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Smoke gas analysis by Fourier transform infrared spectroscopy

The SAFIR project

Edited by

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SAFIR

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Abstract

The determination of toxic components from fire gases is difficult because the environment is hot, reactions are often temperature dependent, and a lot of soot may be produced. Due to the different properties of the gas components, a different time-consuming procedure for each species has traditionally been used. The use of FTIR (Fourier Transform InfraRed) spectrometers as a continuous monitoring technique overcomes many of the problems in smoke gas analyses. FTIR offers an opportunity to set up a calibration and prediction method for each gas showing a characteristic spectral band in the infra-red region of the spectrum.

The objective of this project was to further develop the FTIR gas analysis of smoke gases to be an applicable and reliable method for the determination of toxic components in combustion gases related to fire test conditions. The project included the following tasks: small scale and large scale sampling; analysis, calibration and software techniques; the verification of the method; and an interlaboratory trial.

The optimum probe design, filter parameters and the most suitable sampling lines in terms of flow rate, diameter, construction material and operating temperature have been specified. The gas adsorption onto the filter and the soot have been measured. In the large scale, special concern was given to the probe design and the effects of the probe location in relation to the fire source as well as practical considerations of the sampling line length.

Quantitative calibration and prediction methods have been constructed for different components present in smoke gases. Recommendations on how to deal with interferents, non-linearities and outliers have been provided and a verification method for the spectrometer for unexpected variations and for the different models have been described.

FTIR measurement procedures in different fire test scenarios have been studied using the recommendations of this project for measurement techniques and analysis, and real precision values for specific test scenarios have been estimated. Also a proposal for draft standard of the FTIR method for smoke gas analysis has been prepared.

An interlaboratory trial of the FTIR technique in smoke gas analysis was carried out to define the repeatability and reproducibility of the method in connection with a small scale fire test method, the cone calorimeter.

Preface

This report presents the work performed in the SAFIR (Smoke Gas Analysis by Fourier Transform Infrared Spectroscopy) project within the European Standards, Measurement and Testing programme under Contract no. SMT4-CT96-2136. The project was initiated in February 1997 by the Commission of the European Communities, DG XII, in the SMT research programme.

The objectives of the SAFIR project were:

- to further develop the FTIR gas analysis of smoke gases to be an applicable and reliable method for the determination of toxic components in hot combustion gases related to fire test conditions;
- to produce a code of practice for the FTIR method which includes techniques of sampling, calibration and analysis; to assess the precision and area of application of FTIR in different fire test scenarios;
- to prepare a draft standard (including repeatability and reproducibility data) in a form suitable to be forwarded to the European standards organisations (CEN, CENELEC) as well as to the international standards organisations (ISO, IEC, IMO).

The member institutes and responsible/contact persons of the SAFIR Consortium were:

VTT	VTT Building Technology (coordinator) Esko Mikkola	Finland
Centexbel	Scientific and Technical Centre of the Belgian Textile Industry Jan Laperre	Belgium
GRL	Groupement de Recherches de Lacq Francis Gensous	France
FRS/BRE	Building Research Establishment, Fire Research Station Peter Fardell	UK
LNE	Laboratoire National d’Essais Yannick LeTallec	France
LSF SUD	L.S.F. SUD srl – Laboratorio di Studi e Ricerche sul Fuoco Franco Carradori	Italy
RAPRA	RAPRA Technology Limited Keith Paul	UK

SP	Swedish National Testing and Research Institute Margaret Simonson	Sweden
RUG	Universiteit Gent Caroline Deleu	Belgium
U.Greenw.	University of Greenwich Edwin Metcalfe	UK

The SAFIR project was divided into five work packages:

WP1	Sampling in small scale
WP2	Sampling in large scale
WP3	Data analysis, calibration and software
WP4	Verification in different fire scenarios
WP5	Interlaboratory trial

Acknowledgements

Contributions of the SAFIR partners are summarised in this final report of the project. VTT was responsible for compiling the final report with the assistance of many experts from the participating institutes. The principal authors of the chapters describing the work performed in the work packages are the following:

WP1: Yannick LeTallec, LNE
WP2: Margaret Simonson, SP
WP3: Jan Laperre, Centexbel
WP4: Peter Fardell, FRS/BRE
WP5: Tuula Hakkarainen, VTT

The Commission of the European Communities contributed to the SAFIR project through the SMT research programme. The remaining funding was raised nationally by the partners of the Consortium. A considerable portion of the work was funded by the partners themselves. Additional national sponsors were:

Finland: Centre for Metrology and Accreditation, Nordtest
Sweden: EU/FoUrådet, Nordtest, SRV

Contents

List of abbreviations

%SL	percentage significance level
$\Delta h_{c,eff}$	effective heat of combustion
ASTM	American Society for Testing and Materials
CCT	Classical Chemometrical Techniques
CEN	European Committee for Standardization
CENELEC	European Committee for Electronical Standardization
CLS	Classical Least Squares
CMHR	combustion modified high resilience (foam)
CO	carbon monoxide
CO_2	carbon dioxide
DIN	Deutsches Institut für Normung e.V.
DTGS	deuterated triglycine sulfate
FR	fire retarded
FR ABS	fire retarded acrylonitrile butadiene styrene
FR PVC	fire retarded polyvinyl chloride
FRPE	fire retarded polyethylene
FTIR	Fourier Transform Infra-Red spectroscopy / spectrometer
H_2O	water
H_2S	hydrogen sulphide
HBr	hydrogen bromide
HCl	hydrogen chloride
HCN	hydrogen cyanide
HF	hydrogen fluoride
HPIC	High Performance Ion Chromatography
HPLC	High Pressure Liquid Chromatography
HRR	heat release rate
IC	Ion Chromatography
IEC	International Electrotechnical Commission
IMO	International Maritime Organisation
IND	factor indicator function
INLR	Implicit Non-linear Latent variable Regression
ISE	Ion Specific Electrode
ISO	International Standardization Organisation
MCT	mercury cadmium telluride
MDL	Minimum Detection Limit
NDIR	Non-Dispersive Infra-Red analysis / analyser
NO	nitric oxide
NO_2	nitrogen dioxide
PC	Principal Component

PCA	Principal Component Analysis
PE	polyethylene
PFA	perfluoroalkoxy
PLS	Partial Least Squares
PTFE	polytetrafluoroethene
PU	polyurethane
PUR	polyurethane
PVC	polyvinyl chloride
QTFA	Quantitative Target Factor Analysis
RHR	rate of heat release
SBI	Single Burning Item (fire test method)
SMT	Standards, Measurement and Testing (research programme)
SO_2	sulphur dioxide
SS	stainless steel
THR	total heat release
t_{ig}	time to ignition
TML	total mass loss
TSP	total smoke production
WP	Work Package

1. WP1 – sampling in small scale

1.1 Objectives of WP1

The objectives of Work Package 1 were to define and optimise the FTIR sampling device in connection with different small scale fire tests. For this purpose, the different items of the sampling device were studied:

- the probe to collect effluents from the fire effluent stream,
- the filter to retain particles,
- the transfer line to transport the effluents to the FTIR analysis,
- the gas cell.

The basic requirements for the sampling system are: 1) the fire effluents shall remain unaltered during their passage, and 2) the transport of the gases is as quick as possible. The soot particles shall be mainly filtered out of the gas sample before it flows through the sampling line.

1.2 Participants of WP1

The participants of WP1 were:

VTT	VTT Building Technology	Finland
GRL	Groupement de Recherches de Lacq	France
LNE	Laboratoire National d'Essais	France
LSF SUD	L.S.F. SUD srl – Laboratorio di Studi e Ricerche sul Fuoco	Italy
RAPRA	RAPRA Technology Limited	UK

1.3 Structure of WP1

WP1 was divided into 5 subtasks, listed below with the partner responsible for the work presented.

- the probe: VTT was in charge of this work,
- the filter: LSF SUD was in charge of this work,
- the sampling line: RAPRA was in charge of this work,
- the gas cell: LNE was in charge of this work,
- the validation of the sampling device: GRL and LNE were in charge of this work.

1.4 Work performed in subtasks

The experimental work for each part of the sampling device is described below. The tests were carried out to determine the response of different sampling systems and operating conditions to find the optimal sampling configuration for the FTIR method in small scale fire tests.

1.4.1 Probe

The study of the probes was concentrated on linear probes. The parameters to optimise were the diameter of the holes, the shape of the probe (i.e. number and position of holes), and the orientation of the probe with regard to the stream. Circular probes were not studied due to their technical disadvantages: when holes are blocked by the soot produced during the combustion, this type of probe is difficult to remove and clean.

1.4.1.1 Results

Different simple linear probes were studied to optimise the diameter, position, and number of the holes (see Figure 1.1). All probes were made of stainless steel tube with inner and outer diameters of 4 and 6 mm, respectively. The upper end of the multi-hole probes was closed.

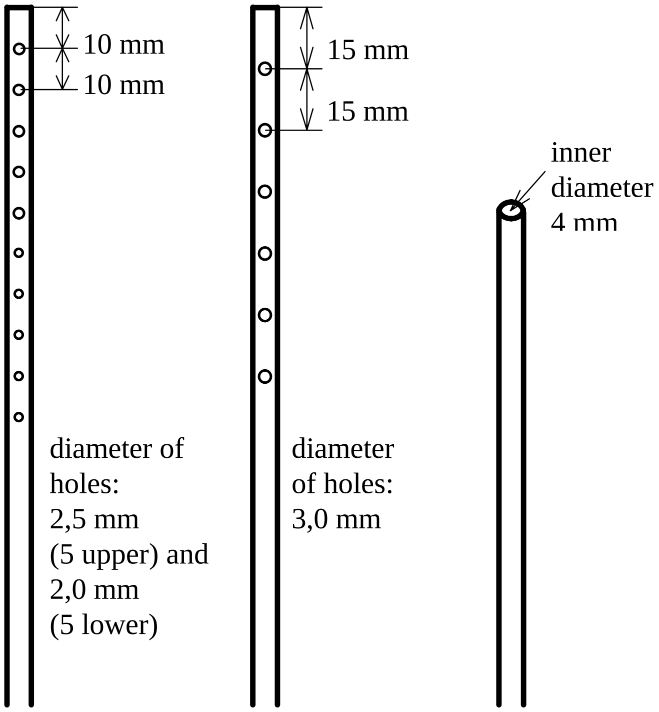


Figure 1.1. Different types of probes tested.

