the tubing with SO$_2$. However, it turned out that the experimental error/uncertainty as calculated in Appendix A1 was not reduced by this strategy. Furthermore, rapid saturation of the tubes with SO$_2$ could also be achieved by short term (few minutes) burning of D-S-0.15.

3.3.1   HFO Analysis based on 3 Point Calibration

The first 10 analyses were performed using a three point calibration with D-S-0.1, D-S-0.125 and D-S-0.15 standards and D-S-0.1-HFO-1 as sample. The resulting sulphur concentration in HFO including the uncertainty range is shown in figure 13. A high degree of scattering is observed and the average value of 1.72 wt.% is clearly below the range reported by DFDS. The average uncertainty is 0.59 wt.% and never below 0.22 wt.%. These values are clearly not satisfactory.
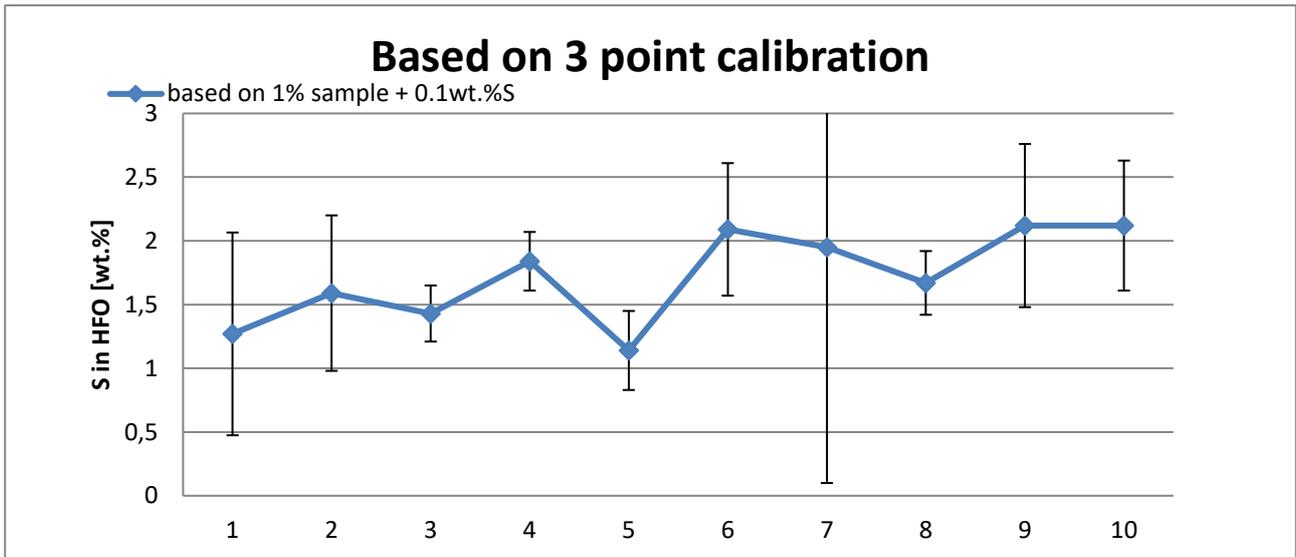
Figure 13: Sulphur concentration in HFO including uncertainty bars. Values derived from a three point calibration (D-S-0.1; D-S-0.125 and D-S-0.15) and D-S-0.1-HFO-1 as sample. SO₂ detection using BINOS ULTRA.sens.

