FTIR Analysis of Nitrogen Species in a Fluidized Bed Combustion Chamber

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ABSTRACT

The present paper shows how the FTIR measurements in the combustion chamber of a commercial fluidized bed boiler was performed and evaluated. Problems with interfering compounds are discussed. It is concluded that the present instrument is not suitable for measurement of hydrogen cyanide. The influence of instrument resolution and the removal of the main interfering component, carbon dioxide are demonstrated. However, the problem with interfering species is much less severe for ammonia, and the present instrument can be used for the determination of this species.

INTRODUCTION

As part of a larger NO/N_2O project concerning the measurement of local concentrations of gaseous species in the combustion chamber of the 12 MW circulating fluidized bed (CFB) boiler[1] at Chalmers University of Technology, nitrogen species have been measured as well. For this purpose an fourier transform infra-red (FTIR) analyser was used. The measurement of reducing nitrogen species such as ammonia (NH_3) or hydrogen cyanide (HCN) is important for the understanding of the nitrogen chemistry in combustion chambers. Measurement of concentration profiles of NH_3 and HCN thereby becomes an important link of knowledge in the area of formation and reduction of nitric oxide (NO) and nitrous oxide (N_2O) during fluidized bed combustion (FBC). From a previous project carried out at the Chalmers boiler[2] it can be concluded that N_2O is partly formed from oxidation of HCN, while NH_3 to a greater extent is oxidised to either N_2 or NO depending on the local oxygen concentration. The purpose of this paper is to analyse the ability of the FTIR technique for measuring NH_3 and HCN in combustion gases containing high concentrations of carbon dioxide (CO_2), water (H_2O) and unburned species such as carbon monoxide (CO) and hydrocarbons (HC).

EXPERIMENTAL

The Boiler. The boiler has been described in detail i earlier publications[2,3]. Of special interest for this project is the measurement holes which are located at the right side of the combustion chamber, Figure 1. Figure 1 also shows a cross-section of the combustion chamber seen from above.

The Operating Conditions. The fuel was the same as that used in ref. 2, a high volatile bituminous coal. Pure silica sand was used as bed material and no lime for sulphur capture was supplied in order to minimise the catalytic effects of the bed material on the nitrogen

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chemistry. The gas-concentration profiles were measured with the boiler operated at typical operating conditions corresponding to a bed temperature of 850 °C, an excess air ratio of 1.20 to 1.25 and a primary air stoichiometry of 0.8. The lowest secondary air register was used.

The Gas Sampling Probe. The gas sampling probe is shown in Figure 2. This probe is specially designed for analysis of wet combustion gases which is important when NH_3 and HCN are to be analysed. The combustion gas first passes through a ceramic filter mounted at the tip of the probe, Figure 2c, shielded and cooled by the cooling shield of the probe. The combustion gas is then transported through the center-pipe which was electrically heated to approximately 200 °C, Figure 2b. In order to control the cooling of the center-pipe heated water was used as cooling medium for the probe, Figure 2a, (temperature between 45 and 95 °C). Downstream the probe the combustion gas is transported to the gas analysers through heated gas sampling lines. In order to clean the ceramic filter from ash and bed material the probe is regularly back-flushed with pressurised air.

The Gas Analysis System. The Chalmers boiler is equipped with on-line conventional flue-gas analysers for continuous monitoring of oxygen (O_2), CO, sulphur dioxide (SO_2), NO, and N_2O in the stack and O_2, NO, CO, CO_2 and SO_2 in the combustion gas from the gas analysis probe. Further details about the analysers can be found in ref. 1. The FTIR analyser is connected in series with the on-line continuous gas analysers. The FTIR is a Bomem M110-D11 with a 500 cm^3 quartz glass gas cell with an optical path length of 3.6 meter. This instrument is equipped with a MCT detector and the maximum resolution is 4 cm^{-1}. This maximum resolution was used in all tests with this instrument. The gas cell was heated to 175 °C during the present tests. The Spectra Calc software package was used for evaluation and control of the spectrometer. Spectra were collected in a continuous mode where 22 mirror scans for each single-beam spectrum stored were sampled. Each scan takes approximately one second and the stored single-beam spectra were added afterwards to form and "average" single beam spectrum. An absorbance spectrum was then produced from the ratio of this average single beam spectrum an a reference spectrum (100% nitrogen) collected immediately before the sampling of the single-beam spectra. Evaluation of spectra was carried out by spectral subtraction using spectra from pure calibration gases.

RESULTS

In Figure 3 a spectrum of a typical combustion gas sample is shown. Calibration spectra for the major components CO_2 and H_2O as well as for trace components such as NH_3, HCN, N_2O, acetonitile (CH_3CN) and isocyanic acid (HNCO) are shown in Figure 4. In an ideal case it is possible to find an isolated wavenumber band where only the substance of interest absorbs. It is clear from Figure 4 that there are no such regions for any of the trace components mentioned. In addition, quantitative analyses of multiple component mixtures can be complicated by interferences (matrix effects) in such a way that the spectrum for the mixture differs from the spectrum obtained if the spectra for all pure components were added. Rudling[4] discusses FTIR analysis of CO_2, H_2O, CO, N_2O, NO, SO_2 and NH_3 and reports matrix effects for mixtures of CO_2 and H_2O and for the system N_2O-CO_2 at 2200 cm^{-1}. In the analyses reported below, matrix effects were assumed to be negligible.

