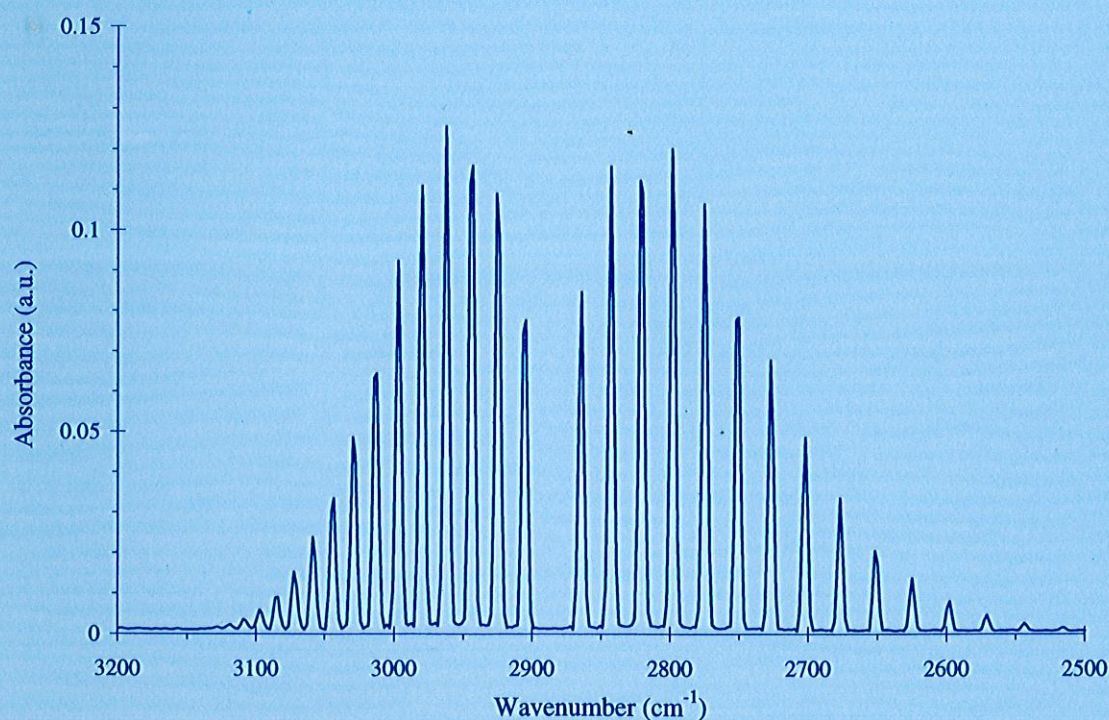


Per Blomqvist, Per Lindberg and Margret Månsson

# TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments

## FTIR Measurements





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## Abstract

Large-scale combustion experiments with amount of material burned in the 100-kg range were performed in the TOXFIRE project to provide results as close to real scale as possible for comparison with results from the smaller scale measurements in the project. The real challenge was to achieve conditions yielding under-ventilated, *i.e.* oxygen-depleted, combustion. Most of the large-scale experiments were carried out in the ISO 9705 room. A few tests were performed in a larger scale test facility built to allow real storage configurations.

Fourier Transform InfraRed spectroscopy (FTIR) was the major technique used to characterise the smoke gases. This report gives a detailed account of the instrumentation, calibration, measurement strategy and method for evaluation of the IR-spectra. Advantages with FTIR are the ability to measure several gases simultaneously and to obtain time resolved concentrations. The evaluation program used presented the concentrations information on-line during the tests. The FTIR equipment was calibrated for the major gases expected to be found in the smoke gases from the different materials tested. The gases calibrated for were CO<sub>2</sub>, CO, HCl, HCN, NH<sub>3</sub> and SO<sub>2</sub>. Also H<sub>2</sub>O was calibrated for, as this is a major combustion product and severe spectral interference is caused by the strong absorbance of water. Univariate peak-height calibration-algorithms were used in the quantitative evaluation of the smoke gas spectra. The calibration algorithms handled interference from H<sub>2</sub>O and from CO<sub>2</sub> in cases where needed.

The sampling of the smoke gases was made directly in the opening of the test enclosure. The idea was to enable measurements of the original combustion products, before any after-burning had taken place.

Generally, valid and interesting chemical information was extracted from the FTIR measurements. The feature of time resolved data from the FTIR turned out to be of great benefit for the assessment of the combustion processes studied. In many cases only short periods of constant ventilation conditions were found. The concentration data from the FTIR measurement could then be evaluated for these periods, which gave very valuable information.

**Key words:** FTIR, on-line measurements, combustion of chemicals, oxygen depleted conditions, large scale tests.

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**Swedish National Testing and  
Research Institute**  
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Postal address:  
Box 857, S-501 15 BORÅS,  
Sweden  
Telephone +46 33 16 50 00  
Telex 36252 Testing S  
Telefax +46 33 13 55 02

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## **Foreword**

The work described in this report has been sponsored by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275), the Swedish National Board for Industrial and Technical Development (NUTEK; project nr P1226) and the Swedish Rescue Services (Räddningsverket; projects P 221-619/94, R 52-106/96).

We would like to thank our colleagues at the departments of Fire Technology and Chemical Analysis for valuable assistance throughout this work. The authors gratefully acknowledge the proficient and generous co-operation of Olle Moberg and Per-Anders Wallin (Olle Moberg AB) during installation and calibration of the FTIR equipment.

We are very much indebted to Borealis Sverige AB, that generously provided the particular quality sample of polypropene.

## Nomenclature

### Greek symbols

$\phi$       Equivalence ratio

### Operators

·      Per unit time [ $s^{-1}$ ]

### Abbreviations

CB	Monochlorobenzene
CNBA	4-chloro-3-nitrobenzoic acid
DTGS	Deuterated triglycine sulfate
FID	Flame ionisation detector
FTIR	Fourier transform infrared spectrometer
GSP	Gas sampling probe
HRR	Heat release rate
Ny	Nylon 66
PMP	Phi meter probe
PP	Polypropene
SPR	Smoke production rate
SSP	Soot sampling probe
THC	Total amount of unburned hydrocarbon
TMTM	Tetramethylthiuram monosulfide

## 1 Introduction

In many countries there are large numbers of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances, *e.g.* pesticides. Chemical fires seem to be one of the most important hazards from these activities. Today only limited documentation is available concerning the assessment of the potential consequences from fires at chemical plants and chemical storage facilities.

The project *Guidelines for Management of Fires in Chemical Warehouses* (TOX-FIRE) was initiated in order to remedy some of these problems. The project has been financially supported by the CEC ENVIRONMENT program (contract no. EV5V-CT93-0275). An international consortium carried out the project during a three years period (1993-1996), including the following partners:

- Risø National Laboratory, Denmark (co-ordinator)
- NERI - Danish National Environmental Research Institute
- South Bank University, United Kingdom
- VTT - Technical Research Centre of Finland
- Lund University, Sweden
- SP - Swedish National Testing and Research Institute
- FOA - Swedish National Defence Research Establishment

Based on a number of characteristics, the substances were classified comprising ignitability, heat release, burning rate, smoke production, combustion products and the influence of the packaging materials on the combustion products. The source characteristics were described by parameters obtained by carrying out combustion experiments at various scales and by studying the effects of scaling. In addition, the fire scenarios were characterised by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. Also the suppression was an important parameter, *i.e.* active and passive suppression and fire brigade tactics.

The consequences to humans as well as the environment were assessed in the project. The existing modelling methods used for risk assessment were studied, along with the handling and prevention of the accidents. These investigations led to the development of the basis for two sets of guideline documents in relation to fires in chemical warehouses: guidelines for the safety engineers and guidelines for the fire brigades. In parallel, a quick decision system to be used by the fire chief in the case of a chemical fire was also developed.

The role of SP in the TOXFIRE project was to determine the source characteristics by carrying out controlled large-scale combustion experiments with amount of material burned in the 100 kg range. The aim was to provide results as close to real scale as possible for comparison with results from the smaller scale measurements in the project. The real challenge was to achieve conditions yielding under-ventilated, *i.e.* oxygen-depleted, combustion. Most of the large-scale experiments were carried out in the ISO 9705 room with different degrees of restrictions of the size of the door opening. A few tests were performed in a larger scale test facility that was built to allow real storage configurations. The SP work was carried out in co-operation between the departments of Fire Technology and Chemical Analysis.



A phi meter was used to define the degree of ventilation. In addition to the common fire test parameters mentioned previously, extensive measurements were carried out to characterise the composition of the smoke gases. On-line measurements, *e.g.* Fourier Transform InfraRed spectroscopy (FTIR) and adsorbent techniques were utilised to measure quantitatively individual components in the smoke. Measurements of the mass loss rate allowed evaluation of yields in relation to amount of material burned for the various species in the smoke gases.

This report gives a detailed account on the Fourier Transform InfraRed spectroscopy (FTIR) measurements made at SP during the project. The instrumentation, measurement strategy and method for evaluation of the IR-spectra are described. Also specific problems and insight accumulated during the project are reviewed. The remaining parts of the SP work is accounted for in a set of five additional reports [1-5], where reference 1 summarises the SP work. The others give detailed accounts of the various parts of the SP measurements.

## 2 Test set-up

The aim of the tests was to study the fire characteristics and smoke gas composition in fires in storage of bulk chemicals. Study of the specific smoke gas composition during under-ventilated conditions was an important issue. FTIR was a key tool in this context. Some of the tests incorporated real storage configurations. The test data were used in scaling comparisons between different test scales as another part of the project [6].

### 2.1 Substances and selection of gases for measurement

The substances for the tests were selected such that a reasonable complexity in the smoke gas chemistry could be expected. For a more in depth discussion on the selection of substances, see reference 2.

