

FTIR measurement of NH₃, HCN, SO₂, H₂S and COS
in pulverized lignite oxy-fuel flames
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Abstract

Nitrogen and sulphur compounds are investigated in the atmosphere of a high temperature oxy-fuel flame, using Fourier Transform Infrared Spectroscopy (FTIR). For this application, evaluation routines have been developed to investigate the concentrations of NH₃, HCN, SO₂, H₂S and COS by analyzing the absorption intensity of characteristic fingerprints within the strong overlapping of the CO₂ rich sample gas matrix. NH₃ and SO₂ was successfully analysed however HCN, H₂S and where not measured. The later species had either low concentration at the specific spatial measurement point or could not be detected due to too strong overlapping from absorption bands other gases in the same wavelength. It is furthermore discussed if decomposition of HCN, H₂S and COS on the filter of the sampling probe or elsewhere during the sampling process could cause the noticed difficulties in detectability of those gases.

1 Introduction

The question of measuring the precursors for nitrogen oxides (NO_x) formation and sulphur compounds in the pulverized lignite flame of the oxy-fuel reactor at CTU was posed within the first part of the Bio-Fuel GS II course, held at the Chalmers University of Technology (CTU) from the 20 to 24 of October 2008. At CTU, one has good experience with FTIR measurements in a circulating fluidized bed boiler (CFB),

however not in oxy-fuel combustion. In oxy-fuel combustion the gas atmosphere differs completely from a CFB combustion atmosphere since oxygen (O_2) is used instead of air to create a flue gas with high concentration of carbon dioxide (CO_2). To reduce the combustion temperature, flue gas is recycled and, as a consequence, the combustion takes place in an atmosphere with high concentrations of combustion products. This has important implications on the combustion reactions.

For example are NO_x emissions reduced by reburning when recycled into the flame. To understand the reduction mechanism, it is important to achieve a good spatial resolution of NH_3 and HCN as the two most important precursors of NO_x . Sulphur compounds like sulphur dioxide (SO_2), hydrogen sulphide (H_2S) and carbonyl sulphide (COS) on the other hand, are of interest regarding to fate of sulphur in an oxy-fuel combustion process. FTIR measurements offer a good possibility for analysis of such compounds. However high concentrations of CO_2 and water vapour (H_2O) in an oxy-fuel flame make the evaluation of infrared spectra complicate, since the two gases have strong overlapping infrared absorbance bands over wide ranges of wave numbers. The H_2O concentration depends on the kind of recycle (dry or wet), the oxygen concentration in the oxidiser and the stoichiometric ratio.

Summarized, there are two additional challenges in FTIR measurements in a pulverized lignite oxy-fuel flame compared to measurements in a CFB boiler: Considerably higher temperatures of up to about 1700K during the sampling in the flame; higher CO_2 concentrations compared to CFB combustion. This makes it necessary to evaluate the retrieved FTIR spectra individually. The aim of the work was to measure nitrogen and sulphur species in an oxy-fuel flame and to give evaluation routines for the concentrations of NH_3 , HCN, SO_2 , H_2S and COS by using the software tool Grams AI.

2 Measurements

2.1 Experimental description

The measurements were performed in the Chalmers 100kW oxy-fuel test unit, firing pre-dried pulverized lignite as fuel. The proximate and ultimate analyse of the fuel is given in Table 1. The heat input was $P_{th}=76$ kW. That is equivalent to a lignite mass flow of 13 kg/h. Oxy-fuel combustion with dry recycle, 40 vol% O_2 in the oxidizer and a stoichiometric ratio of around $\lambda = 1.17$ was established. Dry recycle was chosen as it shows lower water vapour concentrations and thereby limits the influence of water vapour on the FTIR measurements.

Sampling of the gases was performed with a gas suction probe. The probe, which is shown in Figure 1, has an inner electrical heated tube. The temperature is controlled for guaranteeing a temperature higher than the acid dew-point temperature of the sampled gases. Through the outer tubes flows cooling water for lowering the temperature in the sampling gases and protect the probe from too high temperatures. Before entering the sample probe the gases have to pass through a filter of aluminium silicate at the top of the probe. Further on the gases are transported via heated pipes (above acid dew point) and a heated pump to the FTIR instrument (Bomem 9100). As the measurements were performed on about 200°C, all here given concentrations are on wet basis.