NH_3 Analysis. NH_3 has two distinct absorption peaks at 930 cm^{-1} and 965 cm^{-1}, Figure 4. The major interfering component at this frequency is ethene (C_2H_4), whereas CO_2, and for the peak at 930 cm^{-1} also HNCO, propene (C_3H_6), propadiene (C_3H_4) and CH_3CN absorbs weakly, Figure 4. C_3H_4 and CH_3CN were not detectable using the present instrument, while HNCO was subtracted according to ref. 5. The subtraction of ethene (C_2H_4 from a spectrum of a measurement in the lower part of the combustion chamber (0.65 meter above the nozzles) in the Chalmers boiler is shown in Figure 5a. The subsequent subtraction of NH_3 is shown in Figure 5b. At this position in the bed a slightly higher value was obtained when the

subtraction was performed for the peak at 930 cm^{-1} compared to that of 965 cm^{-1}. The difference is not significant, although it can be noted that some combustion gas components such as propene have a higher absorption at 930 cm^{-1} than at 965 cm^{-1}. Subtraction of propene from the sample spectrum did not influence the quantification of NH_3 significantly, and at all other sample positions higher up in the combustor, where the hydrocarbon concentration is lower, the subtractions yield approximately the same number at both frequencies. The peak absorbance versus concentration of NH_3 can be fitted by a second order polynome, Figure 6a. In all subtractions a calibration spectrum of 525 ppm NH_3 was used. The subtraction factors are given in ref. 5. The absorbance (A_{sample}) corresponding to the subtraction of the calibration spectra according to:

$$A_{sample} - F \times A_{525ppm\ NH_3} = 0$$

where F is the subtraction factor and $A_{525ppm\ NH_3}$ is the absorbance for the NH_3 calibration spectrum used. In order to achieve the concentration of NH_3 the calibration plot of Figure 6b was used. The resulting NH_3 concentration *vs.* height in the combustor is plotted in Figure 6c. In Figure 6c the uncertainty in the determination of the subtraction factor (F) on the final NH_3 concentration is indicated.

HCN Analysis. From the calibration spectrum in Figure 4 it can be seen that HCN absorbs in two regions. Its strongest peak at 714 cm^{-1} interferes mainly with CO_2. The subtraction of a calibration spectrum of CO_2 from a sample spectrum is shown in Figure 7a, and the subsequent subtraction of a HCN calibration spectrum is shown in Figure 7b. As discussed in ref. 5,6 caution is needed when the absorbance is high and it is not possible to say whether the apparent absorption at 714 cm^{-1} is due to the presence of HCN in the sample, or if it is an effect of an inadequate subtraction. The "HCN peak" that appears at ca 714 cm^{-1} after the CO_2 subtraction (Figure 7b) may be a result of the subtraction. A higher spectral resolution of the FTIR analyser or a removal of the CO_2 prior to the analysis could favour the use of this absorption band around 714 cm^{-1} for the HCN quantification of combustion gases. These options are discussed in more detail later. Alternatively, the total absorption of the sample can be reduced to acceptable values simply by diluting the sample with a non-absorbing gas such as N_2 prior to the FTIR analysis. This last obtion has not been tested so far.

Although the absorption is weaker, an alternative band for HCN quantification is located at 3200-3375 cm^{-1}. In this region water has to be subtracted from the sample spectrum prior to HCN, Figure 8a. After the water subtraction, the double peak of HCN clearly appears on the spectrum which can be seen more clearly in Figure 8b, where the subsequent subtraction of HCN is shown. The absorbance in this region is low and Beer's law can be expected to be obeyed. Indeed, this is the case as seen in Figure 9, where the peak absorbance at 3343 cm^{-1} for the HCN calibration spectrum is plotted as a function of concentration.

Consequently, the HCN concentrations in the sample spectra obtained from the measurements in the Chalmers boiler were quantified using the band at 3200-3375 cm^{-1}. All subtractions were performed using the same H_2O and HCN calibration spectrum (i.e. the water calibration spectrum corresponding to saturation at atmospheric pressure at 40 °C (7.3% H_2O) and the HCN calibration spectrum to 199 ppm HCN). The main difficulty performing the subtraction in this spectral region is that the signal-to-noise ratio (SNR) is low. The spectral subtractions were carried out manually, and the subtraction factors were estimated by visual observation. In order to estimate the accuracy of the analyses, both minimum and maximum values of the subtraction factors were estimated, as well as a "best" value. Although the low SNR makes absolute concentration predictions difficult, the analysis gives an indication of the magnitude of the HCN concentrations. In relative terms the values obtained can be compared. The result of the spectral subtractions is shown in Figure 10 where also the uncertainty is indicated. The minor interference with the HCN absorption caused by the presence of C_2H_4 and C_2H_2 was not considered. In addition, CH_3CN, C_3H_4

and C_3H_6 would interfere in this region, but the concentrations of these species were found to be below the detection limit.

Removal of CO_2 Prior to the Analysis of HCN. In order to investigate the possibility of removing the CO_2 prior to analysis of HCN, a laboratory investigation has been carried out[7] with three different sorbents: ascarite™, soda lime and calcium oxide. Ascarite consists of solid silicate particles coated with NaOH, while soda lime consists of a mixture of $Ca(OH)_2$ (> 75 weight-%), NaOH (< 3.5 weight-%) and water (< 21 weight-%). The calcium oxide was prepared from Faxe Bryozo limestone, a Danish limestone of relativly high sulphur capture reactivity[8]. The removal of CO_2 was carried out at 180 °C with ascarite and soda lime, while for the calcium oxide a temperature of 410 °C was used. Under these conditions all three materials proved to be effective in removing almost all CO_2 in the gas. Unfortunately, the sorbents also remove all HCN present in the gas. This is illustrated in Figure 11-13 in which a spectrum of HCN when the sorbents was by-passed can be compared with the subsequent spectrum achieved after the passage of the sorbent. For the ascarite case, Figure 11 is it also shown that part of the HCN is converted to N_2O. Initially, formation of N_2O from HCN was even higher for the soda lime, Figure 12, whereas the calcium oxide leads to a conversion of HCN to NH_3 instead, Figure 13. In other words none of the materials tested are suitable for removal of CO_2 prior to the analysis of HCN, since all the sorbents also affect the HCN concentration in the gas.

Analysis of HCN Using a Higher Spectral Resolution. The test of the improvement of evaluation of HCN around 714 cm^{-1} was performed using another Bomem FTIR analyser in series with the one used above. This extra FTIR analyser was equipped with an DTGS detector, instead and could be operated with an resolution down to 1.0 cm^{-1}. For this comparison 1 cm^{-1} was used. An average single-beam spectrum was obtained by adding 3 single-beam spectra, each produced from 5 mirror scans. An absorption spectrum could then be produced using the reference spectrum (100% nitrogen) collected immediately before the combustion gas. Figure 14 shows the result of the subtraction of a calibration spectrum of CO_2, and Figure 14b shows the subsequent subtraction of HCN. Comparing this last subtraction with the result of the similar subtraction in Figure 7 where the instrument resolution was 4 cm^{-1} shows that the HCN peak around 714 cm^{-1} becomes much clearer with a higher resolution. Still, the result is not satisfactory enough for quantification, and dilution of the sample prior to the analysis is probably needed.