A carbon-hydrogen (CH), *polypropene*, a carbon-hydrogen-nitrogen (CHN), *Nylon 66*, a carbon-hydrogen-nitrogen-sulfur (CHNS), *tetramethylthiuram monosulfide*, a carbon-hydrogen-chlorine (CHCl) compound, *chlorobenzene*, and a carbon-hydrogen-nitrogen-chlorine (CHNCl) compound, *chloronitrobenzoic acid*, were chosen for the tests; see Figure 2.1.

Two of the materials are polymers (polypropene and Nylon 66), two are crystalline organic compounds (tetramethylthiuram monosulfide and chloronitrobenzoic acid) and one (chlorobenzene) is a fairly volatile liquid. All of them are used in bulk quantities in industry.

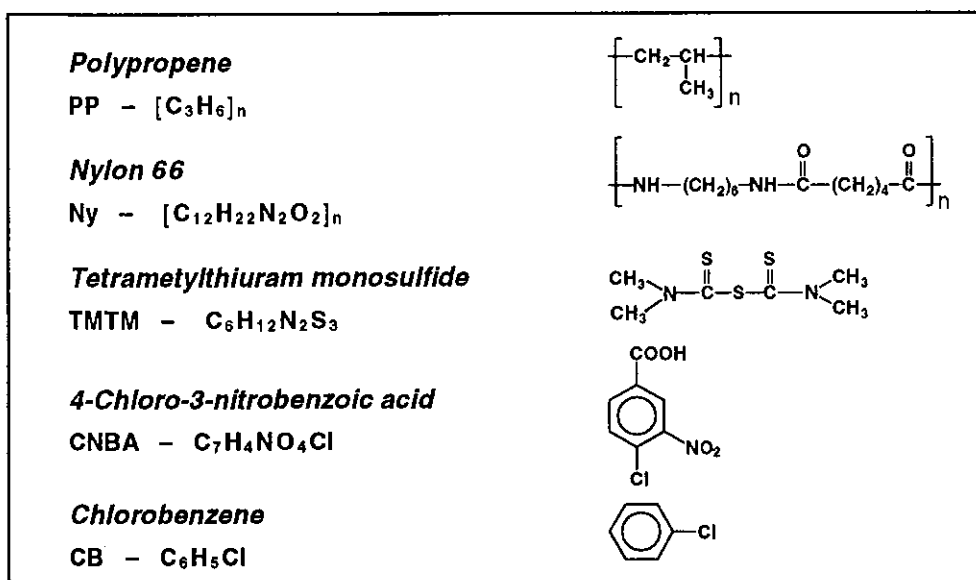
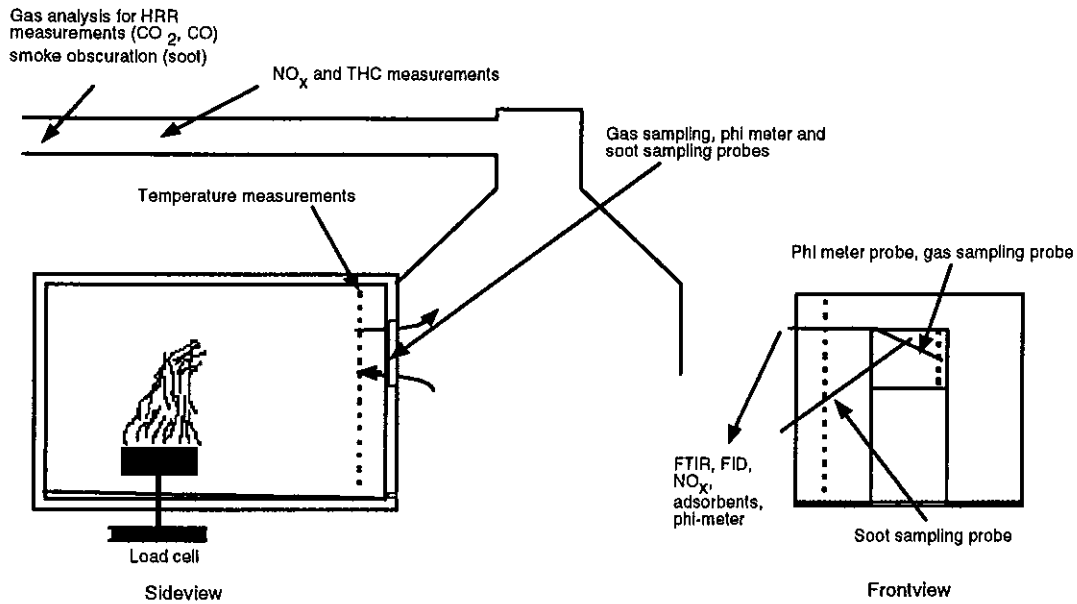


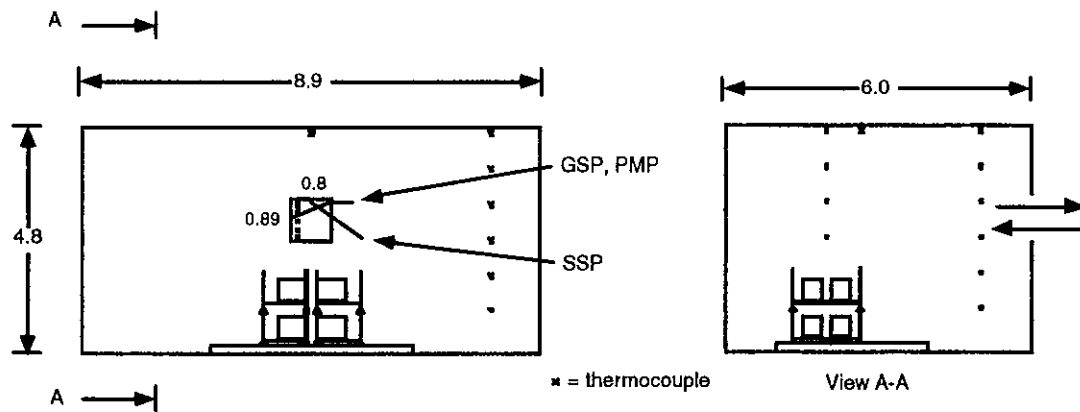
Figure 2.1 Materials selected for the fire tests.

When selecting the different combustion products to be measured by FTIR during the tests, the major products expected from each substance were considered. Also minor but highly toxic products were taken into account.  $\text{CO}_2$  and CO were of course interesting for all the substances, as being important fire parameters.





**Figure 2.2** The experiment set-up in the ISO 9705 room with the dimension  $3.6\text{ m} \times 2.4\text{ m} \times 2.4\text{ m}$  and the probe positions in the opening and in the exhaust duct to the calorimeter system.



**Figure 2.3** The larger scale test enclosure with the storage configuration of the materials, thermocouples and the measurement position in the opening. Dimensions in m.

## 2.4 Test procedure

Before each individual test was started, the condition of the FTIR equipment was tested. This control included test of the energy-throughput of the instrument and optimisation of mirror adjustment. The *BOMEM* software "Align", was used for the mirror adjustment. This procedure was important for assuring wavenumber reproducibility, between calibration and test. The validity of the calibration was checked by measurement on a reference CO-gas mixture.

A typical measurement procedure was as follows:

- A background spectrum was recorded on the FTIR with nitrogen flowing through the cell. 25 scans were recorded for the spectrum to get a high signal-to-noise ratio.
- The duct flow was established.
- All time devices for the experiment time function were synchronised.
- The on-line data acquisition program of the FTIR was started approximately 3 minutes before ignition to collect background data. The collection of data continued throughout the whole test. 4 scans were recorded for each spectrum.
- Ignition.
- If the fire had to be extinguished, normally the sampling to the FTIR and other gas analysis instruments were switched off to avoid clogging problems and excessive water contamination.
- End of test.
- The gas cell of the FTIR was flushed with nitrogen to get rid of contamination *e.g.* corrosive gases.
- A safety back up was taken of the FTIR-data.

### 3 Instrumentation

A measurement system containing a number of critical parts is needed for making on-line gas analysis on hot smoke gases using FTIR technique. The major parts of the system are the spectrometer, the gas cell, the sampling probe, the particle filter, the pump and the sampling lines for transportation of the smoke gases. A procedure for gas sampling and analysis using FTIR technique is described in the NORDTEST METHOD "NT FIRE 047" [8]. The NORDTEST standard has been used as a basis when designing the measurement system, but was not followed in detail. The different components of the measurement system are described in detail in the following sections.

The FTIR instrument was connected to a sampling probe in the door opening of the test enclosure. A number of additional analysis instruments were used for measurement in the opening, as well as in the duct that collect the smoke gases from the test enclosure. The instrumentation set-up was in most parts the same in both test configurations *i.e.* the ISO 9507 room [2] and the storage configuration [3].

#### 3.1 FTIR instrument

The FTIR instrument consisting of: spectrometer, gas cell and computer with software for on-line evaluation, was purchased from the company *Olle Moberg AB, Sweden*. The equipment was bought as a functioning analysis unit including regulating devices for heating of cell and sampling line and measurement of temperature and pressure in the gas cell. The supplier also took part in the calibration and training of users.