Three different measurement points where approached. The measurement points were at 215 cm vertical distance from the burner inlet (position R2 in Figure 1) and at 11, 12 and 13 cm distance from the center line of the cylindrical furnace respectively. Position R2 was chosen because it is a typical position for an early stage in a flame where the high concentrations of the mentioned species are suspected. On this level, measurement points with substoichiometric conditions were

searched, since in such regions the compounds of interest can be most likely available.

Table 1. Analysis of the Lausitz lignite, d.a.f. = dry ash free.

Proximate [wt. %, as received]			Volatile matter [wt. %, d.a.f.]	Ultimate [wt. %, d.a.f.]				
$Y_{moisture}$	Y_{ash}	$Y_{combustible}$		Y_C	Y_H	Y_N	Y_S	Y_O
10.7	4.38	84.9	61.0	67.2	5.36	0.87	0.90	25.7
10.6	4.56	84.8	58.8	67.0	5.37	0.81	0.90	25.9
10.5	4.75	84.7	57.7	66.8	5.39	0.82	0.88	26.1

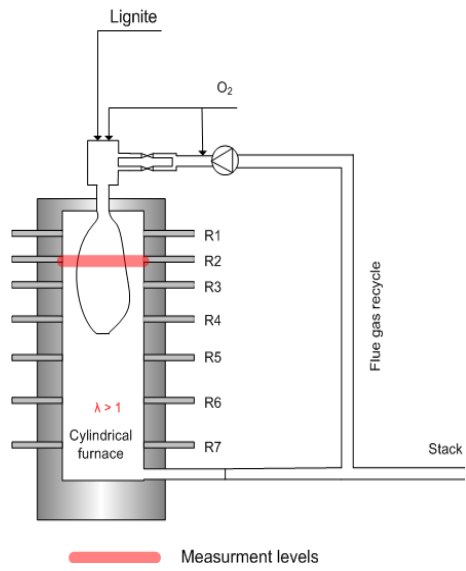


Figure 1. Sketch of the oxy-fuel combustion furnace with top-fired pulverized coal burner at CTU. Measurements were performed in port R2 (marked in red).

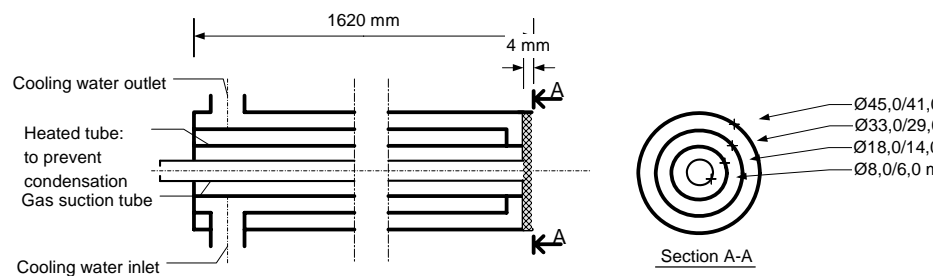


Figure 2. Gas suction probe

2.2 Data Acquisition

Before the measurements in the flame, a background spectrum (0 spectrum) from the used purge gas was taken (nitrogen atmosphere). The FTIR was set up in that way that for each of the three measurement

positions a series of ten single interferograms was taken. These retrieved interferograms of the measured flue gas composition are via Fast Fourier Transform (FFT) transformed into single beam spectra respectively. Of the retrieved ten single beam spectra, a time average spectrum is formed. These average single beam spectra are then converted into absorption spectra, by applying the Bouguer-Lambert-Beer law.

Consequently each measurement point is presented by one absorption spectrum. The spectra are then used to perform spectral subtractions in order to determine the concentration of HCN and NH₃, SO₂, H₂S and COS.

The three measurement points in level R2 (see Figure 1) are named R2_11, which is 11cm from the centreline, R2_12 and R2_13 which are 12cm and 13cm from the centreline respectively. Here, mainly the evaluation of the latter one is presented as the position with the most reducing conditions.

In series with the FTIR instrument the concentrations of CO₂, O₂, CO, NO and SO₂ were measured by standard gas analysis instruments.