CONCLUSIONS

The tests on a FTIR analyser of the combustion gases from the furnace of the Chalmers CFB boiler, show that it is possible to determine the concentrations of NH_3 and HCN. Interference from other components present at high concentrations, such as CO_2, H_2O, CO and a large number of hydrocarbons, complicates the analysis. NH_3 can be detected and quantified using the absorption peaks at 930 and 965 cm^{-1}, where the major interfering components ethene can be subtracted from the sample spectrum. HCN can be detected and quantified at 3200-3375 cm^{-1} where the major interfering component is H_2O. The low signal-to-noise ratio makes the quantification rather uncertain. The major HCN peak at 714 cm^{-1} interferes with CO_2, and could not be used for quantification with the low resolution instrument (4 cm^{-1}). Additional tests with an instrument of higher resolution (1 cm^{-1}) shows a much better possibility for using this peak for HCN determination, but the result is still not satisfactory. Selective removal of CO_2 would improve the HCN analysis. However the laboratory study performed shows that none of the sorbents tested can remove CO_2 without also affecting the concentration of HCN.

ACKNOWLEDGEMENT

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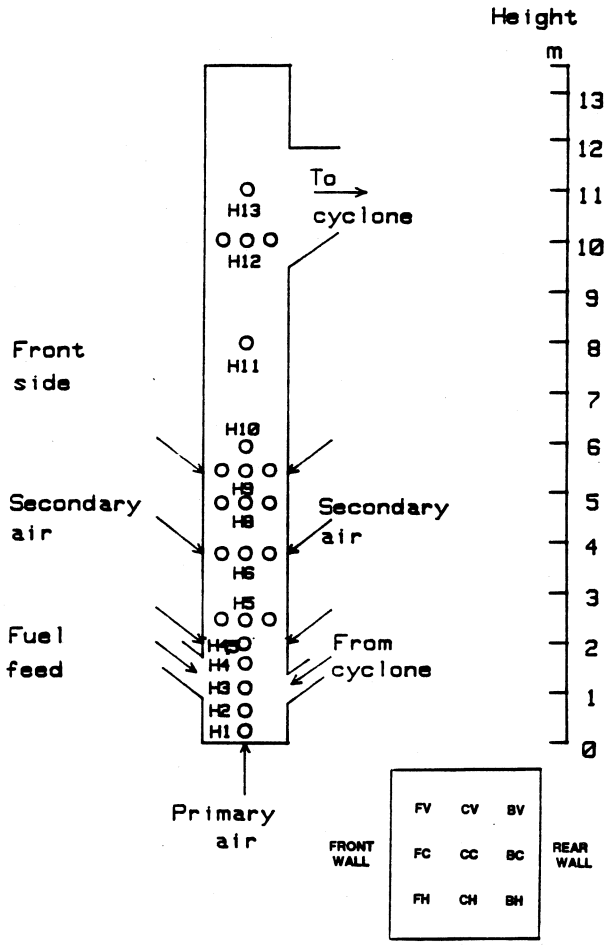

Figure 1. The 12 MW CFB-boiler at Chalmers with measurement holes (H1-H13) indicated. FH, FC, FV, CH, CC, CV, BH, BC and BV in small figure are measurement positions in the cross-section of the combustion chamber.

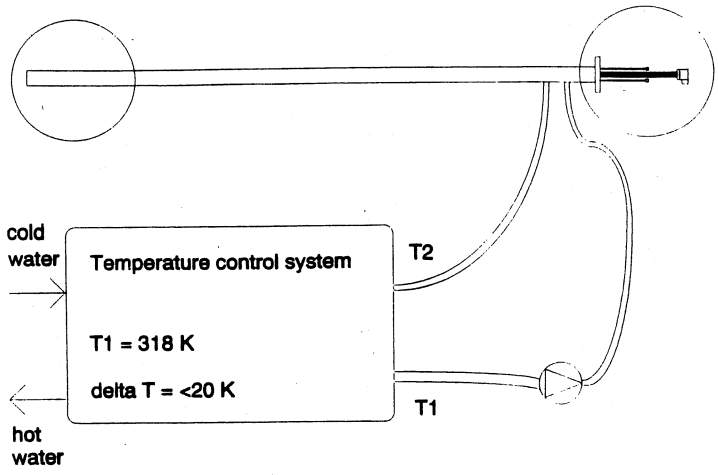

Figure 2a. Gas sampling probe used for analysis of hot flue gases from the combustion chamber.

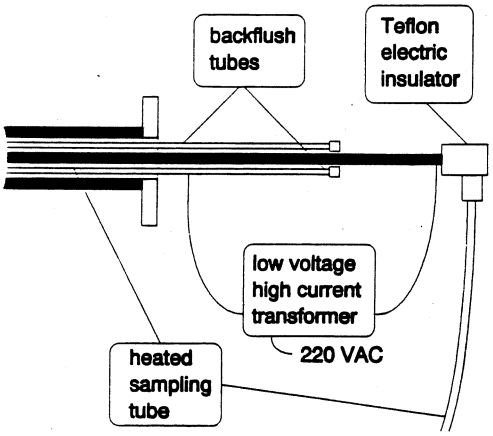

Figure 2b. Rear part of the gas sampling probe.

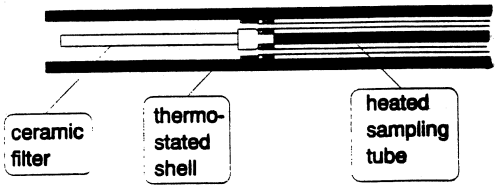

Figure 2c. Front part of the gas sampling probe.