##### 3.1.1 Spectrometer

The spectrometer was a BOMEM MB 100 equipped with a DTGS detector. In Table 3.1 the characteristic parameters for the instrument and the settings selected for this project are described. In determining what settings to use, there is always a trade-off

*Table 3.1 Settings for the BOMEM MB 100 spectrometer.*

Parameter	Range	Selected
Resolution	1 - 128 cm <sup>-1</sup>	4 cm <sup>-1</sup>
Wavenumber	6000 - 350 cm <sup>-1</sup>	4000 - 400 cm <sup>-1</sup>
Apodization	-	cosine
Number of scans	-	4
Time for 1 spectrum	-	18 s



between optimal resolution, detection limits (noise) and measurement frequency. It was judged that a resolution of  $4\text{ cm}^{-1}$  was sufficient for the quantitative work in this project. To make qualitative identification of certain components easier a resolution of  $1\text{ cm}^{-1}$  would be preferred, but this implies longer measurement times. Using a spectral resolution of  $4\text{ cm}^{-1}$  and coadding 4 scans in each spectrum gave sufficient time resolution for the concentration data, in the type of experiments performed.

### 3.1.2 Gas cell

The gas cell used was of the brand *Infrared Analysis M-38H-NK-AU*. The cell was heated by a cylindrical heating element and insulated to maintain a constant temperature. By filling the cell with water and weighing, the exact volume of the cell was determined. For measurement and setting of the path length of the IR-beam inside the cell, the mirror arrangement was extracted from the cell. A small pen laser was used to visualise the path of the IR-beam. The number of paths was counted to give the total path length. Specifications of the cell are given in Table 3.2 below.

Table 3.2 *Specifications of the gas cell.*

Parameter	Specification
Path length	0.8 - 8 m
Path length used	4.8 m
Volume	0.922 L
Maximum temperature	200 °C
Temperature used	150 °C
Windows	2 KBr, $\varnothing 25 \times 4\text{ mm}$
Mirrors	3 Au-plated glass mirrors
Material of cell	Ni-plated aluminium

### 3.1.3 Software

The software for collection and evaluation of the data from the FTIR-spectrometer was *GRAMS/386 v 3.01b (Galactic Industries Corporation)*. An on-line evaluation program written in *Array basic* presented the concentration for selected components on the screen during tests. A database with library IR-spectra bought from *Sadtler (Gases & Vapours)* was used for qualitative identification. The computer used was a *Compaq Deskpro XE 560* with a Pentium processor.

### 3.2 Sampling equipment

The probe in the door opening (see Figure 2.2) used for sampling smoke gases for the FTIR was a multi-hole probe. It was mounted with the holes away from the flow direction of the smoke gases, to reduce the amount of soot sampled.

The gas sampling probe was connected to a heated filtering unit. The filtering unit, model *PSP 4000 H* from *M & C Products Analysentechnik GmbH*, is made of stainless steel having a ceramic filter element with  $2\ \mu\text{m}$  filter porosity. The filter was heated to  $180\ ^\circ\text{C}$ .

Smoke gas samples were drawn from the gas probe through the main 7-m sampling line. The sampled smoke gases were divided to the FTIR and the other measurement equipment (see Section 3.3) at the end of the main sampling line (see Figure 3.1). Short sampling lines were used for the sub flows after partitioning. All sampling lines were heated flexible ones ( $200\ ^\circ\text{C}$ ), having inside removable Teflon tubing. The dimensions of the Teflon tubing were  $8\ \text{mm} \times 6\ \text{mm}$  for the main sampling line, and  $6\ \text{mm} \times 4\ \text{mm}$  for the sub flow sampling lines.

In the start of the test series, a separate pump was connected to the FTIR. After some tests, where problems were experienced with clogging of the filter, the THC and the  $\text{NO}_x$  analysers were connected to draw their sample flows from the outlet of the FTIR cell. Thus omitting a separate pump to the FT-IR gave a reduced total flow through the heated filter. This was a way to prevent the filter from getting blocked by soot. The flow rate through the FTIR cell was in both set-ups approximately  $4\ \text{L/min}$ .

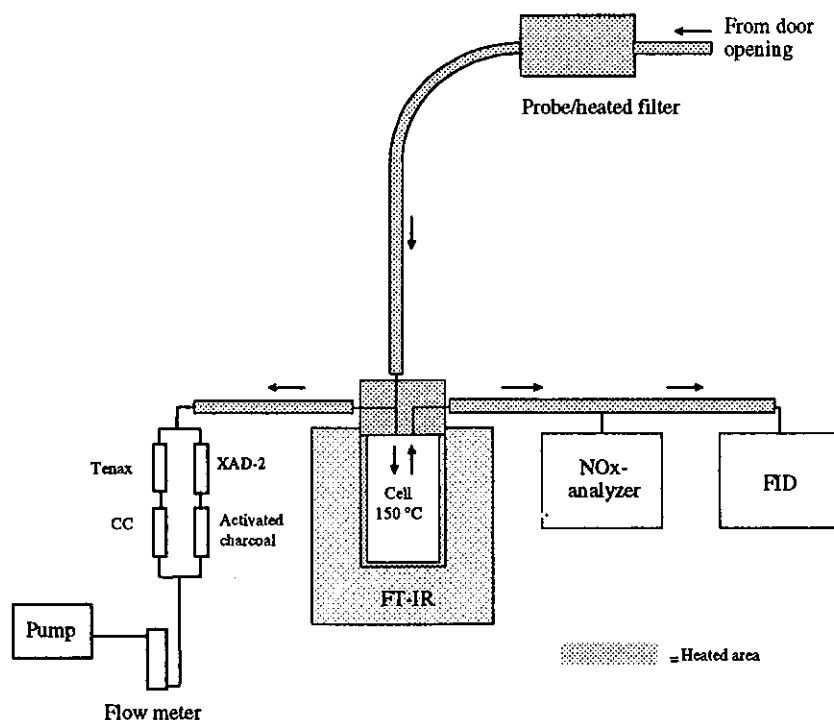


Figure 3.1 Schematic figure showing equipment set-up for measurements in the opening.

A determination of the response time for the complete FTIR measurement system was made. The sampling system was connected to a source of CO<sub>2</sub> gas and the time for 90 % response was measured. The total response time for the system as measured was 22.5 sec. Of the total response time, the response time caused by the cell volume was 19.5 sec.

### 3.3 Additional on-line gas analysis instruments

In the opening a heated chemiluminescence instrument [9] was used for measuring the concentrations of nitrogen oxides, NO and NO<sub>2</sub>, in the smoke gases. The total amount of unburned hydrocarbons, THC, was measured using a heated flame ionisation detector (FID) instrument [9]. Adsorbents were used for integrated sampling of volatile organic compounds [4]. Measurements of the degree of ventilation as equivalence ratio using the phi-meter, were also made in the opening (see section 2.2).

In addition to the normal measurement of O<sub>2</sub>, CO<sub>2</sub> and CO in the exhaust duct [10], an additional probe was used (see reference 2 for the tests in the ISO 9705 room and reference 3 for the storage configuration tests). The smoke gases sampled from this probe were divided using short heated (200 °C) PTFE tubing prior to entering a NO<sub>x</sub> analyser and a THC analyser.

*Table 3.3 On-line instruments used for measurements in the opening and in the duct.*

Instrument	Measurement principle	Measured species	Sampling position
FTIR	IR-absorption	CO <sub>2</sub> , CO, HCl, HCN, NH <sub>3</sub> and SO <sub>2</sub> *	Opening
THC analyser	Flame ionisation	Unburned hydrocarbons	Opening
NO <sub>x</sub> analyser	Chemiluminescence	NO and NO <sub>x</sub> (NO <sub>2</sub> )	Opening
O <sub>2</sub> analyser (Phi meter)	Paramagnetic	O <sub>2</sub>	Opening
THC analyser	Flame ionisation	Unburned hydrocarbons	Duct
NO <sub>x</sub> analyser	Chemiluminescence	NO <sub>x</sub> (or NO)	Duct
CO/CO <sub>2</sub> analyser	IR-absorption, selected bands	CO and CO <sub>2</sub>	Duct

\* Species calibrated for.

## 4 Calibration of the FTIR

When a molecule absorbs the energy of infrared light, this energy turns into motional energy of the molecule. The molecule exhibits both rotational and vibrational motions, which can be seen as specific absorption patterns in the infrared spectrum. The absorption follows certain quantum mechanics selection rules. This gives the basis for selection of suitable absorption bands to use for detection and analysis of an absorbing molecule.

To determine the concentration of a gas component in the absorption cell, the Beer-Lambert's law can be used, under optimal conditions. This law states a linear dependence for absorption versus concentration.

$$\text{Beer-Lambert's law:} \quad A = l \times C \times E \quad (4.1)$$

$A$  = absorbance

$l$  = total path length

$C$  = concentration

$E$  = specific absorption coefficient

The assumption of linearity in Beer-Lambert's law is in many cases not valid in gas-phase FTIR. One of the causes to this is insufficient resolution of the spectral band [11]. As a result, non-linear calibration curves with a number of calibration points have to be established.

### 4.1 Methods for making calibration gas mixtures

The composition of fire effluents is often very complex and changes rapidly with combustion and ventilation conditions. This demands a calibration covering a broad concentration range. Calibration is also needed for species, which create spectral overlap *e.g.* water.

The normal procedure for the recording of a calibration spectrum was:

- Flushing the cell with nitrogen.
- Recording of a background spectrum with nitrogen flushing the cell.
- Flushing the cell with the calibration gas mixture.
- Recording of a calibration spectrum when a constant concentration was established.

The number of scans for the background and the calibration spectra were in both cases 25. This large number of scans was taken in order to increase the signal to noise ratio.