The tests were carried out using the cone calorimeter. The material used was FR ABS (fire retarded acrylonitrile butadiene styrene), producing very large amounts of smoke and soot.

The holes of the multi-hole probes were oriented either downstream or towards the flow. The hole of the open-ended probe was placed to the geometrical centre of the exhaust duct cross section, with the hole opening upwards perpendicular to the duct flow direction. The flow rate in the sampling was about 1 l/min in most tests, since a low flow rate represents the worst case of probe blocking. After each test, the probe used was removed from its socket, examined, and blown clean with pressurised air.

The tests performed to examine the blocking of the probes are described in Table 1.1. The effects of the hole size, hole orientation, and flow rate were studied. The blocking of the probe holes was scored using the following grading system:

0: totally open hole, no traces of soot observed
1: small amount of soot on the edges of the hole
2: significant amount of soot on the edges of the hole
3: totally blocked hole

The blocking indices shown in Table 1.1 were calculated as averages of the blocking scores. A large index indicates extensive blocking of the holes in average.

Table 1.1. Description of probe tests. Probe number key: 1: linear multi-hole, 5 × 2,5 mm and 5 × 2,0 mm holes; 2: linear multi-hole, 6 × 3,0 mm holes; 3: open-ended, 1 × 4,0 mm hole.

Test	Probe	Hole orientation	Flow rate (l/min)	Hole size (mm)	Blocking index
1	1	towards the flow	1	2,0 2,5	3,0 1,8
2	1	downstream	1	2,0 2,5	2,8 1,4
3	1	downstream	5	2,0 2,5	2,2 1,0
4	2	towards the flow	1	3,0	1,5
5	2	downstream	1	3,0	1,0
6	3	upwards	1	4,0	0,0

This study puts forward three main results:

- Decreasing sample flow rate tends to increase the blocking of the holes (comparison of tests 2 & 3),
- Blocking is more severe with the probe holes pointing towards the flow than with the probe holes pointing downstream (comparison of tests 1 & 2 and 4 & 5),
- The blocking index decreases with the increasing of the hole diameter (comparison of tests 1 & 4 and 2 & 5).

The blocking of the holes becomes more significant if several specimens are tested without cleaning the probe between successive tests.

In addition to the cone calorimeter tests, the applicability of the results to other small scale test methods were estimated. The exposed area and thickness of the specimen, the smoke and soot production, the cross area of the exhaust duct, and the burning characteristics of specimens in each test method were considered in the calculations. According to these estimations, the same minimum diameter is applicable to the sampling opening in the DIN furnace method (a probe is traditionally not used in this test method) as to the probe holes in the cone calorimeter method.

1.4.1.2 Main conclusions and recommendations

The main conclusions of the probe study are the following:

- A multi-hole probe made of stainless steel is the best compromise to collect a representative sample of non-homogeneous gaseous products without blocking the holes. The probe shall be long enough to sample over the whole diameter of the duct,
- An open-ended probe can be used if the smoke gases are mixed uniformly or sampling from a single point is appropriate,
- A minimum hole diameter of 3 mm is recommended for the FTIR probe in cone calorimeter experiments as well as for the FTIR sampling opening in DIN furnace tests,
- The probe holes should be placed downstream in order to limit the blocking of holes,
- The probe should be cleaned at least in connection with normal service of the test equipment. If exceptionally sooty tests are performed, cleaning should be carried out more often. Cleaning is recommended also between the test series of different products to avoid disturbance from possible traces of soot.

1.4.2 Filter

This part of the programme was divided in two parts: a questionnaire concerning the filters used by all the partners of the SAFIR programme and an experimental study by LSF SUD.

1.4.2.1 Questionnaire

For both small and large scale tests, a variety of trapping problems of HCl of varying severity was reported by the partners. Significant trapping of HBr was also observed. Trapping of HCN seemed not to be a problem as the HCN amounts detected in filters were negligible.

Cylindrical and circular filters are used with a predominance of cylindrical filters (i.e. glass fibre, ceramic fibre or PTFE). The area of FTIR filter was also presented in an effort to analyse its influence.

1.4.2.2 Experimental results on circular filter

The fire model used for the experimental study was the ASTM E 662 test method. The conditions for the tests were as follows: temperature of sampling line 170°C, sampling line flow rate 7 l/min (measured immediately after the gas cell, the actual flow rate was thus lower), gas cell temperature 170°C, sampling line length 2 m, and filter heating by heating tape with thermocouple and thermoregulator control. The shape of the filtering device was circular for all experiments.

The filter parameters studied were :

- the filter temperature (160°C, 175°C, 190°C)
- the filter diameter (25 mm, 47 mm and 90 mm)
- the porosity of the filter (0,45 µm, 1 µm, 5 µm)
- the membrane material (glass fibre, PTFE)
- the filter holder material (stainless steel, polyamide, PTFE)

Two materials were used: plasticised PVC and expanded rubber. In addition to the FTIR measurements, potentiometric ISE (Ion Specific Electrode) was carried out for chloride and bromine compounds (by washing filter and analysing the solution to determine the amount of gases blocked on the filter).

The following conclusions were drawn:

- HCl detected by FTIR increases with the increasing temperature of the filter device and HCl retained on the filter (determined by ISE) decreases when the temperature increases.
- The filter with lower porosity obstructs the flow rate more. The porosity did not have the same influence for both materials tested. The contradictory situation for the materials evaluated does not permit the best choice. General consideration suggests the choice of 5 μm porosity.
- The PTFE membrane inhibits the sampling flow rate. With PTFE membrane, the FTIR detectability of HCl and HBr is improved for PVC but deteriorated for expanded rubber compared to glass fibre membrane. Having different behaviours depending on the type of the deposit, glass fibre membrane is recommended based on general aspects and evaluations. However, if a considerable amount of HF is expected to be produced in the test, PTFE membranes or ceramic filters are recommended instead of glass fibre filters due to the capability of HF to etch glass.
- The amount of blocked HCl and HBr increases with increasing filter diameter. On the other hand, obstruction of sampling flow rate was decreased with larger filters. The best compromise between the blocking of gases and the flow rate appears to be a filter with a diameter of 47 mm.
- The stainless steel filter holder exhibited the best performance in the tests. The PTFE filter holder was problematic due to its tendency to sealing at high temperatures. The polyamide filter holder showed an intermediate behaviour.

1.4.2.3 Unfiltered systems: “dirty cell” technology

Recent developments have included the so-called “dirty cell” which is claimed to be capable of analysing unfiltered fire gases, i.e. gases which contain soot and other particles. These cells have only become available recently and consequently have not been evaluated in the SAFIR project. However, it should be acknowledged that the presence of soot in the FTIR cell can cause problems such as the absorption and scattering of the infrared beam, and the deposition of soot on the mirrors and windows of the cell. The major advantage of “dirty cells” is that they are easily cleaned.

It is suggested that users of “dirty cells” should assess the performance of such cells in a similar manner to that described for the fire gas sampling system recommended by the SAFIR project.

1.4.2.4 Main conclusions and recommendations

The following conclusions could be proposed for a circular filter:

- holder: stainless steel

- membrane: glass fibre (not suitable if HF is produced)
- diameter: 47 mm
- porosity: 5 μm
- temperature: as high as possible, with the minimum of 150°C and the practical maximum of about 190°C.

On the filter shape only a little information is available; there is no study concerning the comparison between circular and cylindrical filters. The questionnaire answers showed that cylindrical filters are used more frequently.

Further recommendations concerning all types of filters are noted:

- The filter shall be placed between the probe and the transfer line (as close to the probe as possible).
- A second filter could be used between the transfer line and the gas cell to limit the amount of soot into the gas cell.
- If acid gases are analysed or if there are difficulties during the test (e.g. blockage) the filter should be analysed.
- Cylindrical or circular filter can be used depending on the fire test and the amount of soot produced during the combustion. When a lot of soot is expected, high capacity filters are recommended. The area of the filter is probably the most important factor in the efficiency.

1.4.3 Sampling line

Different types of gas sampling lines and conditions for fire gas sampling and FTIR analysis were studied. It was considered that the most important fire gases are CO, CO_2, HCN, HCl, SO_2, acrolein, NO, NO_2, HBr. Of these gases, CO_2, CO, HCN and HCl were considered to be the most relevant in terms of toxicity and different behaviour patterns. These four gases were used for all evaluations. Additional gases from the main list were used for more detailed evaluations.

In the experimental programme, the gas to be studied was passed through gas sampling lines of different materials at pre-set temperatures and flow rates. The gas was allowed to flow for specified time periods, and each period was followed by a similar air purge period. 4 - 5 gas sample doses were used for each test run. The gas concentration vs. time curves were determined using FTIR, and the time to the initial FTIR response and the 90 % response times for increasing and decreasing gas concentrations were determined.

1.4.3.1 Results

The parameters studied were the temperature and material of the gas sampling line, and the sampling flow rate in the line. Three lengths of lines were evaluated.

The selection of the sampling line material depends on the general environment, the temperature of operation and the gases to be sampled. Table 1.2 presents the sampling line materials included in this study with their advantages and disadvantages.

Table 1.2. Advantages and disadvantages of sampling line materials.