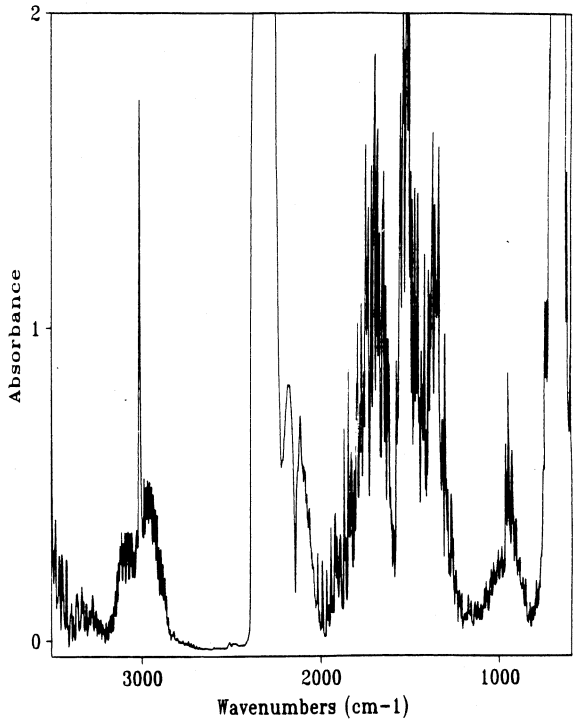

Figure 3. A typical spectrum of the combustion gas taken in the CFB-furnace.

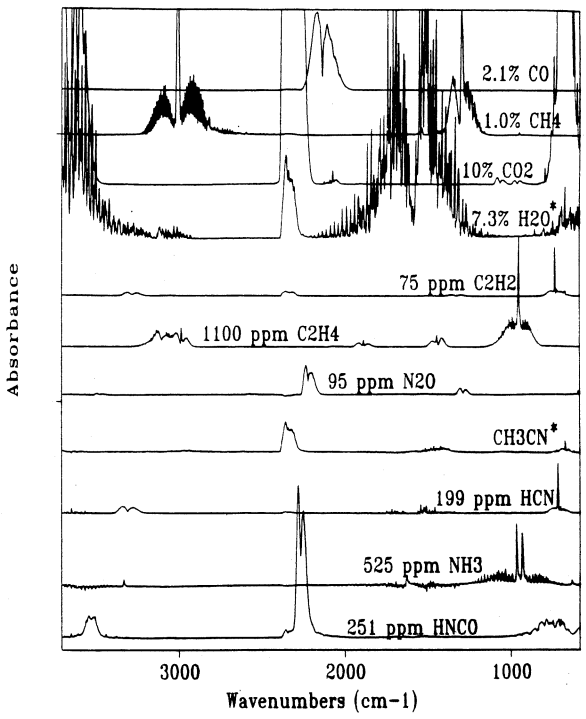

Figure 4. Calibration spectra for some major and minor combustion gas components (all spectra are shown at the same scale in order to enable comparison of absorbencies). *) The peaks at 600-750 cm^{-1} are due to the presence of small amounts of CO_2.

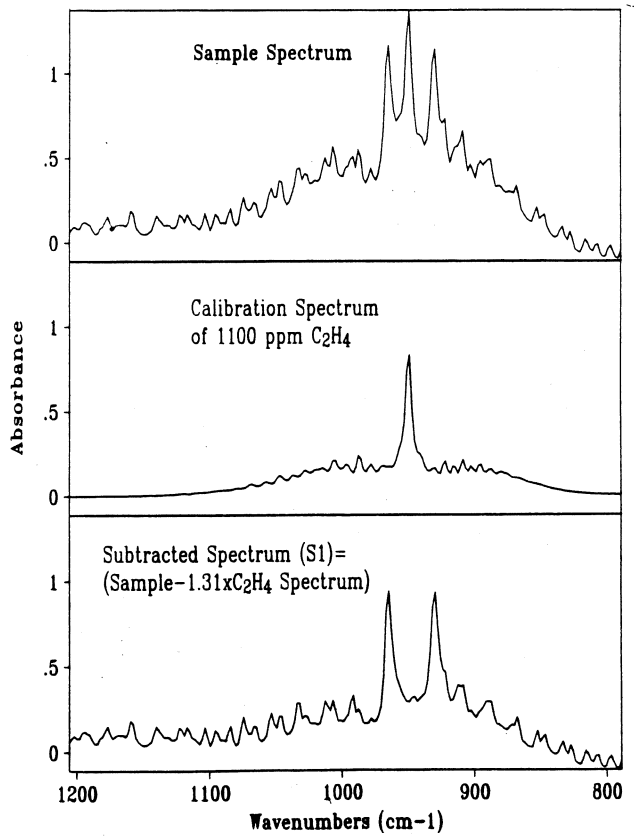

Figure 5a. Subtraction of a C_2H_4 calibration spectrum from a sample spectrum at ca 800-1200 cm^{-1}. Sample position H2cc in Figure 1.

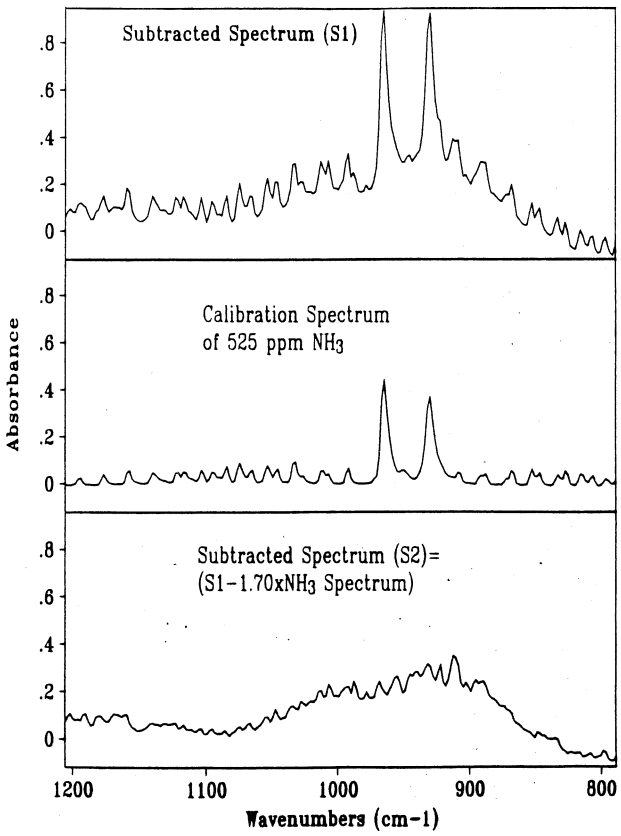

Figure 5b. Subtraction of a NH_3 calibration spectrum from a sample spectrum at 800-1200 cm^{-1}. The peak at 965 cm^{-1} was minimised.