2.3 Spectra Subtraction

The concentrations of HCN, NH₃, SO₂, H₂S and COS, probably present in reducing atmosphere of the flame zone, are determined by successive spectral subtraction of several reference spectra of interfering gas species from the absorbance spectrum of the measured gas sample. As the concentration of species of interest in the sample generally differs from that in the available reference gases, each reference gas spectrum is multiplied by a scaling factor F.

$$A_s - A_R \cdot F = 0 \quad (1) \text{ [Åmand et al.]}$$

Were A_S is the absorbance of the sample and A_R is the absorbance of the reference gas. Following this method, the characteristic fingerprint of the searched gas should be retrieved on a clear baseline.

Combustion gases are a mixture of many different gases. Especially H_2O and CO_2 have absorption bands over wide ranges of wave numbers. Already in flue gases from air combustion, the high CO_2 and H_2O concentrations have wide bands with total absorption, narrowing the possible bands for evaluation significantly down. But even in the more open bands, overlapping CO_2 and H_2O absorption bands give the need for subtraction of reference spectra for these two species. Otherwise equation (1) does not give zero and thus the accuracy of the evaluation is reduced.

3 Results

3.1 NH_3

Ammonia has a characteristic absorption band, or fingerprint, mainly consisting of two distinct absorption peaks at 965 and 930 cm^{-1} respectively. This fingerprint, blue line in **Error! Reference source not found.**, can be clearly identified in the green sample spectrum. In order to be able to evaluate the concentration of NH_3 that is corresponding to the intensity of these absorption peaks, absorption spectra of CO_2 , H_2O and C_2H_4 are subtracted from the initial sample spectrum. **Error! Reference source not found.** shows the subtraction of a calculated (Formula 1) 76 vol% CO_2 (blue spectrum) from the sample spectrum (green). This subtraction is done with a CO_2 reference spectrum of 89.7 vol% CO_2 . A factor $F = 0.886$ was determined on the interval between 997.6 and 909.7 cm^{-1} using the auto-subtract function within the FTIR software Grams AI.

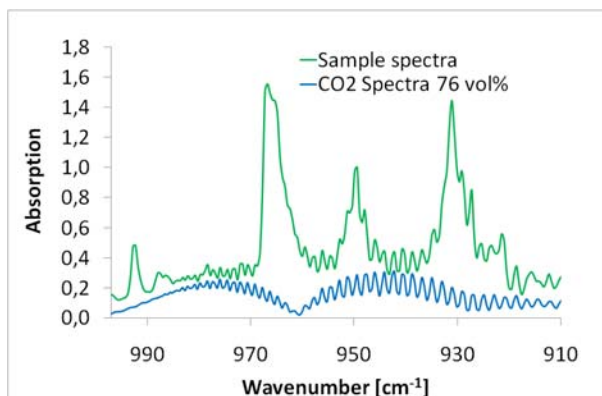


Figure 3. Subtraction of a CO₂ reference spectrum [76.0 vol% (F=0.84729)] (blue) from the flue gas absorption spectrum (green) between 997.6 and 909.7 cm⁻¹ (R2_13)

The result of this first subtraction is shown in **Error! Reference source not found.** as green spectrum. The blue absorption spectrum corresponds to a water spectrum with 11 vol% water. In this wavenumber region the absorbance of water is low. The subtraction of the water spectrum from the measured spectrum (green) has therefore no significant change. The received spectrum (green) is shown in **Error! Reference source not found.**

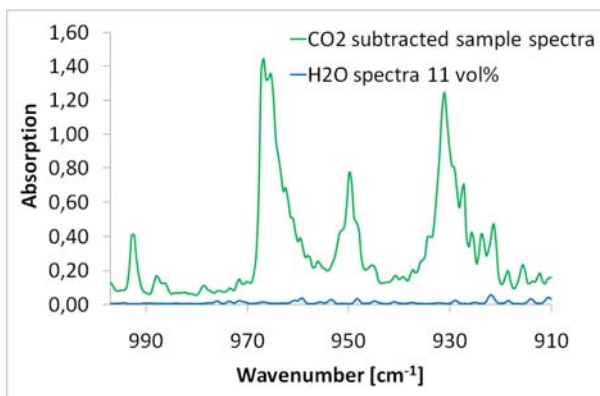


Figure 4. Subtraction of a H₂O reference spectrum [11.0 vol% (F=0.94988)] (blue) from the CO₂ subtracted flue gas absorption spectrum (green) between 997.6 and 909.7 cm⁻¹ (R2_13)