#### 4.1.1 Dynamic mixing of gases

Dynamic mixing with nitrogen of a calibration gas of known concentration was the normal method to make gas mixtures for measurements of a calibration spectrum. The gas flows from the gas cylinders were maintained by means of mass-flow meters controlling each gas flow, one for the calibration gas and one for the

nitrogen. The choice of mass-flow meters depended on the desired gas concentration. The mass flow meters used were all of the brand *BROOKS INSTRUMENT B.V.*, model 5858s. Four mass flow meters with different flow ranges were used. The flow ranges were: 0 - 5 mL/min, 0 - 100 mL/min, 0 - 3 L/min and 0 - 10 L/min. The accuracy of the flow meters were 1 %-relative in all cases, as stated by the manufacturer. A calibration of the flow meters was made before the calibrations, and it validated the stated accuracy. The two PTFE tubes transporting the gases from the mass flow meters were connected by a T-connector, also made of PTFE. After the T-connector, a heated (200 °C) PTFE tube led the mixed gases to the cell of the FTIR. The total flow rate of the mixed gas was kept as close as possible to 4 L/min, which is the normal sampling flow of the FTIR.

The gas mixture was allowed to flush the cell for at least 10 min before a spectrum was recorded. Several successive spectra were recorded in order to make sure that a constant concentration was established. In some cases, *e.g.* low concentrations of HCl, longer times for flushing the cell were needed. The reason for this is probably a tendency of polar species to be retained by adsorption to surfaces of the tubing and the cell.

#### **4.1.2 Static mixing in the cell**

When making calibration for water, the dynamic mixing approach could not be used. The alternative way, which was used, was to let a known volume of liquid water vaporise in the cell. The first step in the calibration procedure was to create vacuum in the cell by means of a pump. When the pressure in the cell was sufficiently low, the valve between the pump and the cell was closed. A specific volume of water was then injected into the cell by a syringe. The needle was put through a septum connected to a second valve to the cell. After injection, nitrogen gas was allowed to slowly fill the cell, until ambient pressure was reached in the cell. When equilibrium was reached (15-30 min), a calibration spectrum was recorded. This method was also used for calibration of high concentrations of CO.

### **4.2 Methods for evaluation of the spectra**

A large part of the work in FTIR measurements is the extraction of information from the spectral data recorded. When only qualitative information is needed, simple comparison of the spectrum with library spectra of known gases can be made. Even in these cases a large set of calibration spectra taken on your own FTIR are required. In measurements on fire gases, spectral overlaps of water and carbon dioxide normally occur. These overlaps have to be accounted for by subtraction from the spectrum before qualitative identification can be made.

When quantitative information is needed, several methods exist to extract concentration data from the spectrum. The more straightforward are peak-height and peak-area methods, where a relationship for the height/area is determined against concentration of the gas in question. The advantages shared by both methods are that they are easy to comprehend, it is fast and easy to build an evaluation algorithm and both methods can handle non-linear cases. One advantage of the peak-height method is that the spectral position of the peak-height measurement can be chosen in such a way that problems with overlap of other gases can be minimised. The drawback,

which both methods have in common, is the lack of robustness for unexpected overlapping or interfering components.

An alternative approach is to use some deconvolution method based on multivariate data analysis. These methods include Classical Least Square (CLS), Partial Least Square (PLS), Principal Component Regression (PCR) and Target Factor Analyses (TFA). These methods are full-spectrum methods and are considered to be more robust [11], and able to handle the presence of overlapping or interfering components better than the methods mentioned above. The drawback of these methods is that they are more complicated to understand and implement, and they also in many cases have difficulties in handling non-linear behaviour.

#### 4.2.1 Peak height

The method that was used for quantitative evaluation of the smoke gas spectra in this project, was the peak-height method. The main reason for this choice was the possibility to quickly build new calibration algorithms and also that the supplier of the equipment had positive and extensive experiences of this method.

When starting to build a peak-height calibration algorithm for a gas, first suitable spectral positions for measurement of peak and baseline absorbance were chosen. The criteria for a good choice of position (wavenumber) for the peak was that it was a position with high absorbance and a minimum of spectral overlap or interference. In some cases a wavenumber on the slope of the peak was chosen to avoid interference, *e.g.* for CO<sub>2</sub>. In such cases, obviously, the wavenumber reproducibility of the instrument was of importance. The procedure for controlling the stability of the instrument was described in section 2.4. The position of the baseline measurement was chosen as close as possible to the peak position to avoid effects of a possibly sloping baseline. Also, the baseline position was chosen in an area where spectral overlap or interference were minimal. The absorbance, defined as the difference between peak and baseline absorbance values of the gas, were measured for different concentrations in the calibration range. The absorbance was plotted against concentration, and a calibration algorithm for the concentration as a function of absorbance was extracted. Often the calibration equation was non-linear and a polynomial fitting function had to be used.

Calibration curves were constructed for each gas calibrated for. Information on the number of spectra, calibrated concentration span and other information on the specific calibration curve can be found in the section of the respective gas. As an example of a typical calibration curve, the calibration curve for HCl at 2798.1 cm<sup>-1</sup> is shown in figure 4.1. The accuracy of the fitted curve is better than 5 %-relative for the calibrated concentration span. 5 % or better, was the normal accuracy in the calibrations in general.

In most cases, there was some degree of spectral overlap or interference from other gases at the peak wave number. This contribution to the absorbance was corrected for by a correction algorithm, yielding a correction factor depending on the concentration of the interfering gas. Especially the overlap of water, which is significant over large parts of the spectrum, had to be handled this way.



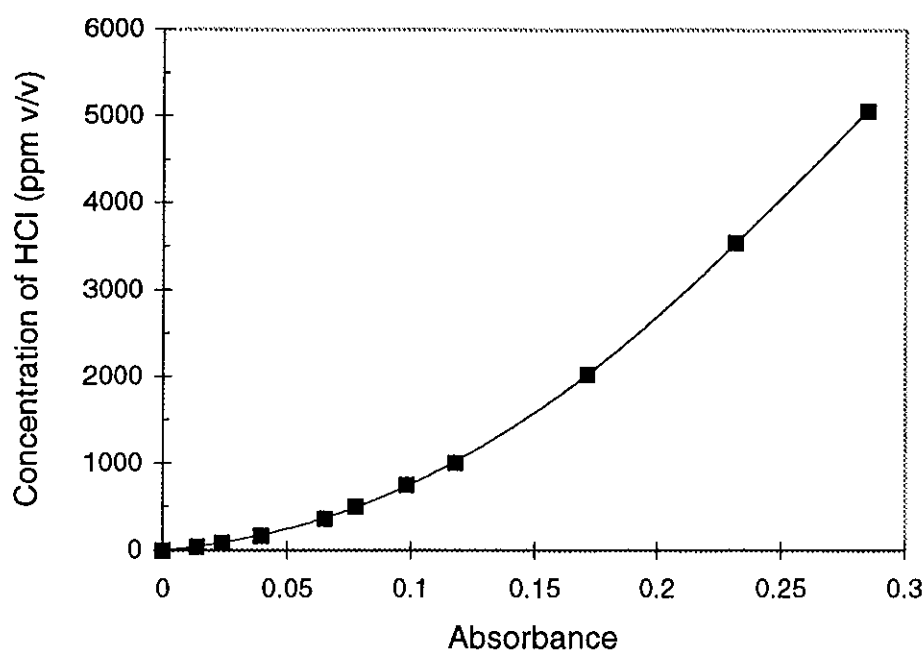


Figure 4.1 Calibration curve of HCl for absorbance at  $2798.1\text{ cm}^{-1}$ .

#### 4.2.2 Spectral subtraction

When manual evaluation of a spectrum was done, the method of spectral subtraction was used. Spectral subtraction is the subtraction of the absorption spectrum of one gas from the test spectrum with *e.g.* a library spectrum or a calibration spectrum. The software used for this also gave a subtraction factor. This factor could in some cases be used for semi-quantitative determination of concentration, if the concentration of the subtraction spectrum was known. Spectral subtraction was frequently used for checking the mathematical evaluation discussed in section 4.2.1.

#### 4.3 Calibration data for the selected gases

An overview of the gases selected for quantitative calibration, and their respective concentration interval for calibration, is shown in Table 4.1. Data on the certified calibration gases used for dilution in the calibrations can be found in Table 4.2.

**Table 4.1** *Gases selected for quantitative calibration and information on calibration intervals and methods for calibration.*

Compound	Lowest calibrated concentration	Highest calibrated concentration	Method for making standard gas
H <sub>2</sub> O	0.1 %	16 %	Static mixing in cell
CO <sub>2</sub>	0.20 %	20 %	Dynamic mixing
CO	100 ppm	80 000 ppm	Static and dynamic
HCl	50 ppm	5100 ppm	Dynamic mixing
SO <sub>2</sub>	10 ppm	26 000 ppm	Dynamic mixing
HCN	10 ppm	2000 ppm	Dynamic mixing
NH <sub>3</sub>	10 ppm	1600 ppm	Dynamic mixing

**Table 4.2** *Data on certified calibration gases used for dynamic mixing. All concentrations in fractions of volume.*

Gas	Supplier	Concentration	Uncertainty
CO <sub>2</sub>	Air Liquide	20 %	2 % (relative)
CO	-"	10200 ppm	2 % -"
HCl	-"	5070 ppm	5 % -"
HCN	Messer Griesheim	2022 ppm	3 % -"
NH <sub>3</sub>	Air Liquide	3180 ppm	2 % -"
SO <sub>2</sub>	-"	2.47 %	2 % -"

### 4.3.1 Water, H<sub>2</sub>O

Water is an important gas when making FTIR measurements in fire tests. In a combustion process water is produced as one of the major products. In our tests, high water concentrations were expected as we were performing our measurements on the undiluted smoke gases in the opening of the test facility. The reason that water is important is the large absorbing features covering much of the IR spectrum. Correction algorithms for water were made for several gases, and a calibration-algorithm for the concentration of water was also made to give an idea of the amounts of water produced in the tests.