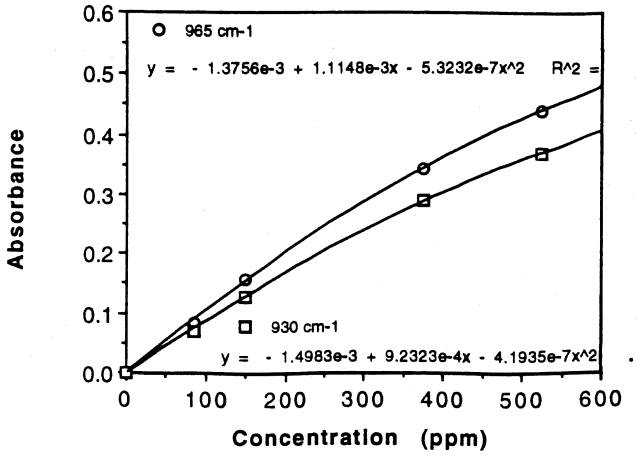

Figure 6a. Absorbance *vs.* concentration of NH_3 at 730 cm^{-1} and 765 cm^{-1}. Second order polynomial fit.

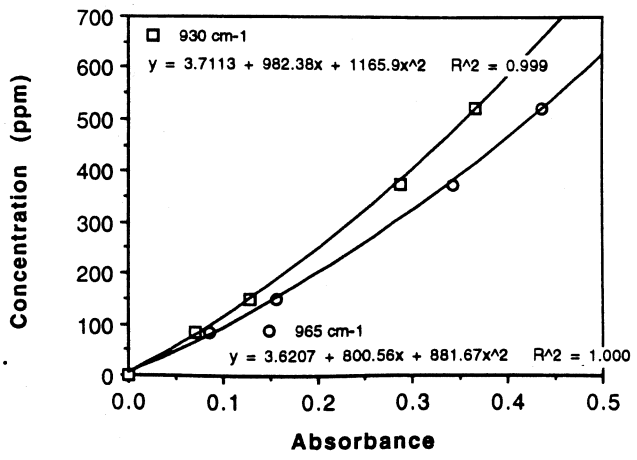

Figure 6b. Calibration plot used in the quantification of NH_3.

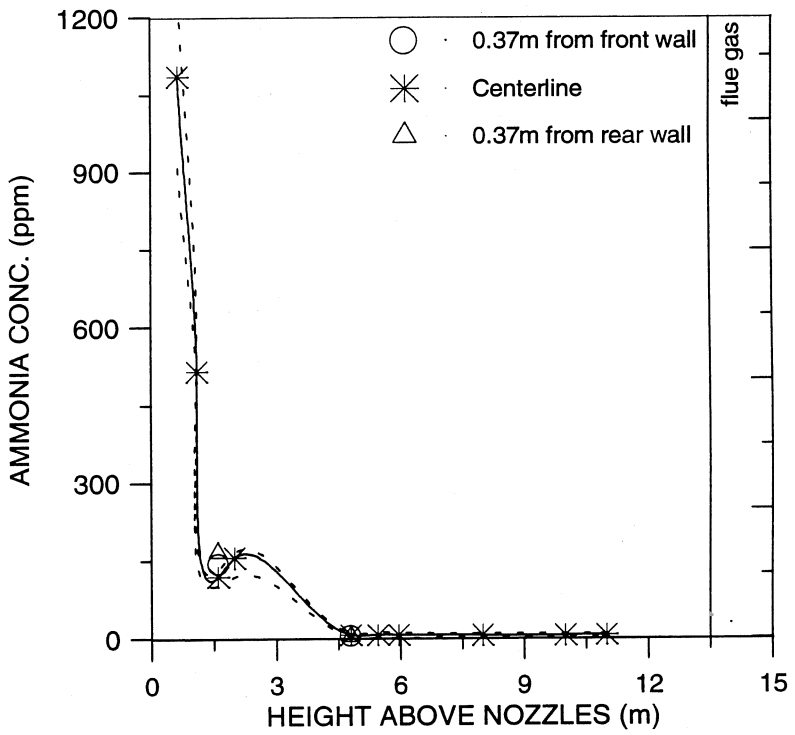

Figure 6c Vertical profiles of NH_3 along the centreline in the combustion chamber. Dotted lines indicate the uncertainty in the NH_3 determination.

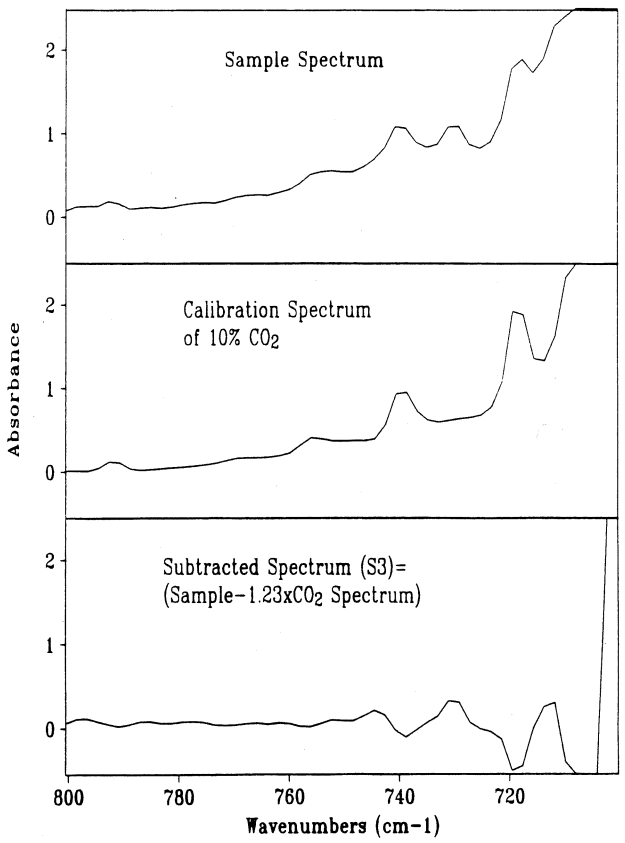

Figure 7a. Subtraction of a CO_2 calibration spectrum from a sample spectrum at ca 700-800 cm^{-1}. Sample position H2CC in Figure 1.