Material	**Temperature of operation**	**Advantages**	**Disadvantages**
PTFE (polytetrafluoroethene)	up to 190 °C	• flexible, easy to install and replace, cheap	• increase of temperature of the effluents may increase the temperature in the line
Stainless steel	no practical limitation for this application		• liable to etching by acid gases • could interfere with NO_x analysis • not easy to install
PFA (perfluoroalkoxy)	up to 190 °C	• flexible, easy to install and replace • slightly superior resistance to HCl compared to PTFE	• expensive

In the main test programme with all three materials, PTFE and PFA offered generally similar performance which was better than that of stainless steel. Since PFA presented no significant improvements compared to PTFE, further tests were carried out with PTFE lines.

The following test programme was performed for PTFE lines:

- In the first stage, tests were carried out using a 4 metre line at three temperatures (140, 160 and 180°C) and at three flow rates (2, 3,5 and 5 l/min). Analysis of the results showed that most gases behaved in a similar manner except HCl which gave significantly longer 90 % response times.
- A pre-aged PTFE line was tested. The adsorption of HCl seemed to be less when the PTFE line was pre-aged. Unfortunately, the experiments did not provide more information on the type or mode of ageing. According to these results, it seems to be sufficient to expose the line to HCl before use.
- In a second stage, tests with PTFE lines with different lengths were carried out: the lengths were 2 m and 10 m. Analysis of results for PTFE lines of 2 and 10 m showed generally similar results to those obtained with the 4 m line for CO_2, CO and HCN. Results for HCl were different and showed longer 90 % response times for both

increasing and decreasing concentration transients. The 4 m line used for the tests had been previously used for fire gas sampling but had been thoroughly cleaned before the tests were carried out. In contrast, the PTFE lines of 2 and 10 m used in the tests were new. Tests with the 4 m PTFE line were repeated using lines taken from the same roll as that used for 2 and 10 m line tests.

- It was noticed that HBr has even longer response times and greater losses than HCl.

1.4.3.2 Main conclusions and recommendations

The recommendations for the sampling line are:

- A gas sampling line made of PTFE offers the best performance.
- A pre-aged PTFE line permitted to limit the problems observed with HCl. However, only a little information is available regarding the method for conditions and duration of pre-conditioning the line. Optimum results require the line to be exposed to fire smoke containing HCl, or at least to HCl, before use.
- The inner diameter of the line could be 3 to 4 mm. The length should be as short as possible: 4 m is acceptable. Problems may arise with longer lines because of greater delays and sample losses (cold points where condensation could arise).
- The temperature of the line shall be as high as possible with a minimum of 150°C.
- The flow rate shall be as high as possible with a minimum value of 3,5 l/min.

1.4.4 Gas cell

This work was divided in two parts: analysis of the gas cells used by the SAFIR partners (questionnaire answers), and the determination of the response time of the gas cell.

The answers to the questionnaire exhibited the large variety of gas cell in use. These answers showed the difficulties to find common working conditions to set for all partners, concerning differences not only between gas cells but also between spectrometers and sampling devices.

1.4.4.1 Results

The procedure for the determination of the time response was based on the introduction of standard CO_2 gas into the FTIR sampling line. The kinetic of concentration versus time allowed the determination of the response time. The acquisition parameters were set by the procedure and the laboratories kept their own sampling configurations.

The analysis of the results showed that the variation of the response time is not directly proportional to the volume of the cell and/or the sampling line.

The main factor in the response time is the gas cell. The delay effects on the transfer line and the filter are usually of minor importance.

The effect of the gas cell pressure on the measured concentration was evaluated. A flow of 10 l/min from a standard gas cylinder with 2000 ppm of CO_2 was passed through the FTIR analyser and the pressure in the gas cell was modified. The results obtained showed a significant effect on the evaluation of concentration as illustrated in Figure 1.2.

According to IR spectroscopy theory, absorbance A can be written:

$$A = a \cdot p \cdot l \tag{1}$$

in which a is the absorbance coefficient of the gas, p is the partial pressure of the gas, and l is the length of the optical path. Thus, a pressure variation in the gas cell is read by the IR analyser as a variation of the absorbance and consequently as a variation of the concentration.

The connection between the absorbance A and cell pressure p is:

$$\frac{A}{A_0} = \frac{p}{p_0} \tag{2}$$

in which A_0 and p_0 are the absorbance and cell pressure during calibration. This relation was used to calculate corrected concentrations, by multiplying the measured concentration by the ratio between the calibration pressure and the actual pressure. As shown in Figure 1.2, the corrected concentration is very near to the actual concentration of 2000 ppm, with a slight decrease when pressure increases. It must be noted, however, that the non-linear behaviour of CO_2 is not taken into account in the correction.

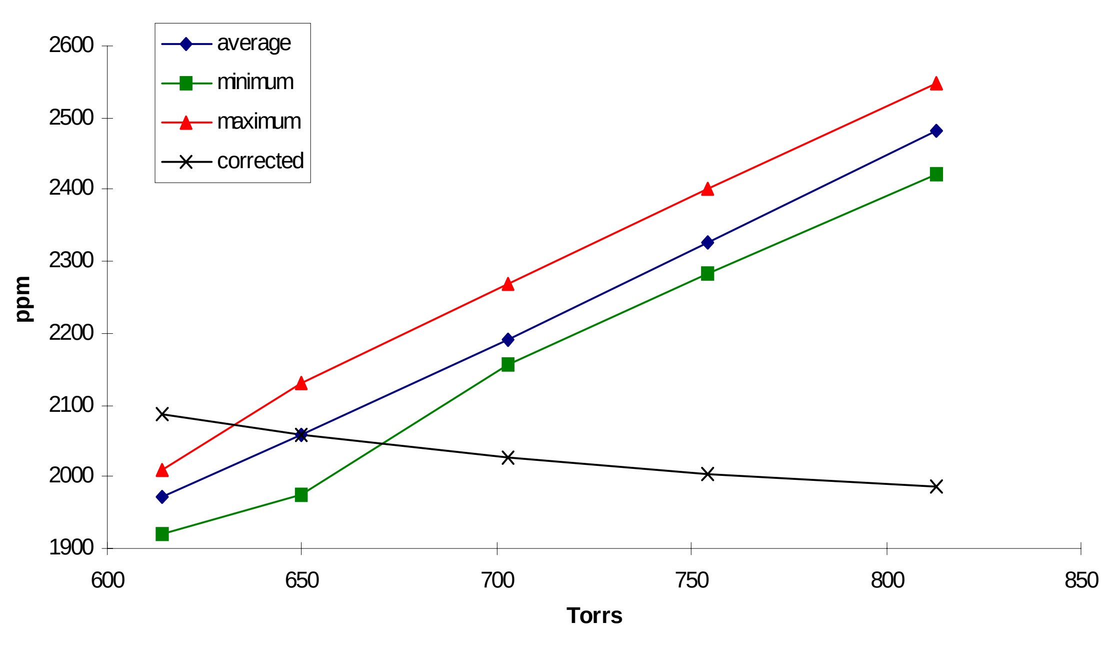


Figure 1.2. Influence of gas cell pressure on measured CO_2 concentration. The calibration pressure is 650 torr.

1.4.5 Optimised sampling device

An optimised sampling device is proposed to follow the recommendations given above. In addition, some further recommendations are suggested:

- The point for gas collection in the exhaust duct shall be placed at a distance where the gaseous mixture is homogeneous and the gas flow is not disturbed.
- The distance between the combustion area and the probe should be as short as possible to avoid condensation.
- The filter must be placed between the probe and the transfer line. Another filter can be used between the line and the gas cell to protect the cell from fine soot particles.
- The flow meter shall be placed after the pump and it is recommended to trap the water between the pump and the flow meter.
- The temperatures of the filter, sampling line and gas cell should be as similar as possible.

Figure 1.3 presents a diagram of the optimised sampling device.

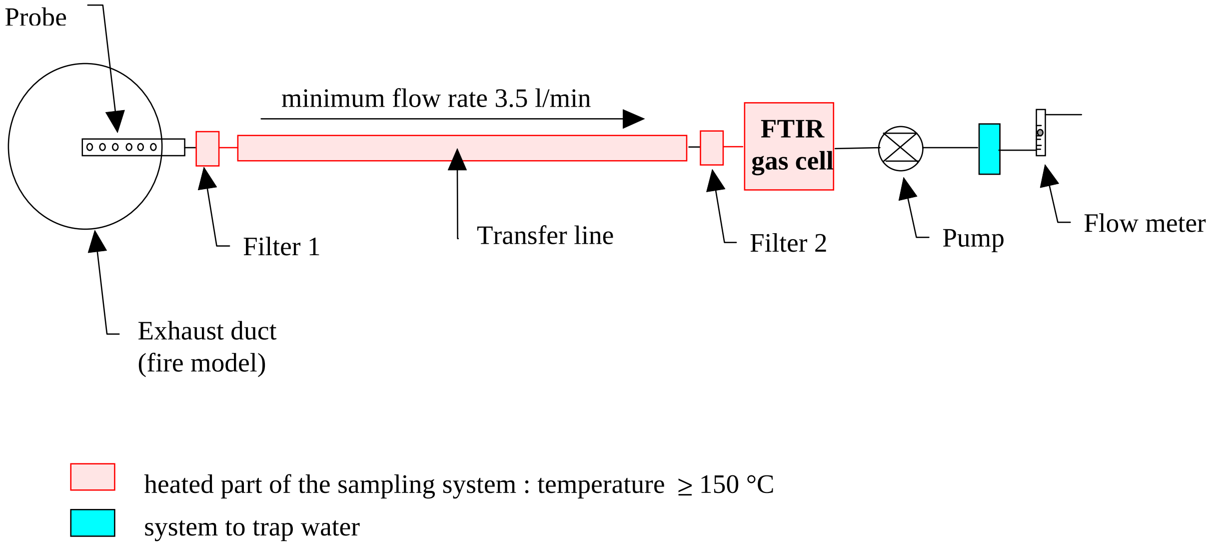


Figure 1.3. Diagram for optimised sampling system.