Also two measurements with HFO dissolved in pure Diesel (D-HFO-1) were conducted, see figure 14. The resulting sulphur concentrations are similar to the average of the 10 D-S-0.1-HFO-1 samples and the range of uncertainty even lower. Henceforth, no more sulphur will be added to the HFO containing blends. Since the range of uncertainty is unacceptably large, calibrations using five instead of three points will be used from now on.
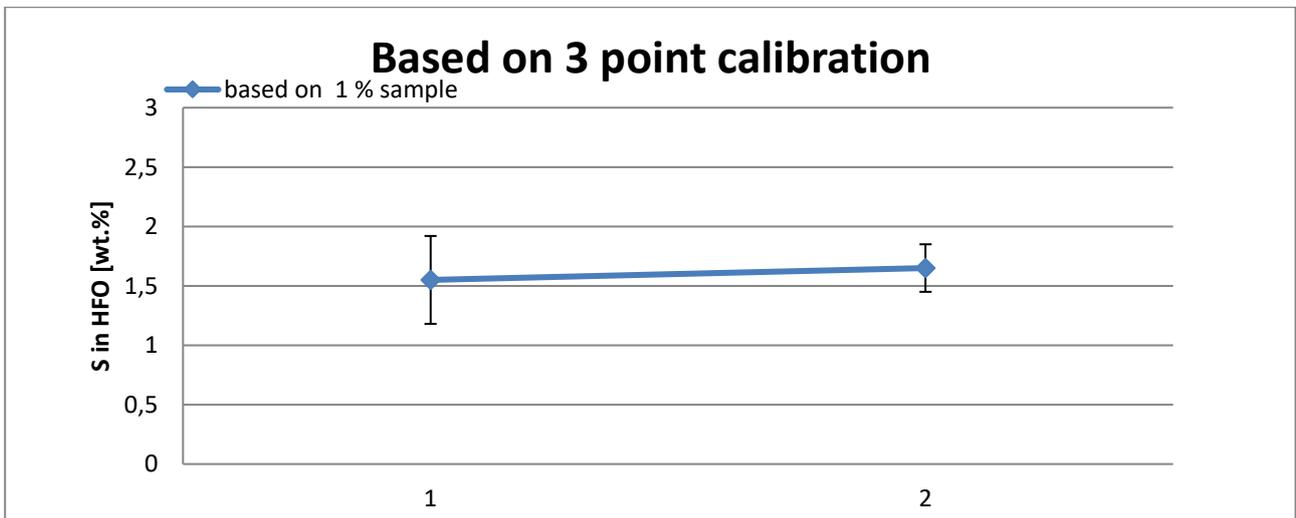

Figure 14: Sulphur concentration in HFO including uncertainty bars. Values derived from a three point calibration (D; D-S-0.025 and D-S-0.05) and D-HFO-1 as sample. SO₂ detection using BINOS ULTRA.sens.

3.3.2   HFO Analysis based on 5 Point Calibration

Two measurements of D-HFO-1 using a five point calibration curve were conducted, see figure 15. Using a five point calibration curve clearly reduces the size in uncertainty. However, the uncertainties are probably still too high. Further reductions can likely only be achieved using higher HFO concentrations. Replacing the throttle with a suction pump might permit this to some extent without causing soot related problems. The average measured sulphur concentration of 1.73±0.16 wt.% is below the range reported by DFDS.
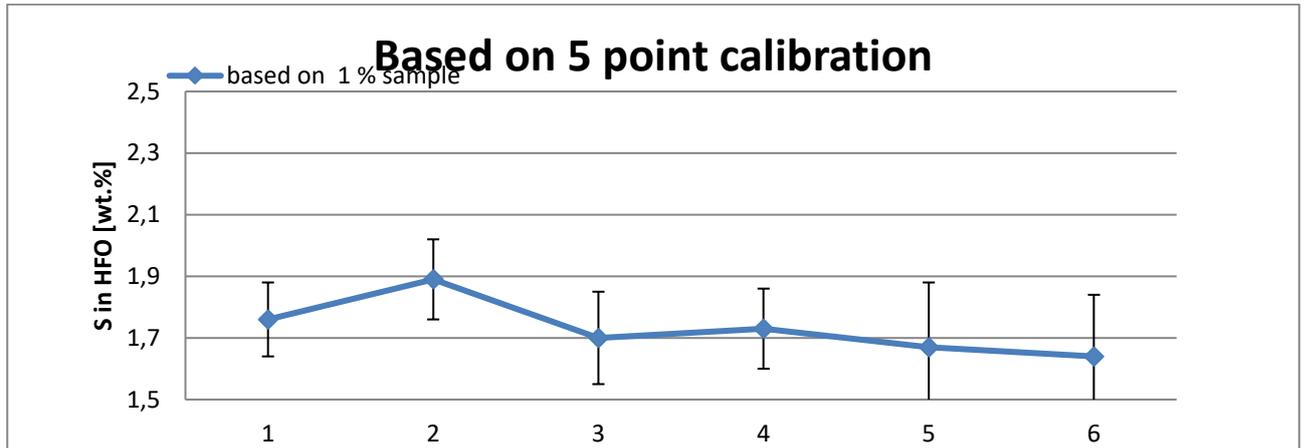