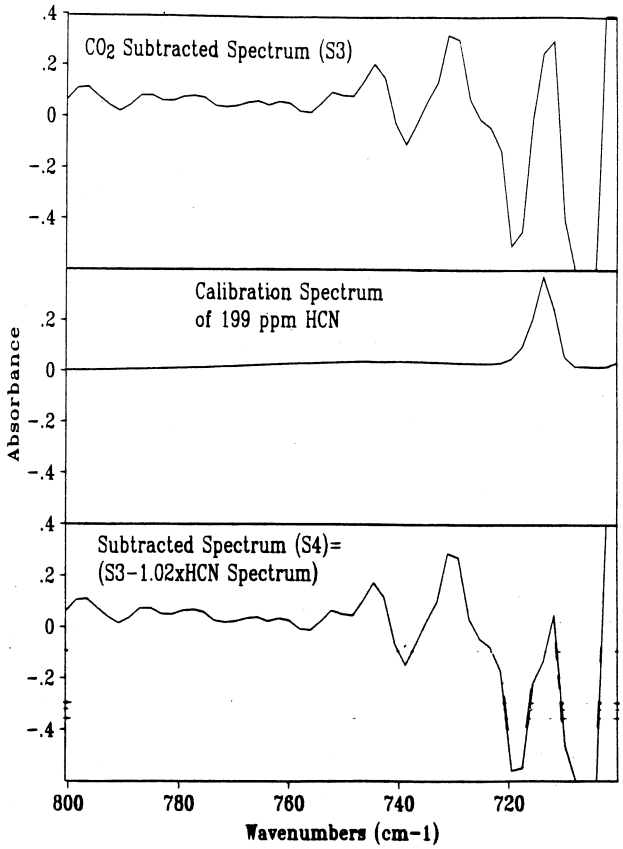

Figure 7b. Subtraction of a HCN calibration spectrum from a sample spectrum at ca 700-800 cm^{-1}.

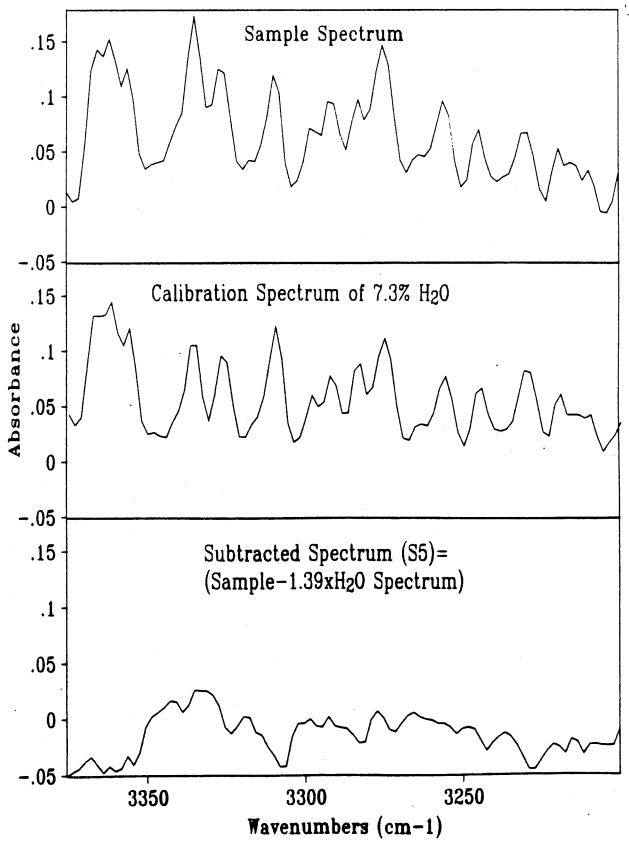

Figure 8a. Subtraction of a H_2O calibration spectrum from a sample spectrum at 3200-3375 cm^{-1}. Sample position H3CC in Figure 1.

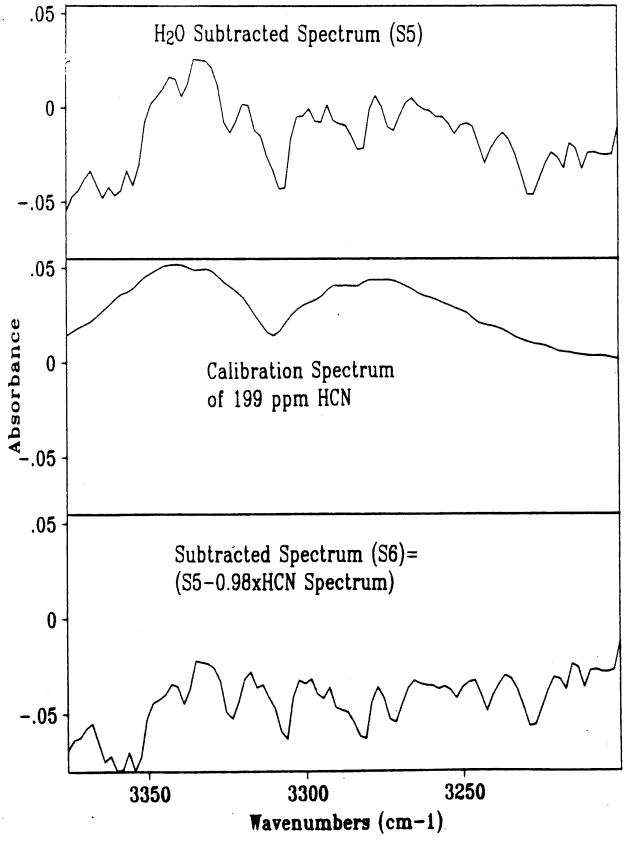

Figure 8b. Subtraction of a HCN calibration spectrum from a sample spectrum at 3200-3375 cm^{-1}.