1.4.6 Validation of sampling device

The validation tests were carried out using the cone calorimeter as fire model. Two types of experiments have been done: the first one according to the definition of the optimised sampling device and the second one with addition of impingers and analysis of the solution by Ion Chromatography (IC).

Before testing the material with the cone calorimeter, the presence of Cl or Br in the filters was studied by washing the filters and analysing the solutions. The analysis of unused filters showed that the cylindrical filters studied contain a non-negligible amount of chlorine.

The cylindrical filters used in the validation study of WP1 were glass fibre filters with a silicate binder. The mass of the filters was about 5,3 g, and inner and outer diameters were 25,4 and 31,8 mm, respectively.

Using the cone calorimeter, three materials were tested: rigid PVC, expanded rubber and PVC foam. Rigid PVC and expanded rubber were tested already in the study of the filter definition.

HCl and HBr quantities retained by the filter are typically rather low (ca. 500 - 1000 µg). The proportion of the acid gas adsorbed on the filter decreases with increasing concentrations. Due to saturation, the retention in the filter causes no major problem at high concentration levels. However, special care is recommended when the production of acid gases is low.

The following conclusions and recommendations can be given for both cylindrical and circular filters:

- Initial quantities of Cl and Br in new filters must be checked. If these quantities are high, and if HCl and HBr retained by the filter during an experiment must be measured, the filter must be washed before use. Washing with hot water followed by drying in an oven is suitable. The washing procedure must be adapted suitable for each type of filter.
- The "time response" of the sampling line is higher for HCl and HBr than for other gases. Therefore, maximum concentrations will be underestimated especially in case of fast concentration changes of these gases.
- All parts of the sampling device must be washed with water when acidic gases are analysed by FTIR, especially when the amount of gas analysed is low.

1.5 Conclusions

The work performed in WP1 has permitted the definition of an optimised sampling system and to give some recommendations.

The main conclusions and recommendations of this study are the following:

- A multi-hole probe is the best compromise to collect a representative sample of non-homogeneous gaseous products. The probe shall be long enough to sample over the whole diameter of the duct.
- The probe shall be made of stainless steel. The minimum hole diameter of 3 mm is recommended.
- A gas sampling line made of PTFE offers the best performance.
- A pre-aged PTFE line reduces the problems observed with HCl. Optimum results require the line to be exposed to fire smoke containing HCl or at least to HCl before use.
- The inner diameter of the line could be 3 - 4 mm. The length should be as short as possible: 4 m is acceptable. Problems may arise with longer lines.
- Two types of filters, circular or cylindrical, can be used. The initial amount of Cl and Br in the filters shall be checked. If non-negligible amounts of Cl or Br are detected, the filters shall be washed before use when acid gases are measured.
- The flow rate shall be as high as possible with a minimum value of 3,5 l/min.
- The temperature of the sampling device shall be as high as possible with a minimum of 150°C. To avoid cold points where condensation could appear, the temperatures of the different parts should be as close to each other as possible. If the same temperature cannot be maintained in all parts of the sampling system, the temperature shall preferably increase towards the end of the device. The practical upper limit of the sampling device temperature is about 190°C.

- When acid gases are analysed by FTIR, it is recommended that the different parts of the sampling device should be washed after the test, especially when the concentrations determined are low. The washing solution should be analysed by appropriate analytical methods to evaluate the total amount of the gas produced in the combustion. Due to saturation, the HCl and HBr retention in the sampling device causes no major problems at high concentration levels.
- The pressure in the gas cell must be checked during the experiments because the variation of the pressure inside the sampling configuration leads to a significant variation in the measured concentrations of gaseous products.

2. WP2 – Sampling in large scale

2.1 Objectives of WP2

WP2 aimed to test the correctness of the concentrations extracted from FTIR spectra measured in large scale tests with possibly high soot concentrations and high temperatures. Thus, the construction of probe, choice of filter, pumping regime, probe temperature, and inlet configuration needed to be optimised taking into consideration the special features of large scale testing. The work relied heavily on the results from WP1.

2.2 Participants of WP2

The participants in this work package were: Fire Technology, Swedish National Testing and Research Institute, Sweden (SP); Fire Research Station, Building Research Establishment, U.K (FRS); and Laboratory for Heat Transfer and Fuel Technology, University of Ghent, Belgium (RUG). SP was responsible for this work package.

2.3 Structure of WP2

WP2 was divided into two parts: duct measurements and door measurements. The door experiments were conducted by SP and all participants were active in the duct measurements. The high soot concentrations and high temperatures were expected to be found in the door.

2.4 Duct experiments

2.4.1 Experimental description

Commercial grade plasticised PVC sheeting was tested in the two duct experiments carried out by RUG in the ISO 9705 Room. Two sheets of PVC were mounted in a corner configuration (1 m × 0,5 m × 0,09 m) with the standard ISO 9705 room burner used as the ignition source. The standard SBI duct probe (described below) was used for all duct sampling in all the labs. The following specific gas sampling arrangement was used for the FTIR apparatus at RUG:

Sampling line	Filter	Probe
Material: PTFE	Material: cylindrical, glass fibre	Material: SS
Temperature: 180°C	Temperature: 170°C	Type: linear, multi-hole
Length: 4 m	Housing: M&C SP 2000	Hole size: 2 mm and 3 mm
Pump flow: 7 l/min	Porosity: 0,1 µm	

One duct measurement was conducted by FRS with the equipment connected to the duct of the SBI room. Polyolefin based communication cables were burnt according to the SBI protocol. The same probe was used in these experiments as that described above for RUG. The following setup was used for the sampling line and filtration system:

Sampling line	Filter
Material: PTFE	Material: cylindrical, PTFE/quartz
Temperature: 160°C	Temperature: >130°C
Length: 8 m	Housing: SS
Pump flow: 8 l/min	Porosity: 0,1 µm

Finally one duct measurement was conducted at SP with FTIR measurements in the duct of the ISO 9705 room using polyolefin based cables. A linear multi-hole probe was used for extraction of the sample as above, while the following setup was used for the sampling line and filtration systems:

Sampling line	Filter
Material: PTFE	Material: cylindrical, ceramic
Temperature: 180°C	Temperature: 180°C
Length: 7 m	Housing: SS, M&C SP 2000
Pump flow: 4 l/min	Porosity: 2 µm

2.4.2 Experimental results

The results of the first experiment conducted at RUG are summarised in Table 2.1. Similar results are not available for the second experiment due to FTIR malfunction.

Table 2.1. Total and average concentrations in the ISO 9705 test of PVC sheeting. Total concentrations were calculated up to 1017 seconds; average concentration were based on the period 552 - 1002 s.

Apparatus	ISO 9705 analysers, Total conc.	FTIR, Total conc.	ISO 9705 analysers, Av. conc.	FTIR, Av. conc.
CO	102 100 ppm x s	73 000 ppm x s	4 ppm	11 ppm
CO_2	248 % x s	296 % x s	0,245 %	0,28 %
HCl	N.A.	452 800 ppm x s	N.A.	450 ppm

The glass fibre filter was found to contain 7,8 mg of HCl while a total of approximately 86 mg HCl went through the FTIR. This corresponds to a retention of about 8,3 % HCl in the filter. The second experiment gave a similar result with approximately 9,6 mg HCl retained in the filter. Assuming that a similar amount of HCl passed through the FTIR in experiment 2 as in experiment 1 this would correspond to a retention of 11 %.

At FRS, cables were burnt according to the SBI protocol. Due to problems with the FTIR spectrometer, no quantitative information was obtained. Spectra were retrieved but sensitivity was too low to allow the extraction of quantitative results. It was, however, possible to see evidence of CO, CO_2 and H_2O but not of HCl. The filter chosen behaved well and showed an adequate capacity with no problem observed with clogging which would have lead to a pressure drop in the FTIR gas cell. Further, the probe configuration provided steady sampling with no build up of soot observed around the holes implying that this probe is indeed suitable for use in this context. Finally, the sampling line was able to be maintained at a constant high temperature and showed no adverse effect of thermal stress. These observations confirmed the results from WP1 concerning this sampling line configuration.

FTIR measurements on the polyolefin based cables tested at SP were made in the duct at the same point that fire gases are extracted for CO_2 and O_2 concentration determination for use in the calculation of the heat release rate. Thus a comparison can be made between the CO_2 measurements made with the FTIR and those made with the standard ISO 9705 room CO_2 analyser. These results are summarised in Table 2.2.

Table 2.2. Comparison between FTIR measurements taken in the duct of the ISO 9705 room and those taken in the duct using the ISO 9705 room analysers.

Apparatus	**ISO 9705 analysers, Av. conc.**	**FTIR, Av. conc.**
CO_2	0,67 %	0,62 %

The FTIR results underestimate the CO_2 concentration by 8 %. Thus the results from RUG and SP show an agreement between the FTIR and ISO room CO_2 analyser of approximately ±15 %.

2.5 Door measurements

2.5.1 Experimental description

The following configuration was used in the experiments. Both filter configurations were tested to determine whether they are suitable for door measurements:

Sampling line	Filter 1	Filter 2
Material: PTFE	Material: cylindrical, ceramic	Material: membrane, glass fibre first followed by PTFE
Temperature: 180°C	Temperature: 180°C	Temperature: 180°C
Length: 7 m	Housing: SS, M&C PSP 4000H	Housing: SS
Pump flow: 4 l/min	Porosity: 2 µm	Porosity: 5 µm
		Diameter: 47 mm

Three different probe configurations were tested. *Probe 1* had a single hole (∅ 6 mm), *Probe 2* had 7 holes with 10 cm between each (∅ 3 mm), *Probe 3* had 7 holes with 10 cm between each hole and with hole size having the following diameter distribution: 1,5 mm, 1,6 mm, 1,8 mm, 2,1 mm, 2,5 mm, 3,2 mm, 5,0 mm.