Table 4.3 Calibration data for H<sub>2</sub>O

Number of calibration points	16
Highest concentration	15.7 %
Lowest concentration	0.1 %
Peak wavenumber	1992 cm <sup>-1</sup>
Baseline wavenumber	1979.2 cm <sup>-1</sup>
Interference corrections	none

When evaluating the spectra from measurements on TMTM and CNBA it was found that the normal spectral range used for water was severely interfered. For these test a water peak in the higher wavelength range was used. The peak position was in these cases 3446.5 cm<sup>-1</sup> and the baseline position was 3428 cm<sup>-1</sup>.

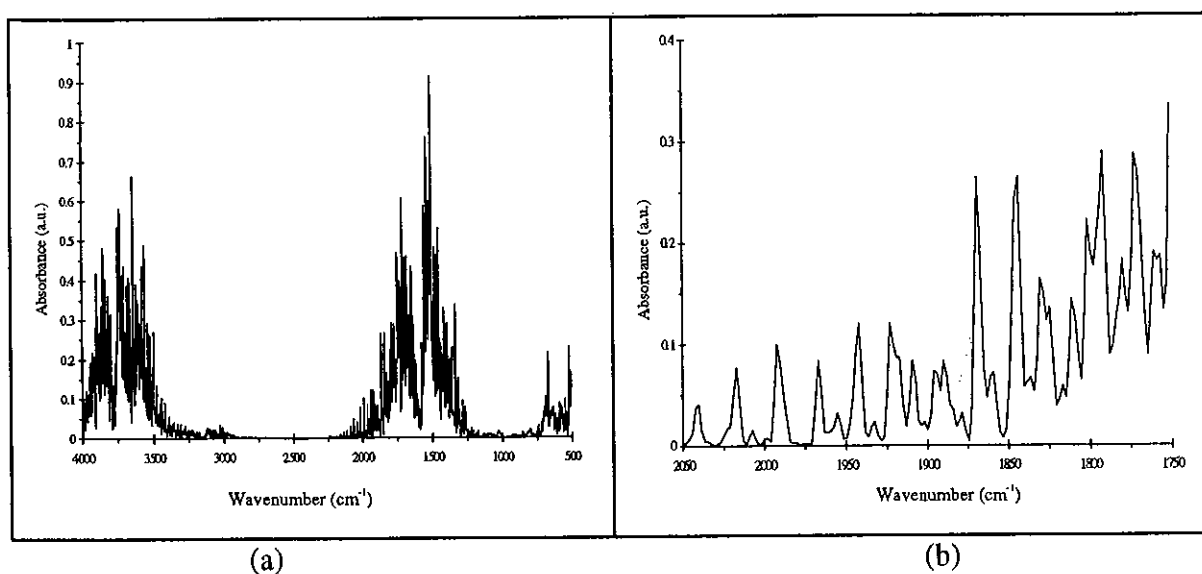


Figure 4.2 (a) Absorbance of H<sub>2</sub>O - full spectrum and (b) spectral range for normal quantification of H<sub>2</sub>O.

### 4.3.2 Carbon dioxide, CO<sub>2</sub>

For CO<sub>2</sub> there exist three different regions in the spectrum that can be used for quantification. The regions round 700 cm<sup>-1</sup> and 3600 cm<sup>-1</sup> both suffer from spectral overlap of water. Even if these regions are possible to use, the peak round 2300 cm<sup>-1</sup> was used. This peak is free from spectral interference. The problem with this peak is the strong absorption, resulting in spectral saturation. To get around this problem a measurement position on the slope of the peak was used for quantification. This method to quantify CO<sub>2</sub> has been proved to give valid results [12].

Table 4.4 Calibration data for CO<sub>2</sub>

Number of calibration points	10
Highest concentration	20 %
Lowest concentration	0.2 %
Peak wavenumber	2392.2 cm <sup>-1</sup>
Baseline wavenumber	2432.6 cm <sup>-1</sup>
Interference corrections	none

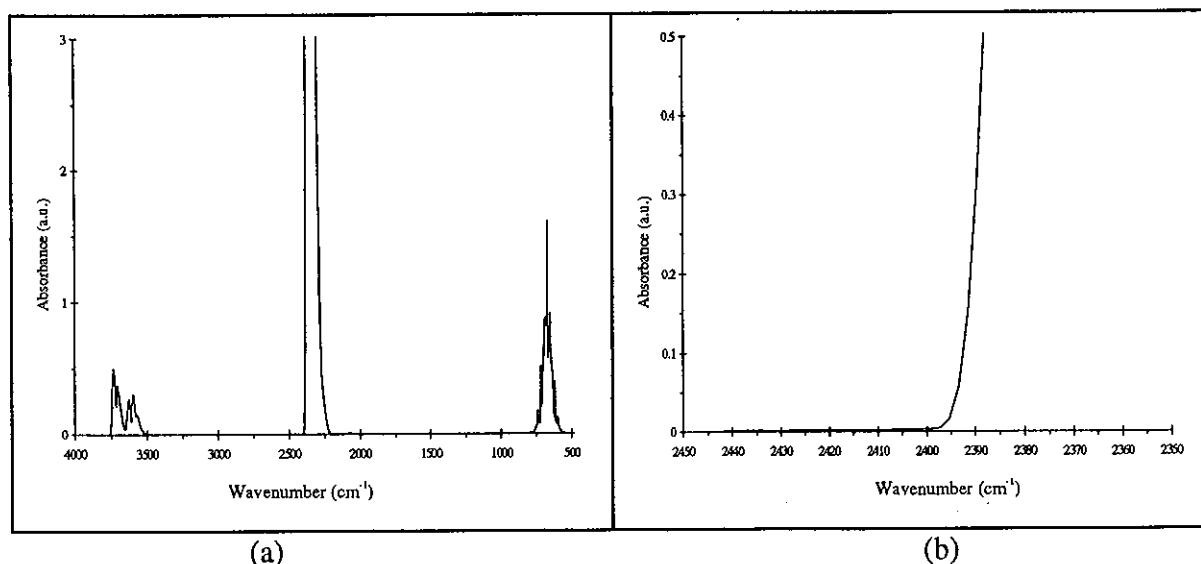


Figure 4.3 (a) Absorbance of CO<sub>2</sub> - full spectrum and (b) spectral range for normal quantification of CO<sub>2</sub>.

### 4.3.3 Carbon monoxide, CO

For CO the main spectral band between  $2000\text{ cm}^{-1}$  and  $2250\text{ cm}^{-1}$  is the only option for quantification. Both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  interfere in varying degrees, depending on the wave number position. The selected wave number  $2133.6\text{ cm}^{-1}$  minimises the interference from these species. The absorbance of CO behaves in a strongly non-linear way. The large concentration interval needed for CO made it impossible to use a single calibration algorithm with maintained good accuracy. Instead, the concentration interval was split into two calibration intervals. One between zero and 10000 ppm, and one between 10000 ppm and 80000 ppm. The results of the two calibration algorithms in the region close to 10000 ppm were approximately equal.

Table 4.5 Calibration data for CO

Number of calibration points	9 and 5
Highest concentration	80000 ppm
Lowest concentration	99 ppm
Peak wavenumber	$2133.6\text{ cm}^{-1}$
Baseline wavenumber	$1979.2\text{ cm}^{-1}$
Interference corrections	$\text{CO}_2$ , $\text{H}_2\text{O}$

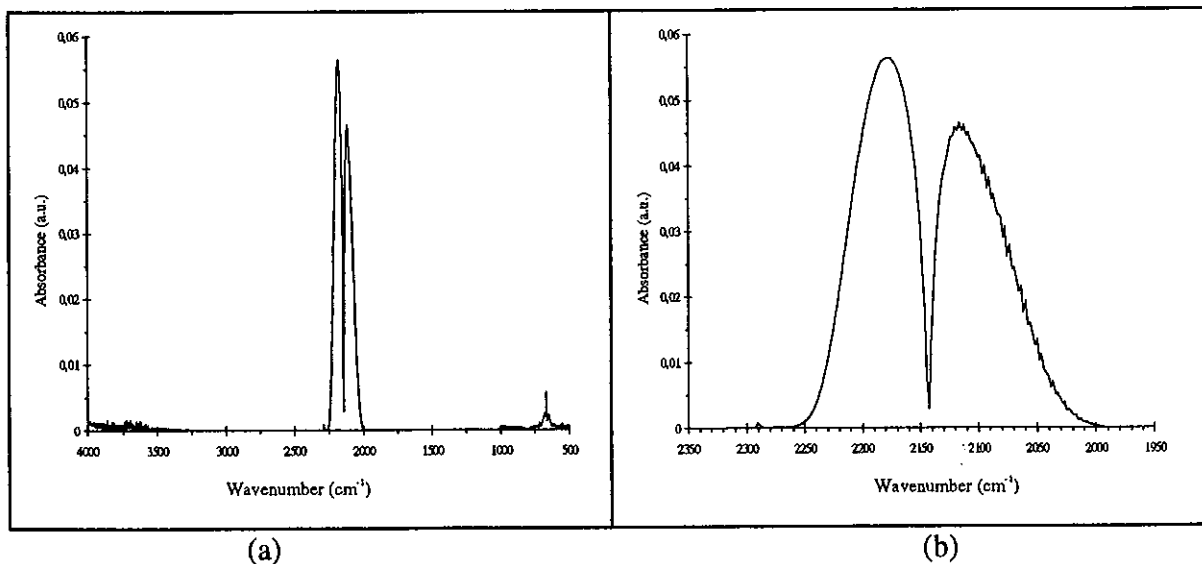


Figure 4.4 (a) Absorbance of CO - full spectrum and (b) spectral range for normal quantification of CO.