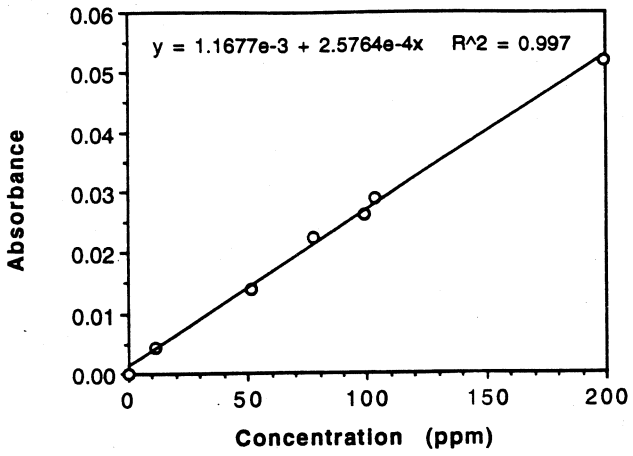

Figure 9. Absorbance *vs.* concentration of HCN at 3343 cm^{-1}.

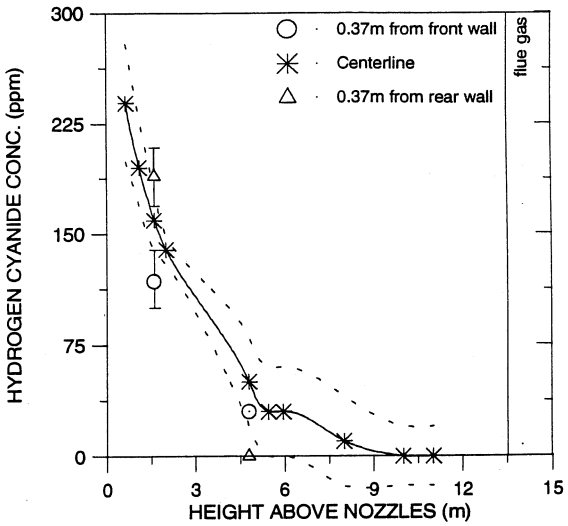

Figure 10. Vertical profiles of HCN along the centreline in the combustion chamber. Dotted lines indicate the uncertainty in the HCN determination.

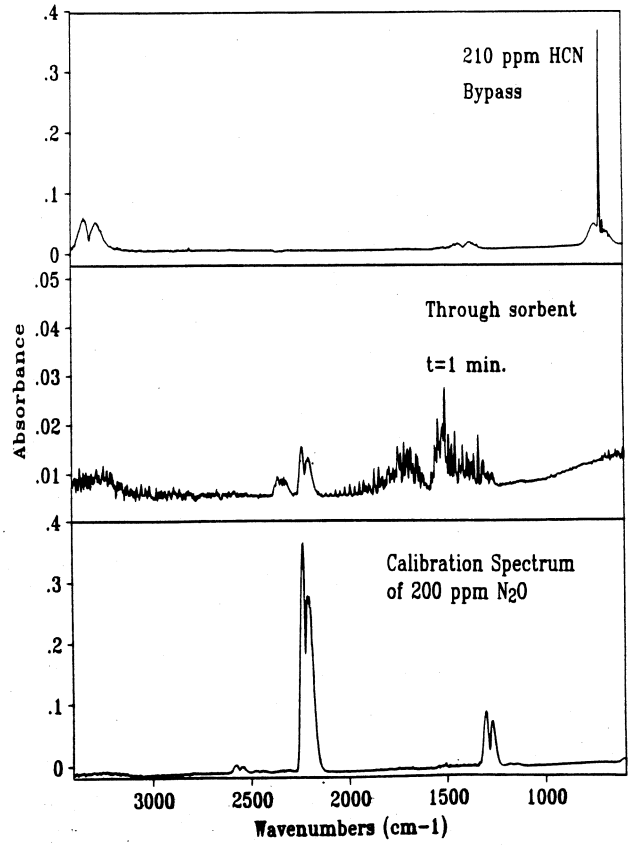

Figure 11. Effect of ascarite™ on the HCN concentration; 210 ppm HCN i N_2. Top figure; HCN at by-pass of sorbent. Figure at middle; after one minute through sorbent. Bottom figure; calibration spectrum of N_2O.

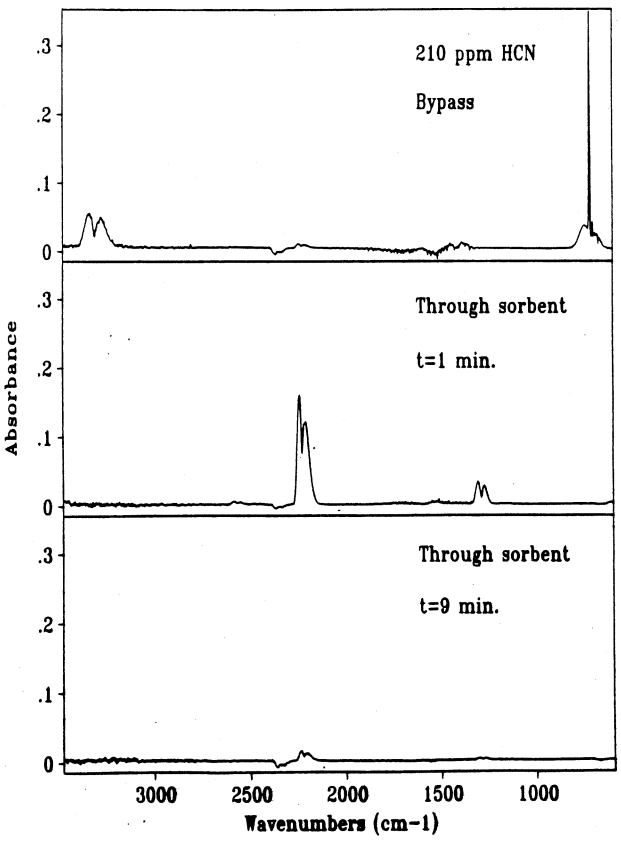

Figure 12. Effect of soda lime on the HCN concentration; 210 ppm HCN in N_2. Top figure; HCN at by-pass of sorbent. Figure at middle and bottom after one and nine minutes through sorbent respectively.