The validation samples were taken in the standard duct sampling position for the ISO 9705 room with the CO_2 measurements being made using the standard ISO 9705 room analyser while the HCl measurements were made using impinger bottles. The gas sample to the impinger bottles was filtered through a cylindrical filter of the same type as that tested in the door. Both the filter in the door and the filter in the duct were changed after each test and analysed for traces of HCl.

The FTIR concentrations were evaluated using peak height to baseline where 2798 cm^{-1} was used as the peak and 2810 cm^{-1} as the baseline for HCl; and 2392 cm^{-1} was used as the peak and 2433 cm^{-1} as the baseline for CO_2 (water was not subtracted in either of these two cases as water does not absorb in these regions).

It was necessary to calculate of the gas flow out of the door to facilitate the comparison between concentrations measured in the door and in the duct. The method used to estimate the flow of the gases out of the door is described in more detail by Drysdale [1]. A list of the experiments conducted is given in Table 2.3.

Table 2.3. Summary of door experiments for WP2.

Experiment	Probe inlet	Filter	Fuel	HCl added	HCl Validation
1	probe 1, position 1*	1	propane	-	-
2	probe 1, position 2**	1	propane	-	-
3	probe 2	1	propane	-	-
4	probe 3	1	propane	-	-
5	probe 3	1	propane	~1000 ppm	Yes
6	probe 3	1	propane	~100 ppm	Yes
7	probe 3	2	propane	~100 ppm	Yes
8	probe 3	2	propane	~1000 ppm	Yes
9	probe 3	1	heptane	~100 ppm	Yes
10	probe 3	1	heptane	~1000 ppm	Yes
11	probe 3	2	heptane	~100 ppm	No
12	probe 3	2	heptane	~1000 ppm	No

* Position 1 has the probe opening centred horizontally and placed 10 cm below the top of the door.
** Position 2 is as above horizontally with the probe placed 30 cm below the top of the door.

2.5.2 Experimental results

Experiments 1 - 4 were used to study the effect of the choice of probe on the reliability of measurements in the door of the ISO room. A comparison between the heat release rate and CO_2 concentration measured in the duct shows that these values are equivalent for all four experiments indicating that the measurements made in the door should also be equivalent. Thus, any differences in the measured concentration in the door must be due to differences in the probe configurations. The FTIR measurements made in the door are summarised in Table 2.4.

Table 2.4. CO_2 concentrations measured in the door for experiments 1 - 4.

Experiment	CO_2 conc.	Probe No.	Position
1	2,54 %	1	1
2	2,29 %	1	2
3	2,34 %	2	crossing gases *)
4	2,30 %	3	crossing gases *)

*) Probes 2 and 3 crossed the top of the door opening with the 7th measurement point being placed ca. 30 cm below the top of the door.

Experiments 1 and 2 indicate that there is a small vertical gradient in the CO_2 concentration across the hot fire gases. The concentration of CO_2 is highest at the top of the door and lower as one approaches the neutral zone. The fact that the CO_2 concentrations are very similar in experiments 3 and 4 indicates that it dips quickly to the lower level measured in experiment 2.

Experiments 5-8 were carried out using the propane burner. These experiments exhibit a constant heat release rate across most of the experimental period (see Figure 2.1a). The concentration of CO_2 has been used to validate the functionality of the FTIR measurements in the door. An average flow through the door was calculated using Rockett's theory [1]. Using this information, measurements in the door can be corrected to correspond to expected results in the duct. These have been compared to actual measurements made in the duct for CO_2, with the results summarised in Table 2.5. The experiments all show an acceptable agreement between the $\%CO_2$ in the door and that in the duct.

Table 2.5. Comparison between CO_2 measurements made in the door and the duct.

Experiment	Time for calc. of mean values	$\%CO_2$ in duct	Corrected $\%CO_2$ in door	% difference
5	9:06 - 22:40*	0,84	0,87	+ 3,5 %
6	5:50 - 23:23*	0,81	0,85	+ 4,9 %
7	5:30 - 23:00*	0,83	0,84	+ 1,2 %
8	5:30 - 16:50*	0,81	0,81	+ 0 %
9	7:00 - 10:00	0,39	0,38	- 2,6 %
10	6:00 - 9:00	0,42	0,40	- 4,8 %
11	5:00 - 8:00	0,42	0,40	- 4,8 %

* Time corresponds to the period for measurement using the impinger bottle.

The propane experiments display extremely stable behaviour for all species and temperature profiles except for HCl. Thus evaluation of CO_2 both in the duct and door is reasonably reliable for experiments 1 - 8. Figure 2.1a shows the heat release rate (HRR) and CO_2 concentration, measured in the duct, for experiment 5. The heptane fires, however, exhibited a less stable heat release and CO_2 production behaviour. Evaluation of species concentration for these experiments is therefore expected to be somewhat less exact. Figure 2.1b shows the HRR and CO_2 concentration for experiment 9.

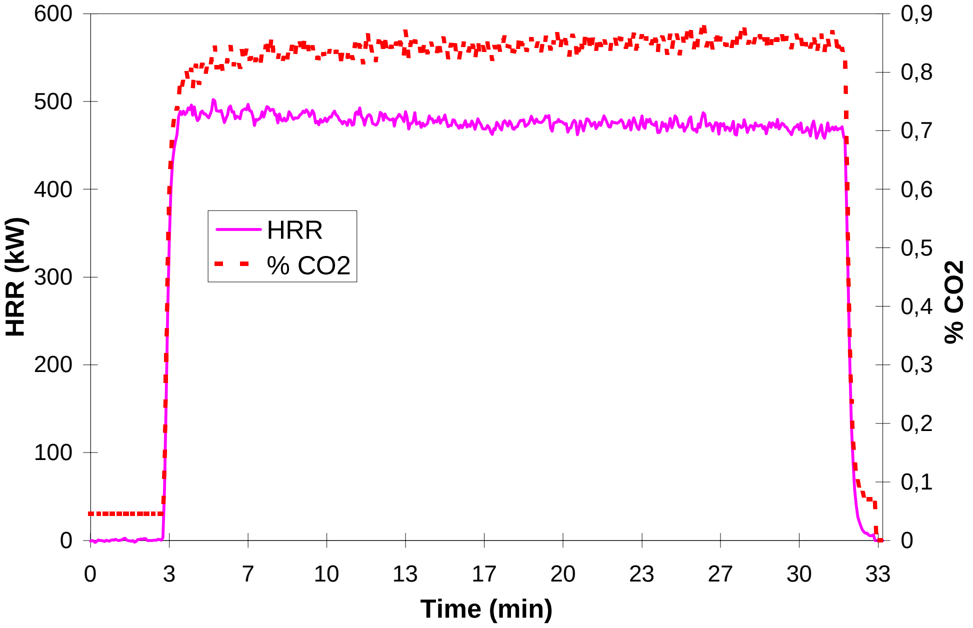


Figure 2.1a. HRR and CO_2 concentration profiles for experiment 5.

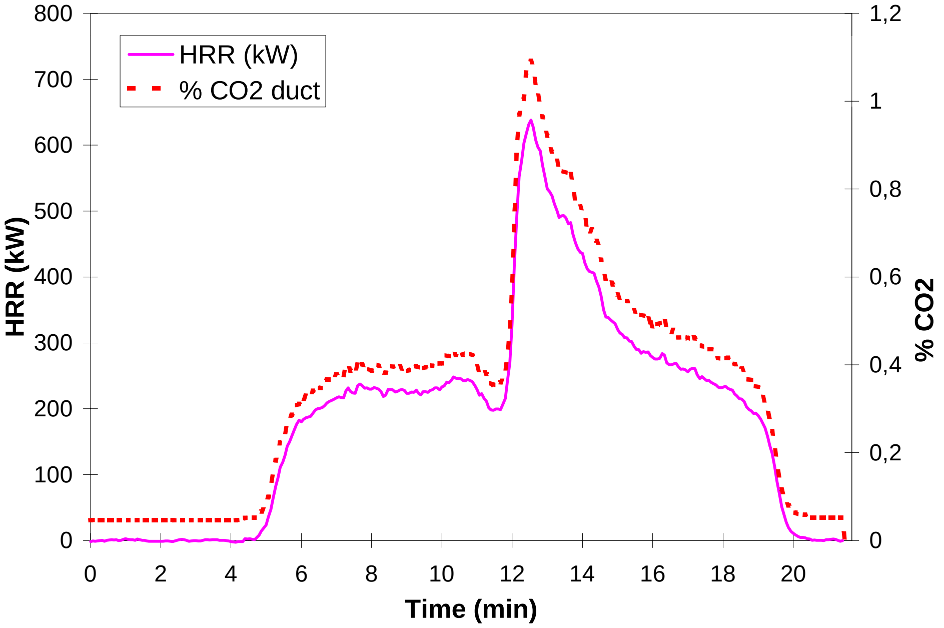


Figure 2.1b. HRR and CO_2 concentration profiles for experiment 9.

Validation of HCl concentrations in these experiments is based on impinger bottle measurements made in the duct. As the HCl concentration has not been stable throughout the experiments but is seen to increase, a comparison is made between the total amount of HCl measured in the door and duct. A representative HCl profile measured using the FTIR is shown in Figure 2.2a for experiments 5 - 8 and in Figure 2.2b for experiments 9 - 12.