The peak between the two NH₃ absorption peaks at 965 and 930 cm⁻¹ in **Error! Reference source not found.** is an absorption peak of ethylene, C₂H₄. The subtraction of 136.6 ppm C₂H₄ (blue spectrum in **Error! Reference source not found.**) leads finally to an absorption spectrum, showing the characteristic NH₃ peaks on a clear baseline (blue spectrum in Figure 6)

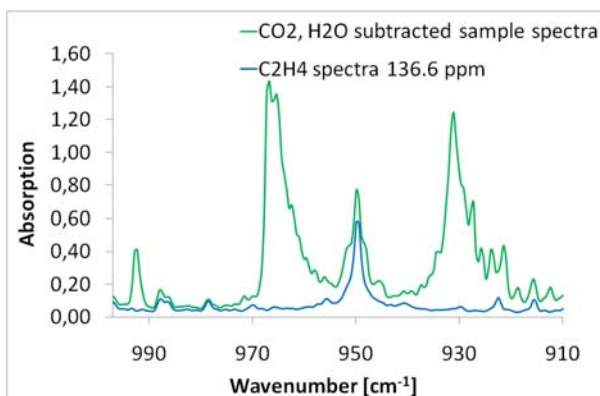


Figure 5. Subtraction of a C₂H₄ reference spectrum [136.6 ppm (F=0.94878)] (blue) from the CO₂ and H₂O subtracted flue gas absorption spectrum (green) between 997.6 and 909.7 cm⁻¹ (R_{2_13})

The final subtraction shown in Figure 6 of 477.5 ppm NH₃ corresponding to the blue spectrum in Figure 6 leads to a clear baseline (red spectra), denoting that the subtractions were correctly done.

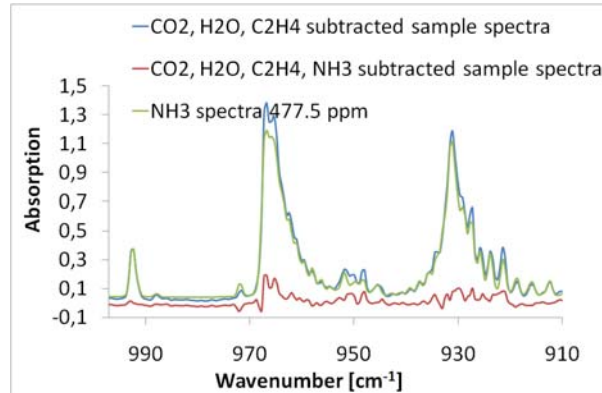


Figure 6. Subtraction of a NH₃ reference spectrum [477.5 ppm (F=0.99485)] (blue) from the CO₂, H₂O and C₂H₄ subtracted flue gas absorption spectrum (green) between 997.6 and 909.7 cm⁻¹. Resulting subtracted spectrum in red. (R_{2_13})

3.2 HCN

The strongest absorption peak of HCN is at 714 cm⁻¹. Unfortunately the overlapping of CO₂ absorption bands is in this region so strong that the signal back from this region is not linear according to the Bouguer-Lambert-Beer law and therefore no evaluation of the concentration of HCN is possible. An other band for HCN quantification can be found

between 3375 and 3200 cm^{-1} . It is less intense than the peak at 715 cm^{-1} but the interference with CO_2 and H_2O is not that severe. In **Error! Reference source not found.** the subtraction of a absorption spectrum of 13.5 vol% H_2O (blue spectrum) is shown. This value differs from that one obtained by water subtraction between 997.6 and 909.7 cm^{-1} (see **Error! Reference source not found.**) and denotes the uncertainty of determining the water content.