#### 4.3.4 Hydrogen chloride, HCl

HCl gives an absorption spectrum with resolved rotational fine structure even at the resolution used,  $4\text{ cm}^{-1}$ . The distinct peak at  $2798.1\text{ cm}^{-1}$  was normally used for quantification. In cases of high absorbance, where the concentration exceeded the highest point of calibration, the weaker peak at  $2597.9\text{ cm}^{-1}$  was used. This weaker peak gives better linearity, and was in such cases used for a linear extrapolation outside the concentration span calibrated for. Quantification of HCl is straight forward in the sense that no spectral overlaps normally occur.

Table 4.6 Calibration data for HCl

Number of calibration points	10
Highest concentration	5070 ppm
Lowest concentration	47 ppm
Peak wavenumber	$2798.1\text{ cm}^{-1}$
Baseline wavenumber	$2809.6\text{ cm}^{-1}$
Interference corrections	none

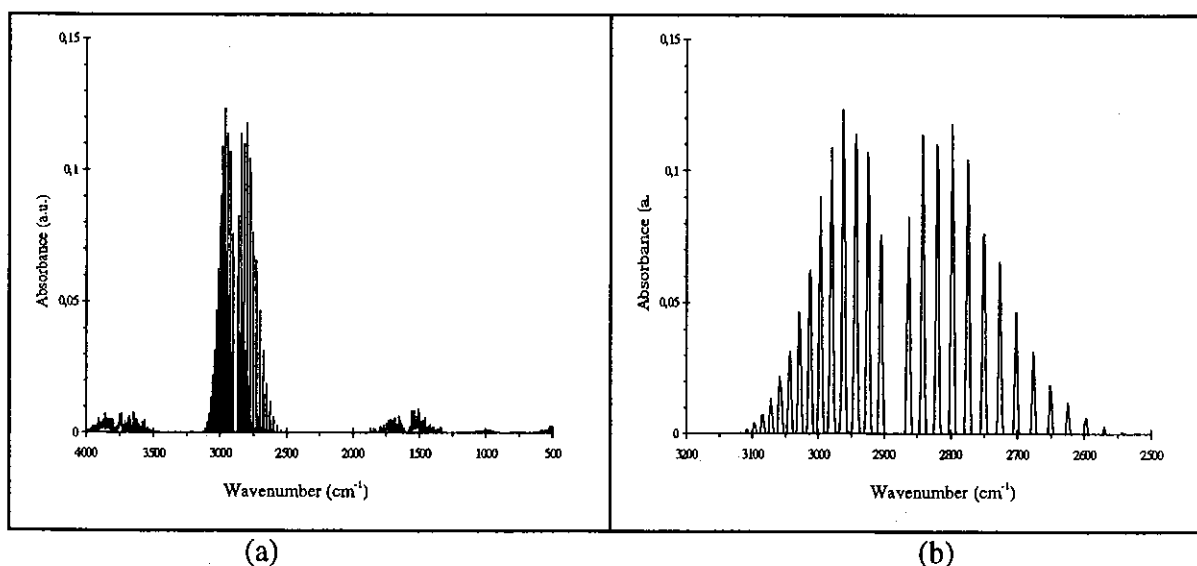


Figure 4.5 (a) Absorbance of HCl - full spectrum also showing some water and (b) spectral range for quantification of HCl.



### 4.3.5 Hydrogen cyanide, HCN

For HCN, two absorption bands can be used for quantification. The strongest band between  $700\text{ cm}^{-1}$  -  $800\text{ cm}^{-1}$  was normally used. The absorbance behaves in a strongly non-linear way here.  $\text{CO}_2$  also absorbs strongly in this region and has to be corrected for. Also  $\text{H}_2\text{O}$  interferes, but not so strongly. For high concentrations, the absorption band in the region  $3200\text{ cm}^{-1}$  -  $3300\text{ cm}^{-1}$  was used. Water interferes strongly in this region, but the interference can be handled at high HCN concentrations. Acetylene (ethyne) also interferes in this region and must be corrected for when present in the smoke gases.

Table 4.7 Calibration data for HCN

Number of calibration points	16
Highest concentration	2022 ppm
Lowest concentration	10 ppm
Peak wavenumber	$713.8\text{ cm}^{-1}$
Baseline wavenumber	$786.9\text{ cm}^{-1}$
Interference corrections	$\text{CO}_2$ , $\text{H}_2\text{O}$

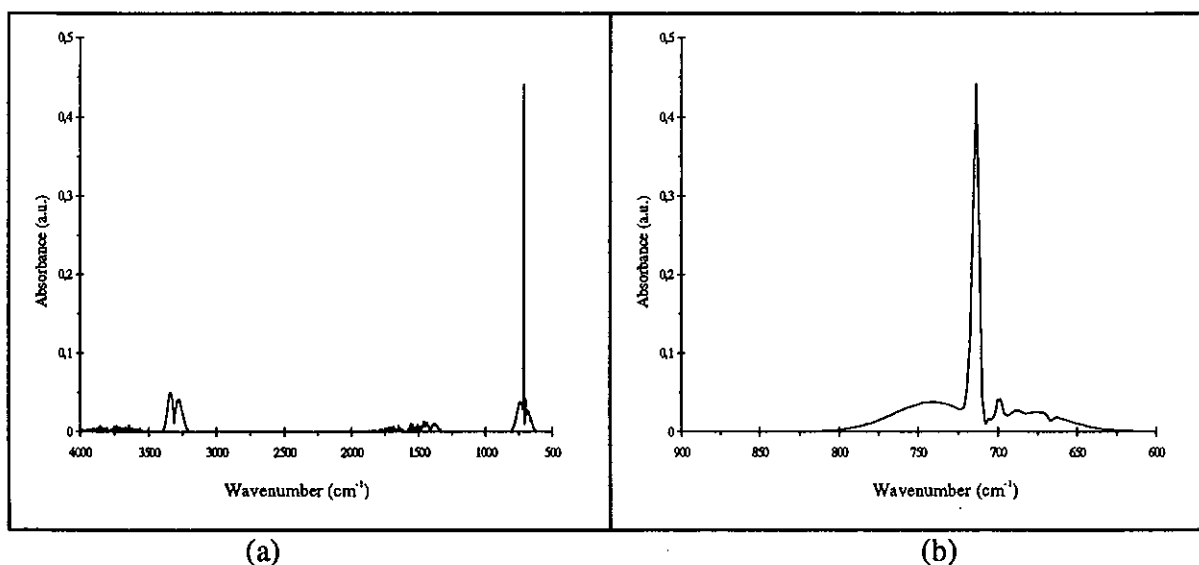


Figure 4.6 (a) Absorbance of HCN - full spectrum also showing some water and (b) spectral range for normal quantification of HCN.

### 4.3.6 Ammonia, $\text{NH}_3$

$\text{NH}_3$  has two strong, well separated absorption bands. The band at  $965.3$  was used for quantification. The absorbance behaves in a strongly non-linear way. Interference from other gases is relatively modest here. No corrections were made.

Table 4.8 Calibration data for  $\text{NH}_3$

Number of calibration points	14
Highest concentration	1590 ppm
Lowest concentration	11 ppm
Peak wavenumber	$965.3 \text{ cm}^{-1}$
Baseline wavenumber	$1000 \text{ cm}^{-1}$
Interference corrections	none

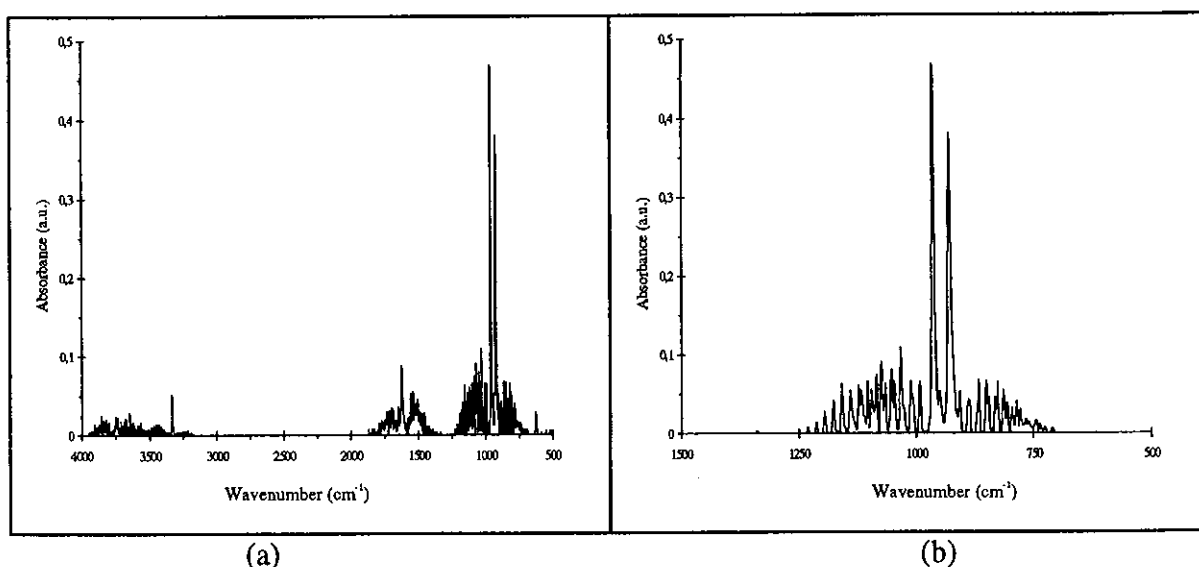


Figure 4.7 (a) Absorbance of  $\text{NH}_3$  - full spectrum also showing some water and (b) spectral range for normal quantification of  $\text{NH}_3$ .