Figure 15: Sulphur concentration in HFO including uncertainty bars (6 experiments). Values derived from a five point calibration (D; D-S-0.015 D-S-0.025, D-S-0.05 and D-S-0.06) and D-HFO-1 as sample. SO_2 detection using BINOS ULTRA.sens.

3.3.3   Summary on HFO analyses

Burning of HFO at concentrations of 2.5 wt.% (in Diesel) can cause heavy soot formation and unstable SO_2 signals. These problems are largely solved by lowering the HFO concentration to 1 wt.%. Calibration curves containing only three points result in very high uncertainties. These can be strongly reduced by using a five point calibration. The measured sulphur concentrations in HFO are below the range reported by DFDS and seems not be affected by the number of calibration points. Adding extra sulphur to the sample makes no significant difference in terms of both the level of uncertainty and the average.

More precise measurements (lower uncertainties) probably entail using higher concentrations of HFO. Using a more suitable burner is an obvious solution, however, procuring a suitably sized one might not be possible without efforts in burner development. Avoiding the backpressure created by the throttle could allow some small increase in the HFO concentration. Likewise, avoiding the flame disturbing effect of the suction (ventilation) system might allow for some small increase in the permissible HFO concentration.

3.4 Light Fuel Oil (LFO) Analysis

The LFO measurements were carried out analogous to the HFO ones. The LFO concentration in the samples was typically 20 wt.% and 0.1 wt.% of sulphur was added in the form of $C_{12}H_{10}S_2$. Figure 16 shows the result of seven measurements. The first measurement (0.083 wt.% S) is probably an outlier. Otherwise, the values seem not to differ beyond the margin of uncertainty which in relative terms is about 11 to 14 %. This margin could probably be easily reduced by increasing the number of standards.
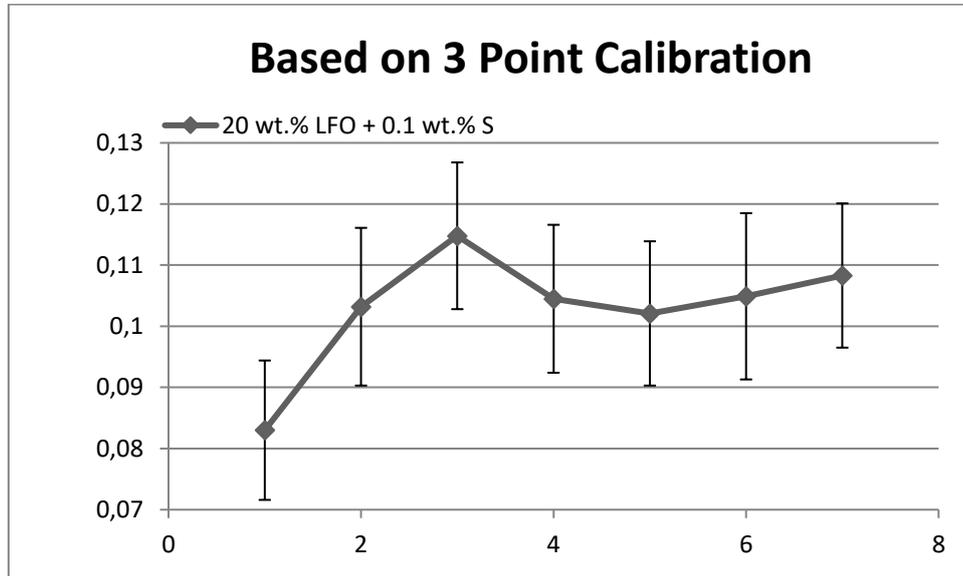