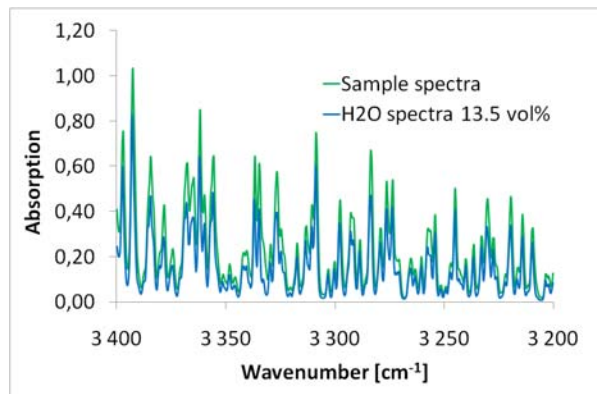
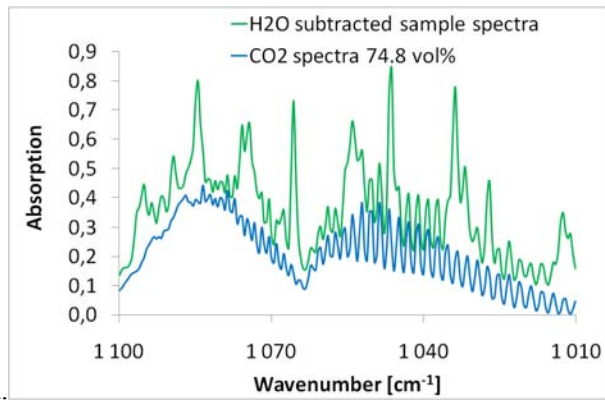


Figure 7. Subtraction of a H_2O reference spectrum [13.5 vol% ($F=0.96159$)] (blue) from the flue gas absorption spectrum (green) between 3400 and 3200 cm^{-1} (R2_13)

The subtraction of 74.8 vol % CO_2 , shown in **Error! Reference source not found.** is done in the spectral range of 1100 to 1010 cm^{-1} as the absorption band of CO_2 is in that region more defined, and better

subtraction results are



obtained.

Figure 8. Subtraction of a CO₂ reference spectrum [74.8 vol% (F=0.83376)] (blue) from the H₂O subtracted flue gas absorption spectrum (green) between 1100 and 1010 cm⁻¹ (R2_13)

The final subtraction of HCN is though still hard to define, as the noise of other absorption bands, most probably resulting from imperfection of the water band subtraction. The result of the subtraction is that only 15 ppm HCN are supposed to be found in the sample. This can be seen by the fact that the pattern of the blue marked HCN absorption band in **Error! Reference source not found.** is hardly to be found in the sample spectrum in green. The uncertainty is high due to the low subtraction factor of $F=0.17364$.

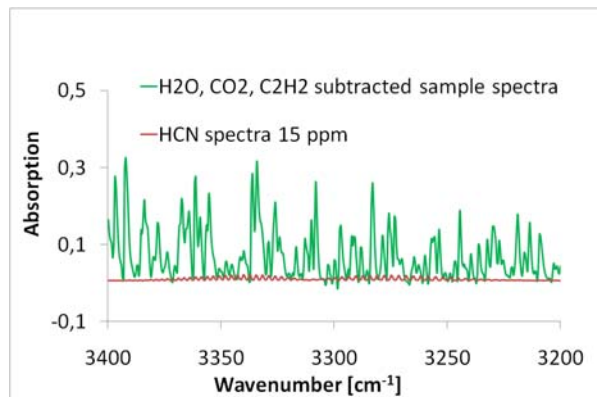


Figure 9. Subtraction of a HCN reference spectrum [15 ppm ($F=0.17364$)] (blue) from the H₂O, CO₂ and C₂H₂ subtracted flue gas absorption spectrum (green) between 3400 and 3200 cm⁻¹ (R2_13)

3.3 SO₂, H₂S and COS

In general it was well possible to analyse the SO₂ content in the gas sample with help of the FTIR because of its relatively high absorbance between 1230 and 1010 cm⁻¹. For example in R2_11 around 2240ppm SO₂ (wet basis) were detected. The procedure for SO₂ analysis is shown in Figure 10 to 12.

Figure 10 shows the subtraction of a 14.2% H₂O reference spectrum (green) with a scaling factor F of 1.251 from the measured spectrum. This yields in a water reference spectrum with theoretical 17.76%. The blue curve is the resulting measured spectrum without water

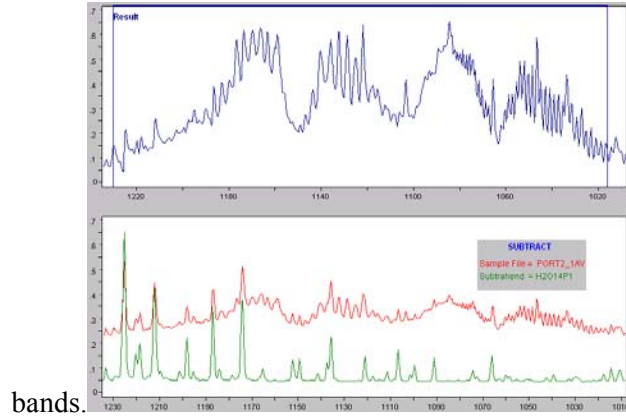


Figure 10. Subtraction of H₂O reference spectrum [14.1% x 1.251] (green) from the sampled spectrum (red) between 1230 and 1016cm⁻¹ (R2_11), resulting measured spectrum blue