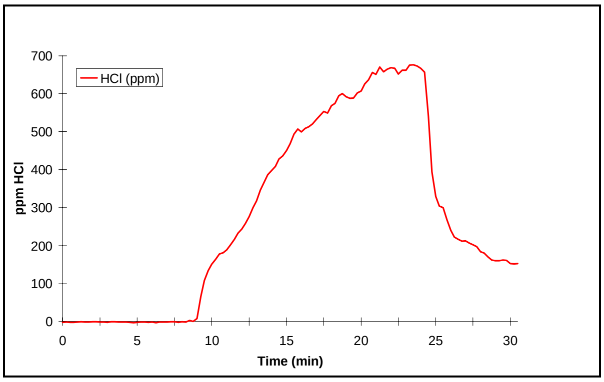


Figure 2.2a. HCl profile for experiment 5 measured in the door of the ISO room using the FTIR spectrometer.

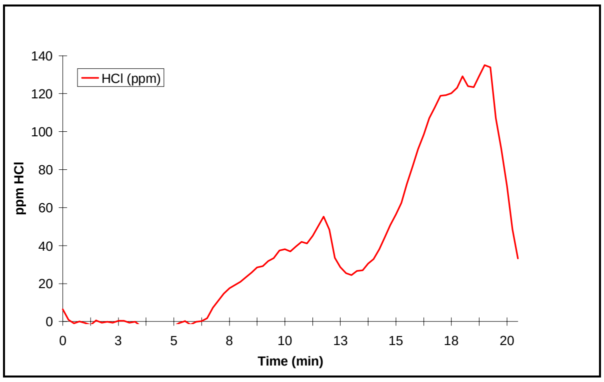


Figure 2.2b. HCl profile for experiment 9 measured in the door of the ISO room using the FTIR spectrometer.

The chemical analysis of the filters both in the door and duct measurements showed that there was no significant retention of HCl in the cylindrical filter in any experiment, i.e., independent of the HCl concentration. There does seem to be a slightly greater retention of HCl in the planar filter, however. In all cases there was a higher percentage retention of HCl when the concentration of HCl was low. This would imply saturation behaviour where a certain level of HCl is adsorbed initially but that once a given adsorption level is reached less of subsequent HCl is adsorbed.

The impinger bottle measurements of HCl in the duct can be adjusted to calculate the amount of HCl in grams that has gone through the duct over a well defined period. Agreement between measurements made in the duct and those made in the door is good when HCl concentrations have been reasonably high and the total amount of HCl to pass through the system is high. This is in agreement with findings of WP1 which indicate that the system becomes saturated after a certain exposure to HCl. In the case of low concentration levels this saturation is not achieved and the HCl measurements both in the door and in the duct are unreliable and the relationship between the two is unclear. The results are summarised in Table 2.6.

Table 2.6. Results concerning HCl measurements in the duct and door.

Exp.	Time for calc. of total	Tot. HCl from gas cylinder (g)	Tot. HCl in duct (g)	Tot. HCl in door (g)	% difference
5	9:06 - 22:40	598	415	356	- 14 %
7	5:30 - 23:00	127	14*	44	+ 214 %
8	5:30 - 16:50	626	271	283	+ 4 %
9	6:20 - 19:00	99	45	40	- 11 %
10	4:45 - 15:30	649	281	241	- 14 %

- The amount of HCl measured in the impinger bottle was very small and thus the accuracy of this value is correspondingly low. The % difference is an indication of this.

2.6 Conclusions

An optimal sampling system for large scale testing can be recommended based on the combined results from WP1 and WP2. Most of the recommendations from the small scale investigations carried out in WP1 are applicable to the large scale. There are, however, some features of the measuring system that are specific for large scale testing. The conclusions are, therefore, divided into a list covering general features and a discussion more specifically related to large scale testing.

General

- A multi-hole probe is recommended, with the holes downstream from the fire gases.
- A minimum hole size of 3 mm is recommended unless clogging of the probe is not expected to occur.
- The probe should be cleaned regularly.
- PTFE is recommended for the sampling line.
- The sampling line should be kept as hot as possible (min. 150°C) and as short as practical (max. 4 m if possible).
- Either cylindrical or membrane filters are recommended between the probe and the sampling line.
- Filters should be kept at as high a temperature as possible (min. 150°C).
- Should one have reason to suspect the retention of acid gases or other species in the filter then the filter should be analysed. In this case the filter should be changed between each test and inert material chosen for the filter where possible.
- Pump speed should be as high as possible (recommended level of at least 3,5 l/min for most applications).
- The temperature of the whole sampling system should be kept as even as possible.
- If the same temperature cannot be maintained in all parts of the sampling system, the temperature shall preferably increase towards the end of the device.

Special features for large scale tests

- When measuring in the inhomogeneous fire gases the probe holes should increase in size away from the pump. The specific holes sizes depend on the length of the probe and hole spacings.
- Due to the size of the testing facilities it may be difficult to keep the sampling line short. In cases where the sampling line is very long and acid gases are being studied it is advisable to wash the line to check for adsorbed species.

3. WP3 – Data analysis, calibration and software

3.1 Objectives of WP3

The objective of work package 3 was to study different techniques for the prediction of concentration of toxic gases, such as SO_2, HCl, Acrolein, HCN, NO, NO_2, HBr, CO and CO_2, in smoke gases.

The prediction of gas concentration generated during a fire test involves several steps which can be summarised as follows:

Model building step
- recording reference spectra
- building and validation of models

Prediction step
- predicting gas concentrations
- detection of outliers

These steps were the central items which have been studied in this work package.

3.2 Participants of WP3

The main participants of WP3 were Centexbel and the University of Greenwich with contributions of LSF SUD. Centexbel was the work package leader.

3.3 Structure of WP3

A method for the determination of the **minimum detection limits** based on the noise level has been given. For this it is assumed that a spectral line of a particular gas can be detected when it is approximately as high as the noise level present in a real smoke gas spectrum.

For **building models** two approaches have been followed. The first approach uses classical chemometrical techniques such as CLS, PLS and INLR. The second approach, QTFA, does not build a multivariate model but uses multivariate techniques to resolve the spectra of smoke gases and identifies each individual gas components. Univariate models are then used to predict the concentration of the component.

The **prediction** of the concentration of toxic gases requires linear or non-linear multivariate techniques or models. Unless the smoke gas spectrum is resolved in its individual components, univariate models are not suited because water vapour, present in various wavenumber regions, covers the gas components of interest. Univariate models can be used on conditions that the spectra have been resolved and that each component is identified (QTFA).

In general non-linear models are necessary. Only in the case of SO_2 and Acrolein linear models can be used. Gases such as CO, CO_2, NO, NO_2, HCl and HCN require non-linear models.

The models which are used for the prediction of the gas concentration should also be able to warn for inaccurate results or outliers. Inaccurate results can occur when another unknown gas is present in the wavenumber region used for prediction. With classical chemometrical techniques, the comparison of the unexplained information during calibration with unexplained information during prediction is a well-known technique and we have shown that it is also suited for smoke gases. In QTFA the unknown component is resolved and the spectrum of the component is presented.

Good laboratory practice requires that models need to be validated. **Validation** can be done by using pure reference gases. However, mixing the reference gas with water vapour is preferable.

Although several excellent **software** packages exist, it has been found necessary to write additional software which is better fitted for building models and analysing test results.

3.3.1 Minimum detection limits

The pathlength and the signal-to-noise ratio determine the minimum detection limit. The noise level is a function of the source intensity, the number of scans, the spectral resolution, type of optical filters used, stability of the optical components, and the quality of the detector.

Choosing a low noise detector such as the MCT detector reduces the noise level. This type of detector has a noise level which is approximately 100 times less than the noise level of the DTGS detector. Increasing the number of scans can also reduce noise whereas increasing the resolution leads to an increase in noise.

To estimate the minimum detection limit of a particular gas component it is assumed that a spectral line can be detected when it is approximately as high as the noise level. We also assume that a linear relationship exists between the absorbance and the concentration for low concentrations. Under these assumptions a procedure to estimate the minimum detection limit for a particular gas component is as follows:

1. From at least 10 different real smoke spectra determine the peak-to-peak noise level (pp) of the spectra in a region free of peaks. Calculate the average $< pp >$.
2. Obtain the spectrum of the reference gas with the lowest concentration (c) and determine the highest absorbance value ($abs_{\mathbf{max}}$) of the spectrum in the region you use for building the model.
3. The minimum detection limit is given by the ratio of the peak-to-peak noise level to the highest absorbance value times the concentration of the reference gas.

$$MDL = \frac{< pp >}{abs_{\mathbf{max}}} c \tag{3}$$

3.3.2 Building models

In this project the applicability of several multivariate techniques for smoke spectra analysis has been studied. A first class of techniques, which we refer to as "classical chemometrical techniques", includes Classical Least Square (CLS), Partial Least Squares (PLS) and Implicit Non-linear Latent Variable regression (INLR). An alternative technique, Quantitative Target Factor Analysis (QTFA) which uses a different approach, has also been found suited for gas spectra analysis.

Before we discuss the different techniques for analysing smoke spectra we first present a brief survey of FTIR spectra of the different toxic smoke gas components: CO_2, CO, Acrolein, NO, NO_2, SO_2, HCN, HCl, HBr and HF. In Figure 3.1 we present the wavenumber regions for each gas where the absorption peaks appear. From this figure, it is easily deduced in which regions absorption peaks of different gases overlap.