Figure 16: Sulphur concentration in LFO including uncertainty bars. Values derived from a three point calibration (D-S-0.1 D-S-0.125, D-S-0.05 and D-S-015) and D-S-0.1-LFO-20 as sample. SO$_2$ detection using BINOS ULTRA.sens.

A separate batch of four experiments with D-LFO-20 samples was conducted, each with a four-point calibration, see figure 17. The S content in LFO is 0.092±0.005 wt.% and 0.093±0.009 wt.% according to the four-point and two-point calibration, respectively. Increasing the number of calibration points reduces the uncertainty margin as expected. However, the measured S content in LFO is practically insensitive to the number of standards in four out of the five experiments. This means that a two-point calibration should suffice and considerably lowers the time requirement of the experiment.
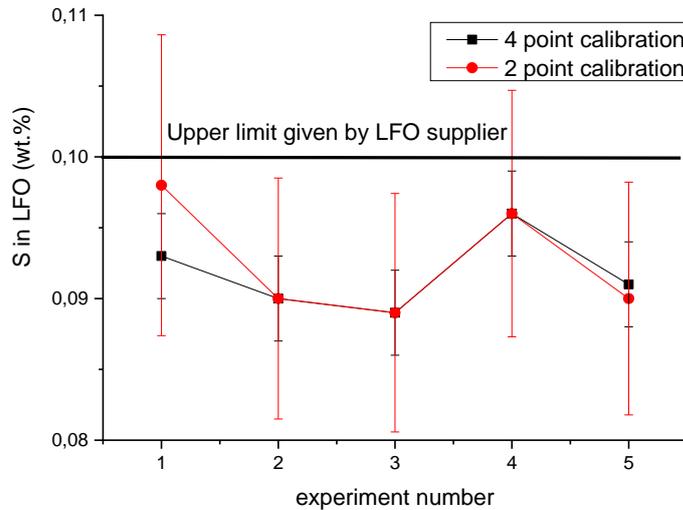
Figure 17: Sulphur concentration in LFO including uncertainty bars. Values derived from a four point calibration (D-S-0, D-S-0.15, D-S-0.025, D-S-0.05 and D-S-0.06) or two point calibration (D-S-0.015 and D-S-0.025) and D-LFO-20 as sample. SO_2 detection using BINOS ULTRA.sens.

3.5 Summary on S Determination in HFO and LFO

Sulphur content determination of HFO and LFO samples proved to be challenging. The major issue turned out to be formation of particulates and soot, especially when burning HFO. Inexpensive electrochemical SO_2 analysers were affected too much by particulates, even when a particulate-removing unit was used upstream. Therefore, a relatively expensive UV-vis analyser had to be used which, in conjunction with a soot filter, showed acceptable performance. Soot formation causing plugging of the combustion chamber was another major problem. This was especially the case when burning blends containing HFO and can largely be explained by the fact that the burner is not designed for fuels heavier than standard diesel. Other soot generating factors were the use of a throttle and a strong suction to remove the flue gas from the laboratory. The throttle can probably be exchanged with a suction pump. The latter issue can probably also be avoided by designing a suction system of appropriate strength.

The sulphur content of LFO was determined rather accurately whereas the one of HFO was significantly lower than the actual value.

In order to fully avoid issues of soot formation use of a more suitable burner seems to be unavoidable. The next section describes the efforts that were made in that direction.