Figure 11 shows the subtraction of a 89.7% CO₂ reference spectrum with a scaling factor F=0.8733 from the resulting spectrum in Figure 10 between 1100cm⁻¹ and 1010cm⁻¹. The blue curve denotes the new resulting measured spectrum.

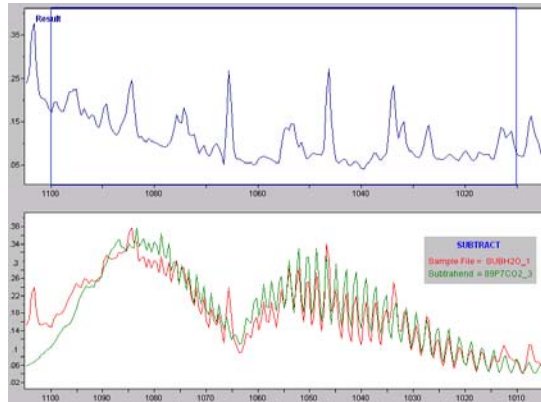


Figure 11. Subtraction of CO₂ reference spectrum [89.7% x 0.8733] (green) from the resulting spectrum from Figure 10 between 1100 and 1010cm⁻¹ (R2_11), resulting measured spectrum (blue)

Figure 12 shows the subtraction of a 1994ppm SO₂ spectrum (green) with a scaling factor F=1.1187, from the resulting measured spectrum in Figure 11 between 1230 and 1016 cm⁻¹. This corresponds to a SO₂ concentration of 2231ppm on wet basis. If also a subtraction of a methane reference spectrum was done a SO₂ concentration of 2242ppm was gotten.

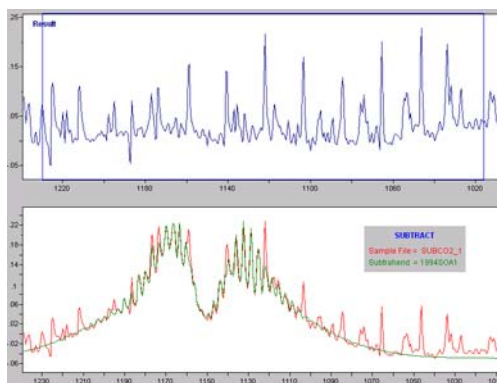


Figure 12. Subtraction of SO₂ reference spectrum [1994ppm x 1.1187] (green) from the resulting spectrum from Figure 11 between 1230 and 1016cm⁻¹ (R2_11), resulting spectrum after subtraction (blue)

Correspondingly, a SO₂ concentration in the same range was measured in the flue gas (furnace outlet). However in the measurement point R2_13 only around 300ppm SO₂ was measured. A reference spectrum with 1017ppm and a scaling factor of 0.2934 was used. The relatively low scaling factor gives a higher uncertainty compared to the scaling factor used in point R2_11. Anyway the SO₂ concentration was significant lower compared to that in point R2_13.

H₂S and COS are in general difficult to analyse because of their weak absorbance. The absorbance takes place between around 2080 and 2010cm⁻¹. It was not possible to analyse H₂S and COS in the gas samples. For example in R2_11 neither H₂S nor COS was noticeable. Figure 13 shows the subtraction of a H₂S reference spectrum from the measured spectra (H₂O, CO₂ and CO reference spectra are already subtracted). A scaling factor of -4.3 was received which means that H₂S is not detectable. In Figure 14 the subtraction of COS from the measured spectra is shown. Here a scaling factor of -0.06 was received which means that COS is not detectable.