### 4.3.7 Sulfur dioxide, SO<sub>2</sub>

SO<sub>2</sub> has several absorption bands that can be used for quantification. For the lower concentrations (< 1000 ppm), the strongest band at 1382.7 cm<sup>-1</sup> was used. Water interferes here, but can be handled at the selected wave number. For higher concentrations, the wave number 2512.3 cm<sup>-1</sup> was used. This weak band is free of interference and proved to be a good choice for high concentrations of SO<sub>2</sub>. In both cases the baseline wavenumber 1978.1 cm<sup>-1</sup> was used. This wavenumber is undisturbed by water, and a good choice in this respect. The relatively large distance to the peak wavenumber could lead to problems in case of a strongly sloped baseline, but no significant errors caused by this effect were found here. A nice feature of SO<sub>2</sub> is the linear dependency of absorbance versus concentration, which implies that fewer calibration points could have been used.

Table 4.9 Calibration data for SO<sub>2</sub>

Number of calibration points	17
Highest concentration	24700 ppm
Lowest concentration	11 ppm
Peak wavenumber	1382.7 cm <sup>-1</sup>
Baseline wavenumber	1978.1 cm <sup>-1</sup>
Interference corrections	H <sub>2</sub> O

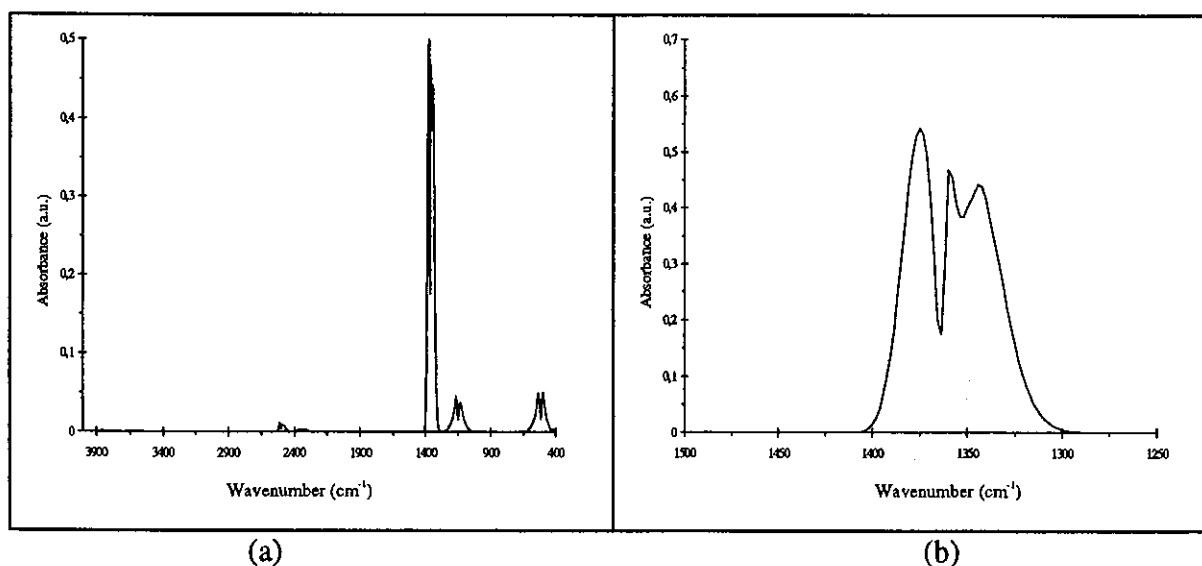


Figure 4.8 (a) Absorbance of SO<sub>2</sub> - full spectrum and (b) spectral range for normal quantification of SO<sub>2</sub>.

## 5 Summary and discussion of results

In this section, general results and trends on the gases measured will be discussed. The results discussed are all from the tests in the ISO 9507 room. This test series was the more extensive, both regarding the number of tests and in variation of the ventilation conditions during the tests. For a complete account of the results from the tests, see reference 2 for the tests in the ISO 9705 room and reference 3 for the tests in the storage configuration enclosure. A comparison between results from the two different test configurations can be found in reference 1.

### 5.1 Expression of results

The output from the evaluation of the FTIR data was as gas concentration, expressed as volume concentration *e.g.* ppm (V/V). The gas concentrations, in this form, were used for comparison with limiting values [2, 3] to assess the risks regarding toxicity in the fire situations studied.

To be able to better compare results from different time periods - within a test, from different tests with the same substance, or from tests with different substances - the measured concentrations of a number of species were converted into yields, *i.e.* the mass of a certain species produced ( $m_i$ ) is divided by the mass of the fuel consumed ( $m_{fuel}$ ):

$$Y_i = \frac{m_i}{m_{fuel}} \quad (5.1)$$

where  $i$  represents an individual species.

### 5.2 Results from the fire tests

#### 5.2.1 Results on CO<sub>2</sub> and CO

CO<sub>2</sub> and CO are the two fire gases normally measured during a fire test. The ratios of these are often used to reflect the fire conditions. Normally on-line measurements are made using a dedicated IR-analyser.

The measurement of CO<sub>2</sub> was not accompanied with any specific problems regardless of what type of substance that was tested. No unexpected interference occurred at the selected wave number 2392.2 cm<sup>-1</sup>. The concentration of CO<sub>2</sub> in the door opening was normally between 8 % and 10 % during a fully developed fire. The accuracy of the FTIR measurements of CO<sub>2</sub> in the door opening, compared with measurements using a normal CO<sub>2</sub>/CO-analyzer (IR) in the duct, was investigated after the test series was completed [12]. This investigation shows that the difference normally is less than 10 % (relative). One has to take into account that the uncertainty of the calculation of the flow through the opening is included in this difference [5].

CO is a combustion product that is produced during incomplete combustion, and consequently, could for all substances tested be found in high concentrations in the under-ventilated parts of the tests. Average concentrations of CO for the different substances, and the dependency of the ventilation degree is shown in Table 5.1.

*Table 5.1 Average concentrations of CO (ppm(V/V)) in the opening for different ventilation scenarios.*

Substance	Ventilation	CO/ppm
PP	$\phi < 1$	1300
	$\phi > 1$	10000
Ny	$\phi < 1$	1200
	$\phi > 1$	9000
TMTM	$\phi < 1$	260
	$\phi > 1$	8500
CNBA	$\phi < 1$	4100
	$\phi > 1^*$	3000
CB	$\phi > 1$	38000

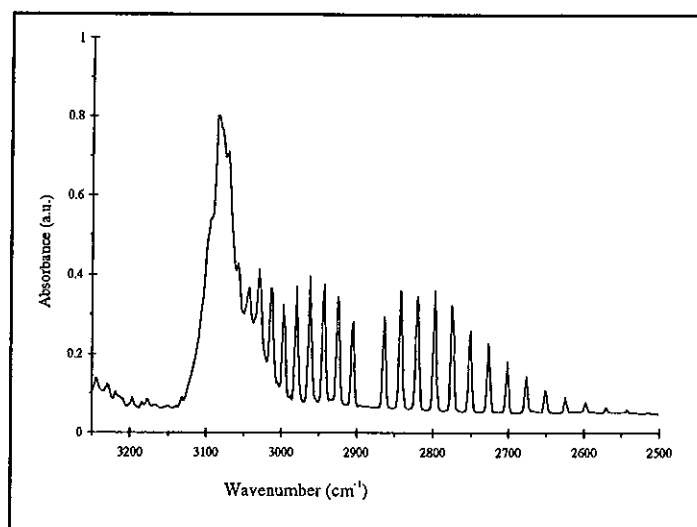
\* Test where CNBA was mixed with PP to achieve better combustion.

In most cases the selected wave number,  $2133.6 \text{ cm}^{-1}$  for CO, proved to give reliable results. An exception was the tests on TMTM, where the spectral region was severely interfered during under-ventilated conditions. The interfering specie was identified as carbonyl sulfide (COS), which was produced from the sulfur containing substance TMTM during oxygen depleted conditions. In Figure 5.1, a spectrum from a test on TMTM shows the interference of COS.





and this makes it important to choose a background position as close to the chosen peak as possible. The choice of the peak wavenumber  $2798.1\text{ cm}^{-1}$  reduces the problems with this type of interference.



*Figure 5.2 Interference of HCl in a spectrum from a fire test on CB, the interference is probably caused by chlorobenzene.*

### 5.2.3 Results on HCN

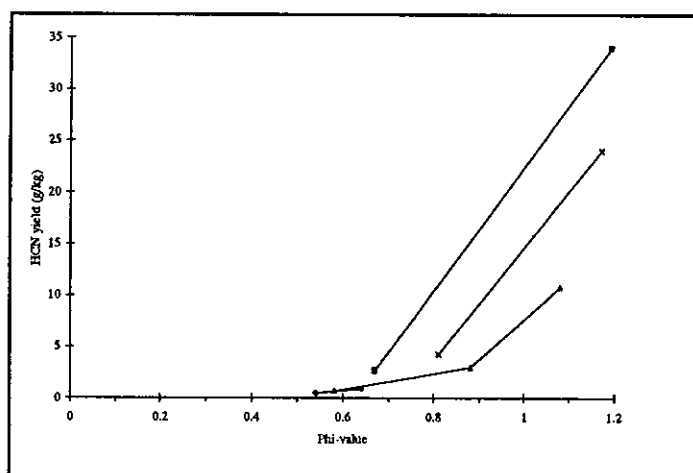
HCN is a highly toxic combustion product that is produced in high yields during incomplete combustion of nitrogen containing substances. All three nitrogen-containing substances tested, *i.e.* Ny, TMTM and CNBA, produced HCN in considerable quantities. Low concentrations of HCN were also found in some tests on PP. As PP does not contain nitrogen, HCN must be produced from reactions of ambient nitrogen. Average concentrations of HCN for the different nitrogen containing substances and the dependence of the ventilation degree is shown in Table 5.2. As can be seen in the table, the dependence on the ventilation degree is strong. Figure 5.3 illustrates this dependence even more clearly. In this figure the yield of HCN for different time periods in four different tests on Ny is plotted against the degree of ventilation.