4. Partnering with companies to develop a miniature burner

Sourcing a suitably sized burner capable of burning blends containing sufficiently high HFO contents turned out to be very difficult. Since we could not find such a device on the market we contacted several companies, among them Eberspächer, in order to establish a partnership regarding burner modification/development.

The only positive response came from AlfaLaval. At present, this company only produces burners of much larger size, but owns a unit in Monza which specializes in fuel conditioning equipment. We had one personal and two skype meetings with employees of this unit and discussed both the actual need for a sulphur determination system and the real world demands to such a system. The following summarizes what we have learned from them.

i)   Safety issues with use of burner

Using a burner in the engine room might be a safety issue, according to AlfaLaval. This is a non-smoking area, hence use of a flame, even inside of a burner, may constitute a substantial hurdle to a security clearance of the envisioned device – although the commercial burner we use is certified for use on board sailing and motor boats.

ii)   Measuring SO_2 content during "fuel change-over"

Measuring and documenting the average sulphur content of the fuel blend burned during the hours before entering the emission control areas is of interest. Since HFO, which is burned outside the emission control areas(possibly diluted HFO after 1/1-2020 to meet new regulations of max. 0.5 w% S fuel at High Sea), and LFO, which is burned inside these areas, have vastly different properties regarding e.g. viscosity, a gradual change in the fuel composition needs to be performed. The change over from HFO(or diluted HFO) to more expensive low sulphur LFO is typically commenced earlier than actually needed in order to be on the safe side regarding sulphur compliance. This "safety margin" is ultimately costly and might be reduced by rapidly measuring the sulphur content of the actual fuel mixture. This could either be done by diverting a small stream of fuel blend (≈5mL/min) to a separate burner, or by measuring the CO_2 and SO_2 contents of the flue gas generated by the vessel's engine after combustion. The latter option was favoured by AlfaLaval due to the before mentioned safety issues with flames in the engine room. Therefore, we spent the project's last period on exploring suitable solutions, see section 5.

5. Fuel Control by Flue Gas Sulphur Determination

Our Quantek Model 906 IR based CO_2 analyser (0-50 vol.%) was installed downstream of the ULTRA.sens SO_2 analyser. The SO_2 analyzer was recalibrated with 50 ppm SO_2 in dry air. The CO_2 analyser had not been re-calibrated since receiving it in early 2016.

We tested the following three samples:

i)   Undiluted LFO
ii)   Diesel-LFO (80/20 w/w)
iii)   Diesel with 0.1 wt.% S (as $C_{12}H_{10}S_2$)

Table 2 gives the measured CO_2 and SO_2 concentrations and the resulting S concentration in the burned fuel. For the LFO sample, both the undiluted and diluted sample give LFO sulphur concentrations significantly lower than the 0.09-0.10 wt.% obtained with calibration curves, see figure 17. Also the sample with known sulphur content (0.1 wt.% as $C_{12}H_{10}S_2$) yielded a concentration which was about 10 % too low. Possible causes for these discrepancies are issues with the two analysers and adsorption of SO_2 onto soot particles. The last

mentioned cause is the least likely one because the relative deviation is insensitive to the fuel mixture burned. Therefore calibration by a fuel standard seems necessary and the corrected values based on the 0.1 wt% standard in the scheme below leads to the values in parenthesis.

Table 2:

Fuel	SO$_2$ Signal (ppmv)	CO$_2$ Signal (vol.%)	S in undiluted fuel (wt.%)
Undiluted LFO	38.824	11.36	0.078 (0.088)
Diesel-LFO (80/20 w/w)	7.036	10.01	0.080 (0.090)
Diesel with 0.1 wt.% S (as C12H10S2)	42.28	10.84	0.089 (0.100)

These values are close to the values measured in Fig. 17 and show that the two-component analysing system used by us in principal are of high enough quality to allow for reliable sulphur content determination in the combusted fuel. Further improvement of the set-up seems promising for an attractive alternative to the direct measure of sulphur in fuels by gasification.