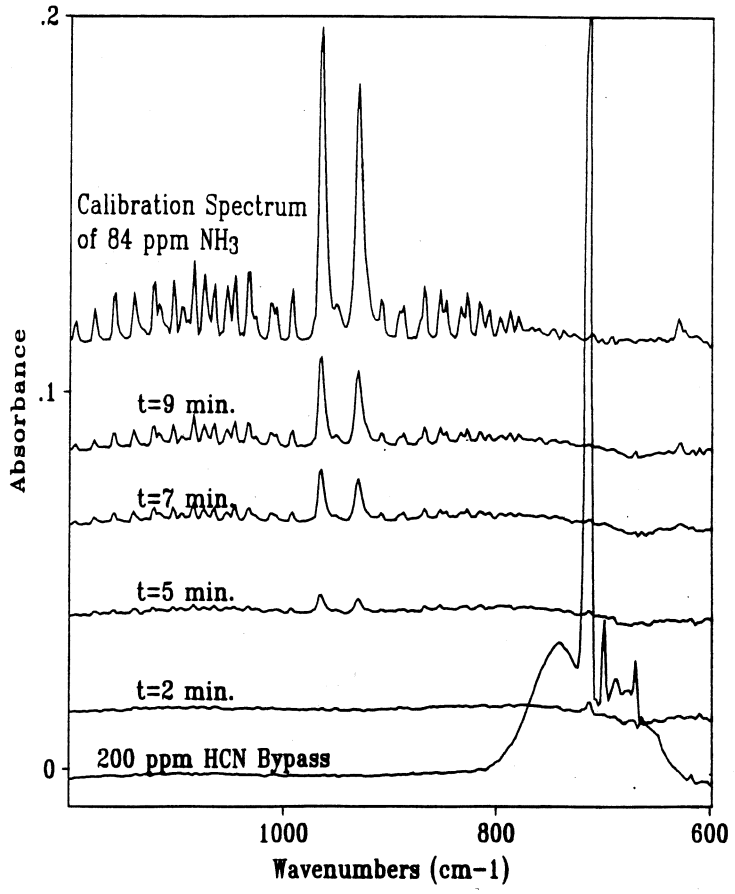

Figure 13. Effect of CaO on the HCN concentration; 160 ppm HCN in N_2 Top spectrum; calibration spectrum of NH_3. Bottom spectrum; HCN at by-pass of sorbent. Other spectra show result of passing 200 ppm HCN through sorbent after 2 to 9 minutes.

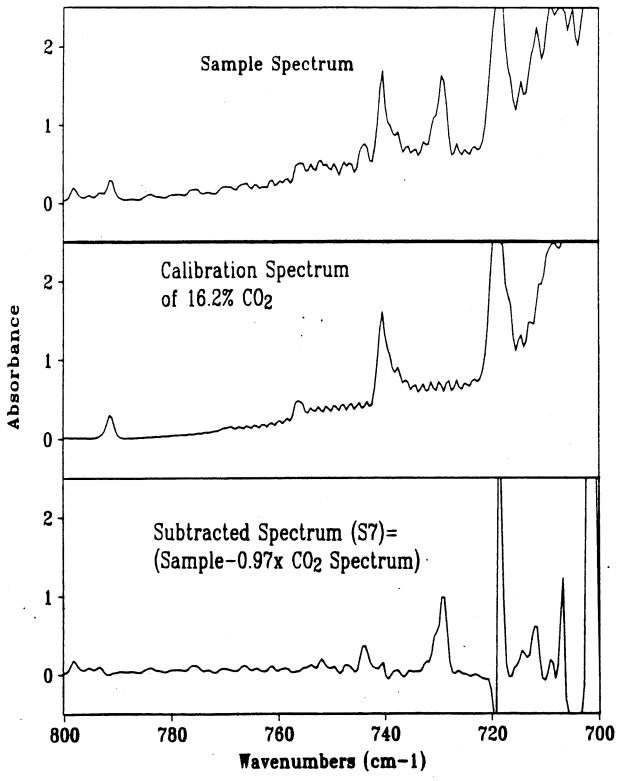

Figure 14a. Subtraction of a CO_2 calibration spectrum from a sample spectrum at ca 700-800 cm^{-1}. Instrument resolution=1cm^{-1}. Sample position H2CC in Figure 1.

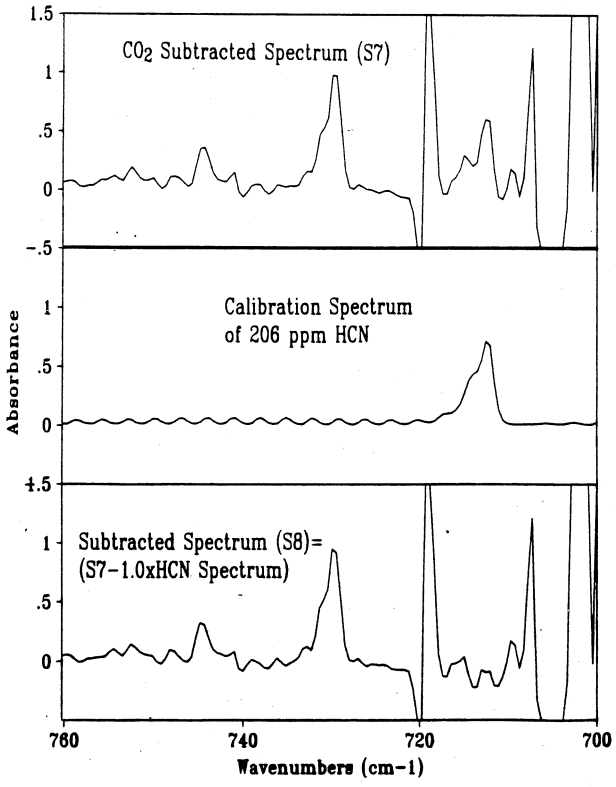

Figure 14b. Subtraction of a HCN calibration spectrum from a sample spectrum at ca 700-800 cm^{-1}. Instrument resolution=1cm^{-1}.