When using the wave number  $713.8\text{ cm}^{-1}$  for HCN, there were no problems with interference noted other than from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . For high concentrations, where HCN exceeded the calibrated concentration span, the alternative spectral position at  $3345\text{ cm}^{-1}$  had to be used (see Section 4.3.5). At this position interference from acetylene ( $\text{H}_2\text{C}_2$ ) can be a problem, and has to be corrected for if it occurs. In those cases when this spectral position was used, the concentration of acetylene never was high enough to cause any significant interference.

**Table 5.2** Average concentrations of HCN (ppm(V/V)) in the opening for different ventilation scenarios.

Substance	Ventilation	HCN/ppm
Ny	$\phi < 1$	220
	$\phi > 1$	2800
TMTM	$\phi < 1$	160
	$\phi > 1$	6300
CNBA	$\phi < 1$	370
	$\phi > 1^*$	190

\* Test where CNBA was mixed with PP to achieve better combustion.



**Figure 5.3** Yields of HCN from four different tests on Ny plotted against the degree of ventilation.

#### 5.2.4 Results on $\text{NH}_3$

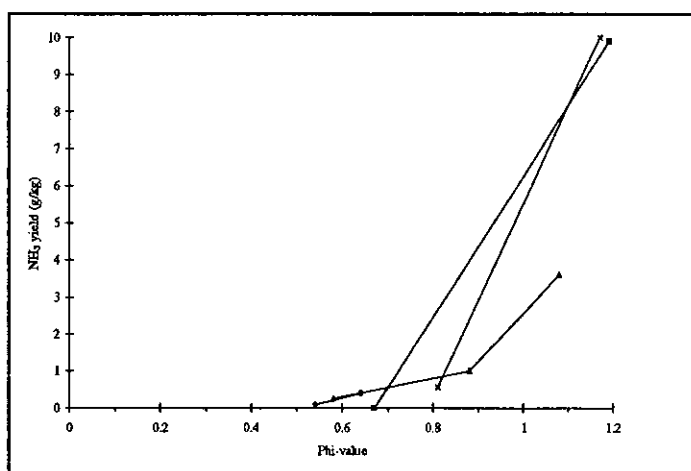
Two of the three nitrogen-containing substances tested, Ny and TMTM, produced  $\text{NH}_3$  in measurable quantities. Low concentrations of  $\text{NH}_3$  were also found in some tests on PP. As PP does not contain nitrogen,  $\text{NH}_3$  must be produced from reactions of ambient nitrogen. Average concentrations of  $\text{NH}_3$  for the different nitrogen containing substances and the dependence on the degree of ventilation is shown in Table 5.3. As can be seen in the table, the dependence of the ventilation degree is strong. Figure 5.4 illustrates this dependence even more clearly. In this figure the yield of  $\text{NH}_3$  for different time periods in four different tests on Ny is plotted against the degree of ventilation.

The wave number selected for  $\text{NH}_3$  was in most cases free from interference. In some spectra in tests on PP the peak position was interfered by some unidentified specie. This was not so serious, as high concentration of  $\text{NH}_3$  was not expected from PP. In some periods of the tests, especially for TMTM, the calibrated concentration span was exceeded. In these cases a linear extrapolation was made.

*Table 5.3 Average concentrations of  $\text{NH}_3$  (ppm(V/V)) in the opening for different ventilation scenarios.*

Substance	Ventilation	$\text{NH}_3$ /ppm
Ny	$\phi < 1$	80
	$\phi > 1$	1800
TMTM	$\phi < 1$	< 5
	$\phi > 1$	1000
CNBA	$\phi < 1$	< 5
	$\phi > 1^*$	< 5

\* Test where CNBA was mixed with PP to achieve better combustion.



*Figure 5.4 Yields of  $\text{NH}_3$  from four different tests on Ny plotted against the degree of ventilation.*

### 5.2.5 Results on $\text{SO}_2$

Only TMTM of the tested substances contained sulfur. The measurement of  $\text{SO}_2$  was fairly straight forward as high concentrations of  $\text{SO}_2$  were produced during the tests. The high concentrations exceeded the calibrated concentration span at several occasions. But, given the fact of the linear absorption behaviour of  $\text{SO}_2$ , an extrapolation can be expected to be rather accurate. The concentration maximum reached in several of the tests was close to 60 000 ppm. As can be seen in Figure

5.5, the production of  $\text{SO}_2$  was close to its maximum (923 g  $\text{SO}_2$ /kg substance) at stoichiometric conditions ( $\phi=1$ ).

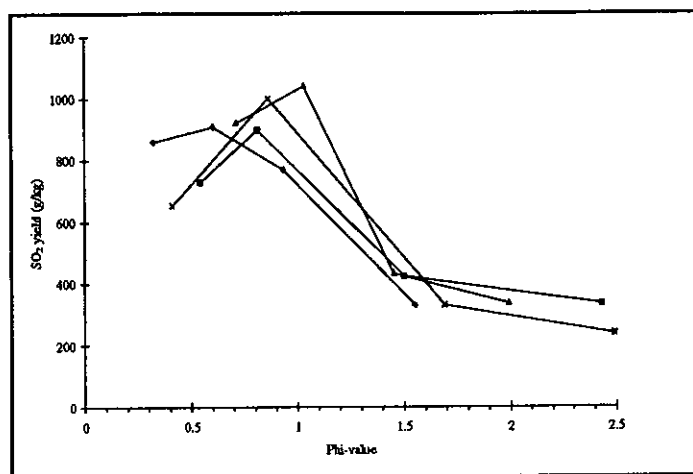


Figure 5.5 Yields of  $\text{SO}_2$  from four different tests plotted against the degree of ventilation.

### 5.2.6 Results on other gases

A valuable advantage of the FTIR technique is the possibility to find information in the spectrum on "unexpected" species. An example of this is the identification of COS in the under-ventilated parts of the tests on the sulfur containing substance TMTM. The finding of this specie has also been verified in the small-scale tests performed at Risø [13]. Other sulfur containing species were also searched for, *e.g.*  $\text{H}_2\text{S}$  and  $\text{CS}_2$ , but these species could not be found. In the tests on the chlorine containing substances, CNBA and CB, the spectra were investigated for  $\text{COCl}_2$  (phosgene). But no trace of phosgene was found. The presence of methane in many of the tests was verified by FTIR. This was valuable information used in the interpretation of the results from analysis of organic species [4] in the smoke gas. When finding unexpected species in the spectral data, it is possibility to calibrate the FTIR for these species even after the test. This has not been done in this project.

## 6 Observations and conclusions

For the evaluation of yields at different equivalence ratios for each of the chemicals studied, it was necessary to select short time periods within a test with reasonably constant  $\phi$  values and calculate yields for these periods. The choice to use on-line FTIR measurement as the main analysis technique turned out to be a sound one, since this allowed assessing the concentrations of the individual components for precisely these time-periods of the constant  $\phi$  values.

The sampling and evaluation strategies chosen for the FTIR measurements worked well in most parts. The gases selected for calibration proved to be the major gaseous combustion products in the fire tests. In some cases gases were produced in higher concentration than what was expected, so that the calibrated concentration span was exceeded. This was a problem, and complementary calibration had to be made. In cases where this was not possible, due to limited economic recourses, extrapolations were made. The method used for the evaluations gave valid results when no unexpected interferences occurred. As there was no way to know this in advance, time consuming manual evaluation had to be made afterwards on a selection of spectra from each test.

One gas with properties that makes measurements difficult is HCl. Due to the fact that HCl readily dissolves in water, losses on cold surfaces, *e.g.* walls of the test enclosure, probably made us underestimate the production of HCl.

The choice to perform the sampling of the smoke gases in the door opening instead of in the duct where more stable conditions can be expected was based mainly on:

- The objective of the project was to measure what was produced from under-ventilated combustion.
- In the door opening no after-burning of the smoke gas products has yet taken place.
- The degree of dilution is low in the door opening compared to the duct, and this could be an advantage regarding detection limits.

Sampling in the opening of the test enclosure proved to give some problems. The high concentration of soot and water blocked the filter and the probe in some tests, *e.g.* tests on CB and CNBA, and only limited chemical information was extracted from these tests.

To calculate yields etc. for the reaction products, the mass flow is required for the smoke gases leaving through the opening, where the sampling was performed. It is a difficult task to use velocity and temperature sensors in the opening plane in order to establish the mass flow rates experimentally. Instead the mass flow was computed [5]. The model used for these calculations is based on temperature measurements and mass loss rates. The flow conditions in the opening was a source of error, especially in the beginning of the tests, before a neutral plane separating the hot smoke gases leaving the room and the inflow of the cooler fresh air was established. In some of the first tests dilution with fresh air of the sampled smoke gases was suspected. The probe position was then adjusted to avoid this problem.

Despite the problems mentioned above, generally, valid and interesting chemical information was extracted from the FTIR measurements. The feature of time resolved data was vital for the assessments of the ventilation dependency of the species produced during the combustion experiments. Also, additional information on species produced was found from the FTIR data, *e.g.* COS and CH<sub>4</sub>.

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SP Swedish National Testing and Research Institute  
Box 857, SE-501 15 BORÅS, Sweden  
Telephone: +46 33 16 50 00, Telefax: +46 33 13 55 02  
E-mail: [info@sp.se](mailto:info@sp.se), Internet: [www.sp.se](http://www.sp.se)

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