6. Summary

A test-rig was constructed with an Eberspächer Airtronic as the burner and an UV-vis based SO$_2$ instrument from WITEC (Germany) as the two major components. Lowering of the water and particulate contents in the analysis gas is achieved using simple methods (ice cooled condenser and automotive soot filter). Samples of LFO and HFO were obtained from DFDS.

Since the burner is designed to use pure Diesel, HFO can only be burned at very low concentrations (≈ 1wt.%) because otherwise too much soot is formed. Soot can plug the equipment and too high levels of particulates can influence the SO$_2$ analysis.

Because of the need for a high dilution factor, the margin of uncertainty attached to the measured sulphur concentrations in HFO is rather high. A five point calibration curve is necessary to bring this value to below 0.2 wt.%. The measured sulphur concentration in HFO was about 1.7 to 1.8 wt.% on average, which is clearly below the lower bound of the range reported by DFDS. Further improvements probably necessitate the burning of blends containing more HFO.

Analysing LFO turned out to be less problematic. Samples containing 20 wt.% of LFO were combusted with fewer soot related problems. A two-point calibration curve was good enough to yield realistic sulphur concentrations with relative uncertainties of just about 10 %.

To be of general interest, our equipment absolutely needs to include a burner that can efficiently burn LFO and HFO at relatively high concentrations. No such device was found and establishing contacts to potential partners in the field of burner development proved to be very difficult. So far we only established a contact to the "fuel conditioning" division of AlfaLaval. However, use of a burner inside the engine room might be a safety issue. Measuring the fuel's sulphur content during change-over between restricted areas is probably

of interest to shipping companies, according to AlfaLaval. This should optimally be done by measuring the SO_2 and CO_2 contents of the engine's flue gas. At the end of the project, we added a Quantek Model 906 IR based CO_2 analyser to our test rig. Both LFO, diluted LFO and a diesel standard containing 0.1 wt.% of sulphur were tested. Using the 0.1 wt% S-standard for calibration the measured sulphur content was for both LFO samples close to the values obtained by our direct measurement of sulphur by gasification of the fuel. Thus two promising tracks may be followed beyond this project, i.e. attempts to develop a burner allowing for stable combustion of both HFO and LFO for direct measure of the sulphur content in the fuel and alternatively measure of the sulphur content by analyzing both the SO2 and CO2 content simultaneously in the flue gas obtained after the combustion engine.

We are currently in dialog with AlfaLaval regarding possible further progress of the technology and if it will be commercially realized and/or patents are issued, DMF will be informed accordingly.

No scientific publications have been submitted in order to be able to work out possible patent applications.

Also for this reason the project have only been presented very briefly at conferences to get possible additional partners attracted by the technology.

Appendix

A1: Calculation of error (uncertainty) margins

$$Error_{total} = \sqrt{\left(Error_{Intercept}\right)^2 + \left(Signal * Error_{Slope}\right)^2 + \left(Error_{Signal} * Slope\right)^2}$$

Y axis: concentration of standards (wt.% S)

X axis: Signal measured by Witec UV-vis instrument

n: number of calibration points (here n=3 or 5)

y(calc): concentrations of calibration curve as calculated from the calibration

$Error_{Signal}$: ± 2% of Signal or 0.5 ppm, whatever is bigger.

1: $Error_{Intercept}$

$$Error_{Intercept} = \sqrt{\frac{\sum_{i=1}^{n} x_i^2}{n * \sum_{i=1}^{n}\left(x_i - x_{average}\right)^2}} * \sqrt{\frac{\sum_{i=1}^{n}(y_i - y(calc)_i)^2}{n - 2}}$$

2: $Error_{Slope}$

$$Error_{Slope} = \sqrt{\frac{\frac{1}{n-2} * \sum_{i=1}^{n}(y_i - y(calc)_i)^2}{\sum_{i=1}^{n}(x_i - x_{average})^2}}$$