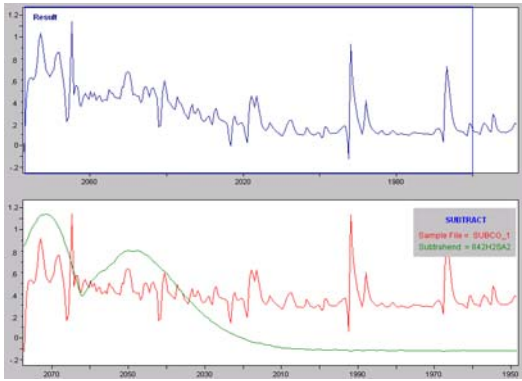


Figure 13. Unsuccessful subtraction of H₂S reference spectrum [842ppm x -4.3] (green) from the measured spectrum in R2_11 (red) , resulting spectrum after subtraction (blue)

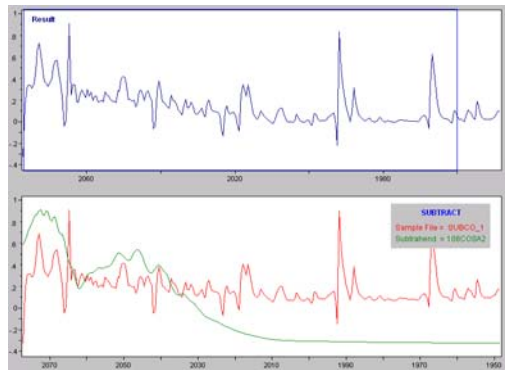


Figure 14. Unsuccessful subtraction of COS reference spectrum [108ppm x -0.6] (green) from the measured spectrum in R2_11 (red) , resulting spectrum after subtraction (blue)

In the measurement point R2_13 the overlapping of other gases (probably CO) was too high so that no subtraction was possible, see Figure 15.

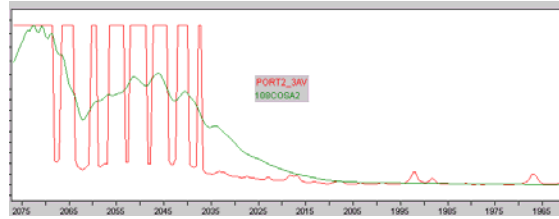


Figure 15. Disturbance in the spectral range where COS or H₂S could be analysed, red: measured spectrum, green: COS reference spectrum (R2_13)

4 Discussion and conclusions

The FTIR measurements at the Chalmers pulverized lignite boiler have shown that it is possible to identify small amounts of NH₃. On the specific measurement point, a peak with 134.1 ppm was clearly identified. This was the fact even though the matrix in the sample gases from oxy-fuel combustion is from a data evaluation point of view much more complicated than in samples from air combustion because of the high CO₂ concentrations. Overlapping of absorption bands is even at the very high CO₂ of the oxy-fuel flue gases not so severe that it would interfere with the evaluation of the characteristic NH₃ absorption peaks at 930 and 965 cm⁻¹.

Only insignificantly low concentrations of HCN were detected. Beside data evaluation problems as high interference with the water absorption bands, there seems to be a problem with the data acquisition as well. One would expect that at reducing conditions as found in the measurement point P24, where about 477.5 ppm NH₃ and several percent CO have been found, some HCN should be present as well. The fact that in the sampled gases almost no HCN was found could be explained with two different hypotheses:

- There is now HCN present in the specific measurement points (In this case the choice of sample positions should be re-accessed)
- The HCN present in the flue gases is destroyed during sampling, for example due to catalytic reaction with the sample probe material or the filter cake of char at the tip of the sampling probe

The second hypothesis is based on the findings of Bassiakos et al. They describe that once formed HCN can react with coal hydrogen towards NH_3 , if the contact time between gas and particles is long enough, and if little oxygen is present to compete against the HCN on the coal hydrogen.

It was always possible to analyse the SO_2 concentration in the gas sample. In measurement point R2_11 around 2240ppm SO_2 was measured and in point R2_13 only around 300ppm SO_2 was measured. Such low SO_2 concentrations can denote substoichiometric conditions and other sulphur compounds like H_2S and COS could be expected. However it was not possible to detect H_2S or COS in the point R2_13 because of too strong absorbance bands from other gases, probably CO . In the measurement point R2_11 no H_2S or COS were seen in the spectrum. For the last case similar questions like for HCN can be asked.

References

Åmand, L-E. et al. **The theory behind FTIR analysis**, Application Examples From Measurement at the 12 MW Circulating Fluidized Bed Boiler at Chalmers (course material, Lund university)

Bassilakis, R et al. **Sulfur and nitrogen evolution in the Argonne coals. Experiment and modeling.** Energy & Fuels (1993), 7(6), 710-20.