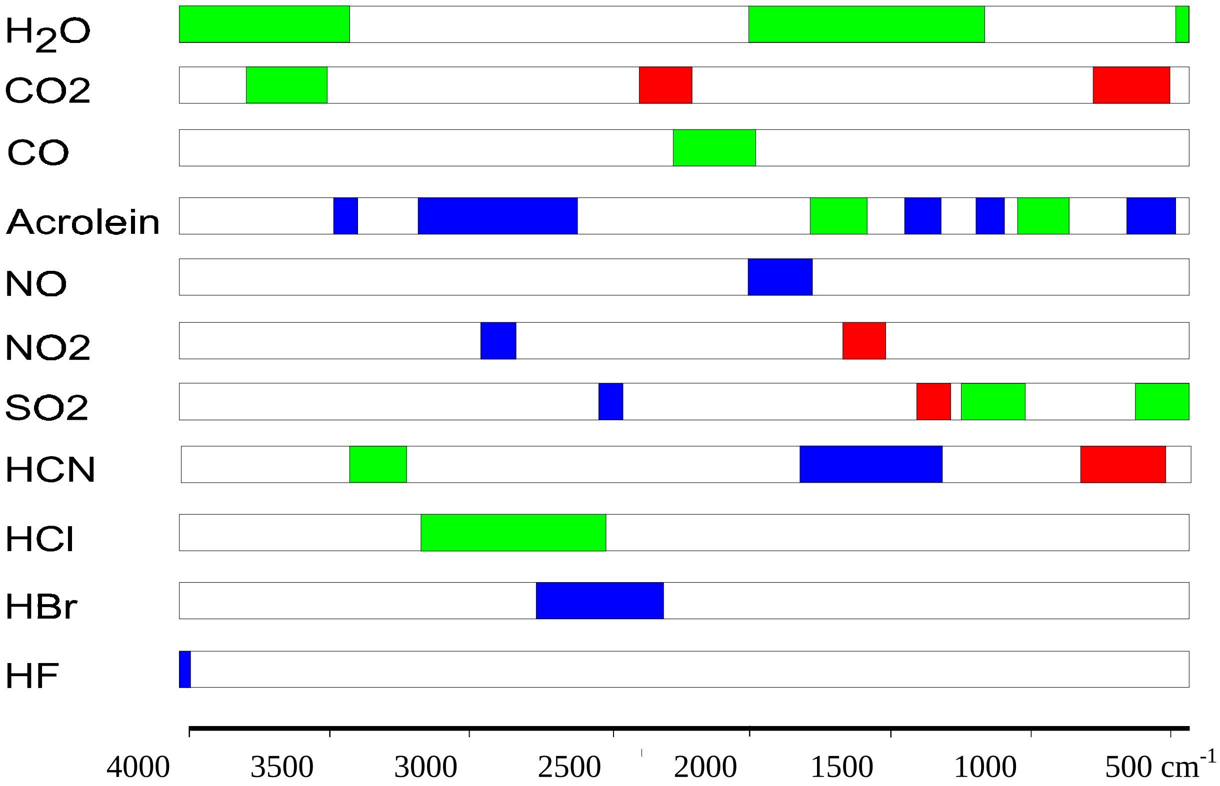


Figure 3.1. Wavenumber regions with relative absorption activity of each gas component.(Key: black: absorbance < 0,1; light grey: 0,1 < absorbance < 1; dark grey: absorbance >1.)

3.3.2.1 FTIR spectra of toxic gas components

Each gas component exhibits a characteristic FTIR spectra. In Figures 3.2 a - h we present a typical reference spectrum of each gas component.

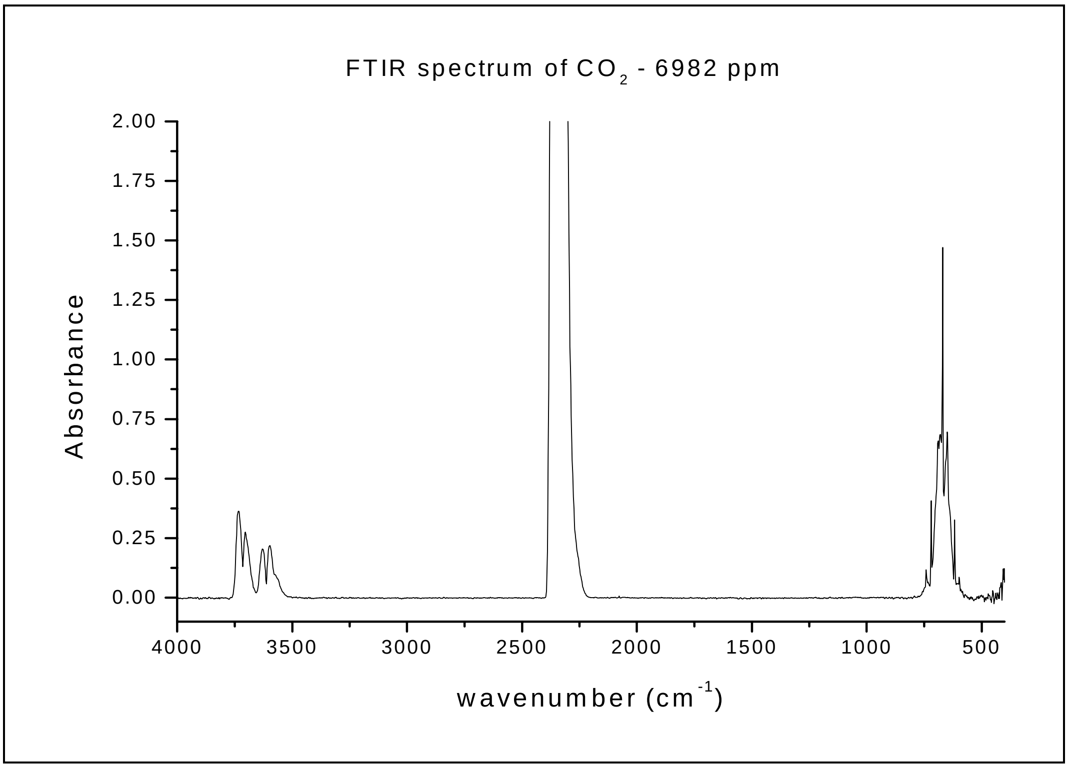


Figure 3.2 a. Referece spectrum of CO_2 .

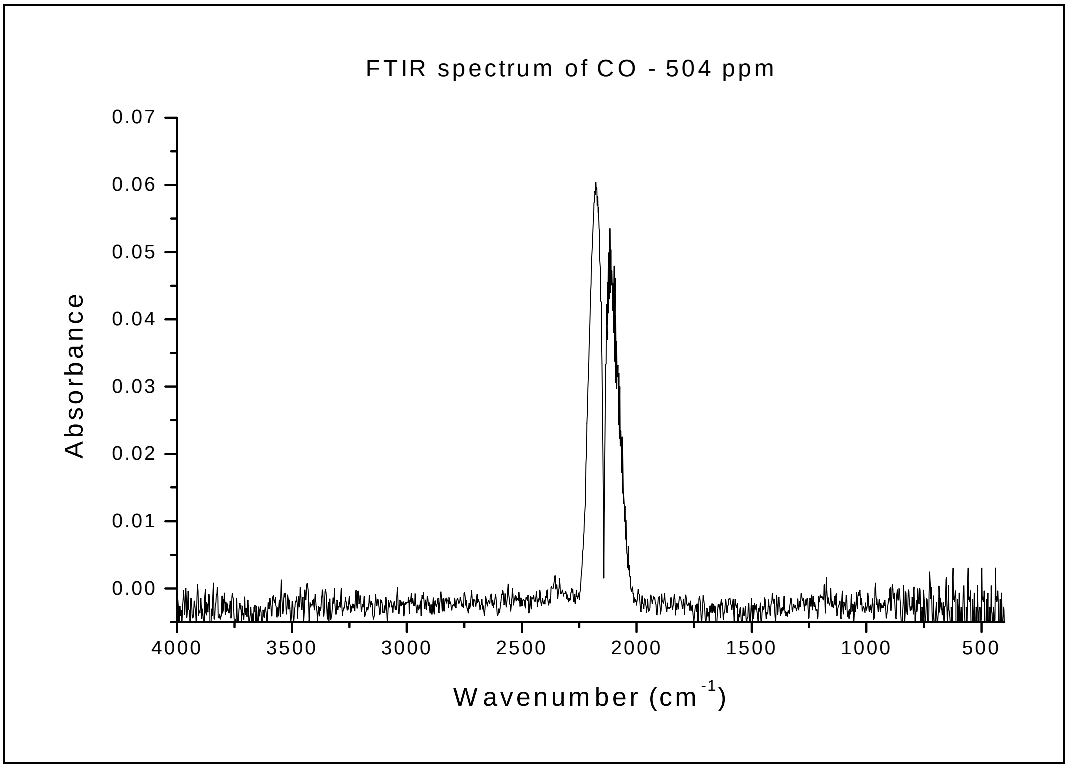


Figure 3.2 b. Reference spectrum of CO.

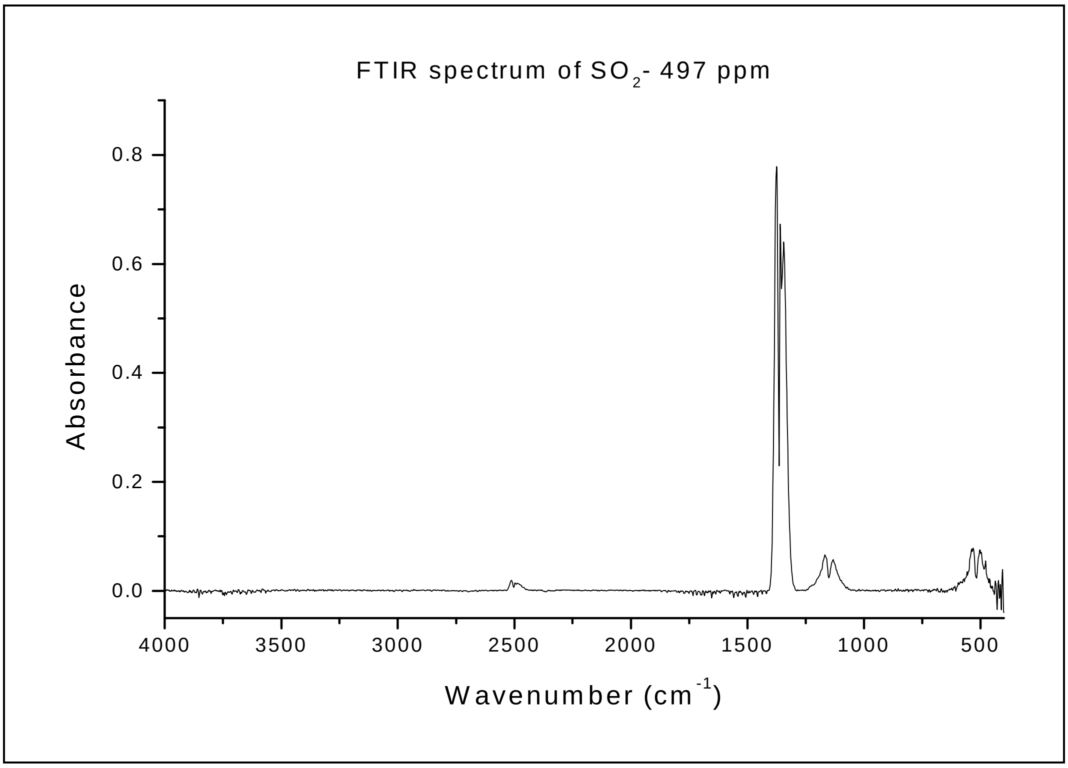


Figure 3.2 c. Reference spectrum of SO_2.

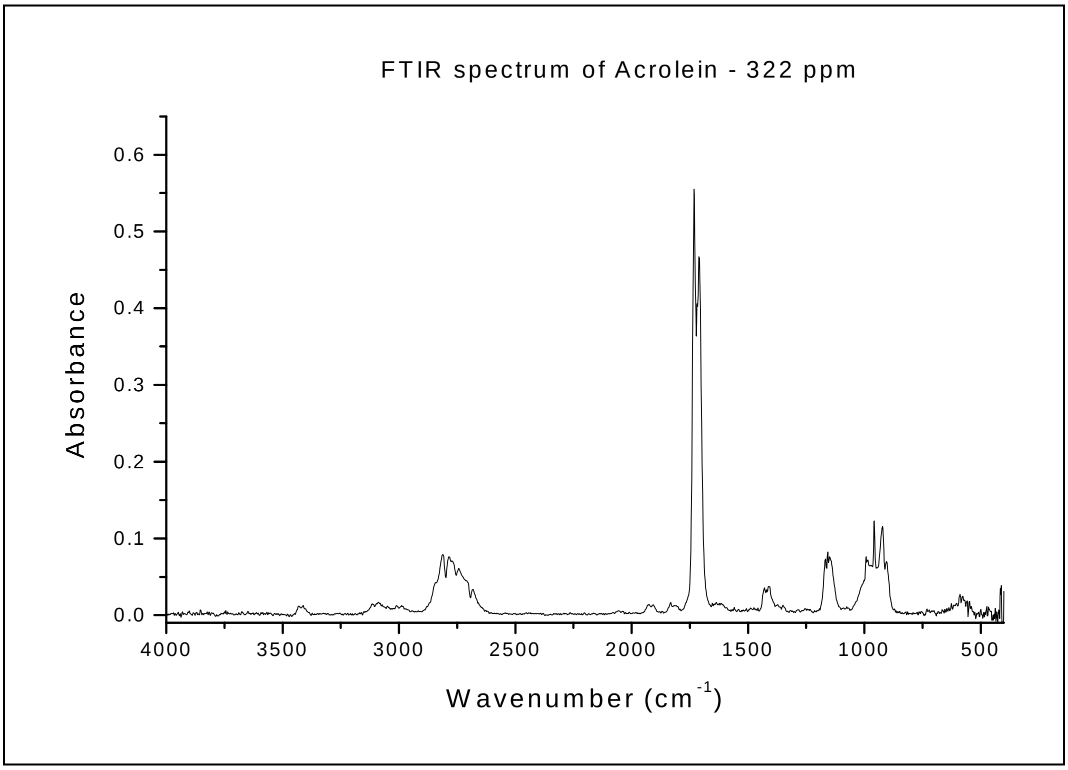


Figure 3.2 d. Reference spectrum of Acrolein.

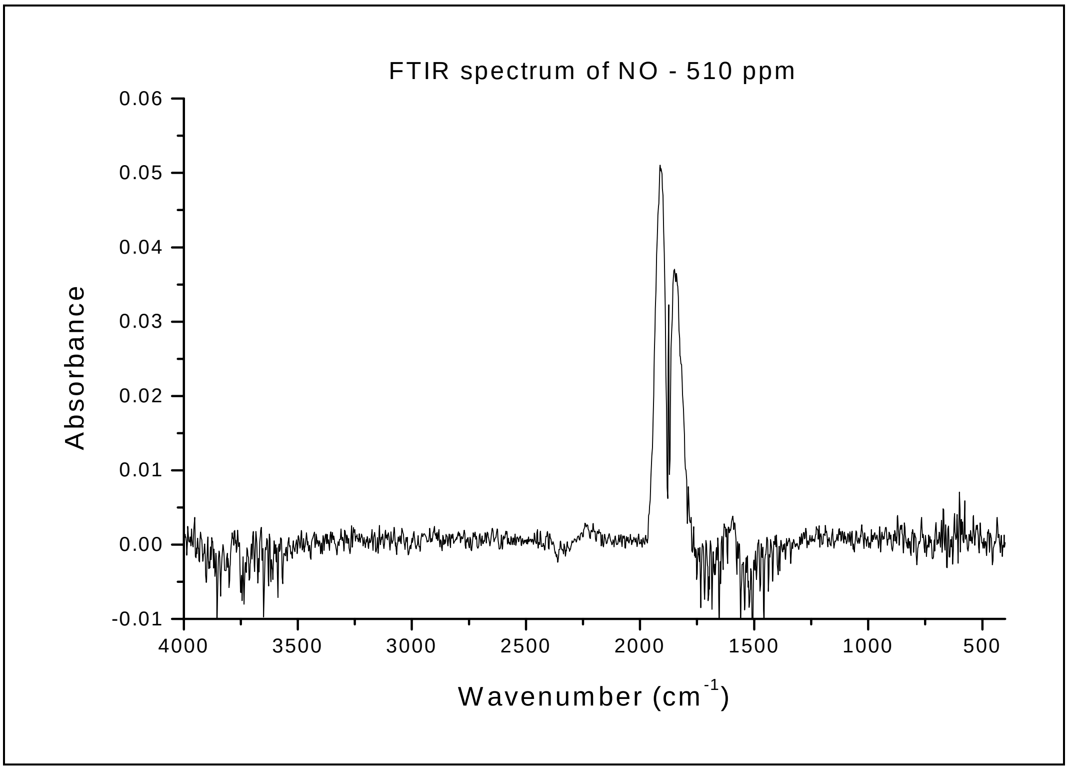


Figure 3.2 e. Reference spectrum of NO.

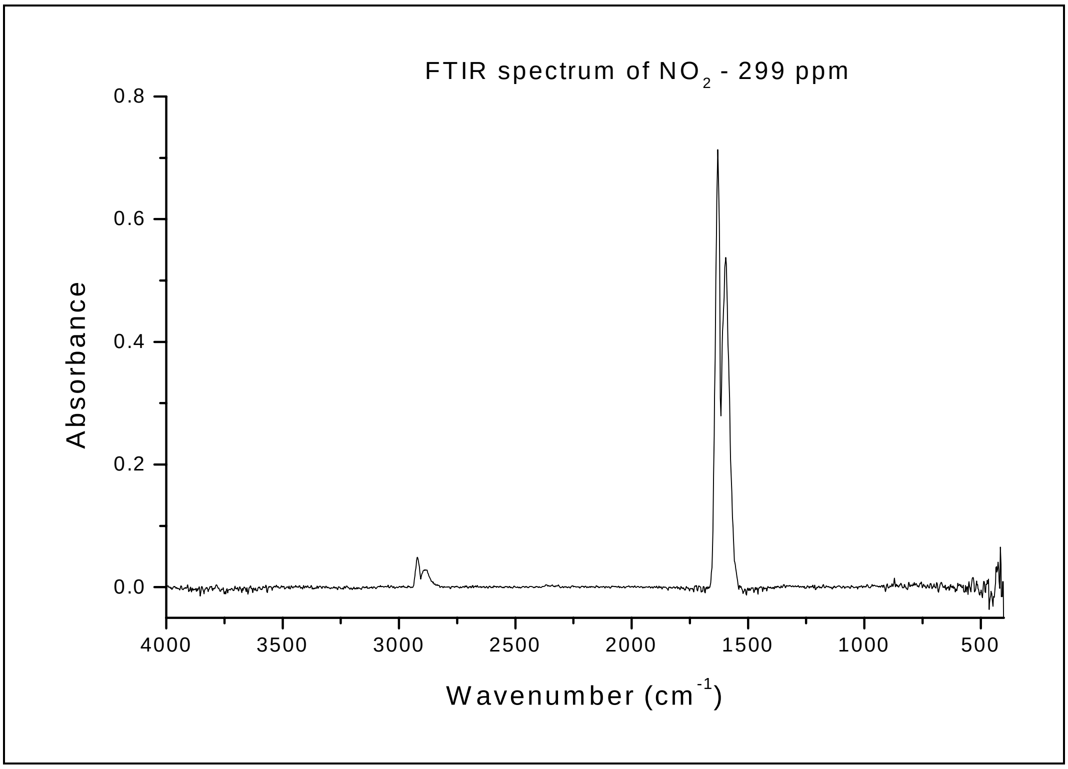


Figure 3.2 f. Reference spectrum of NO_2.

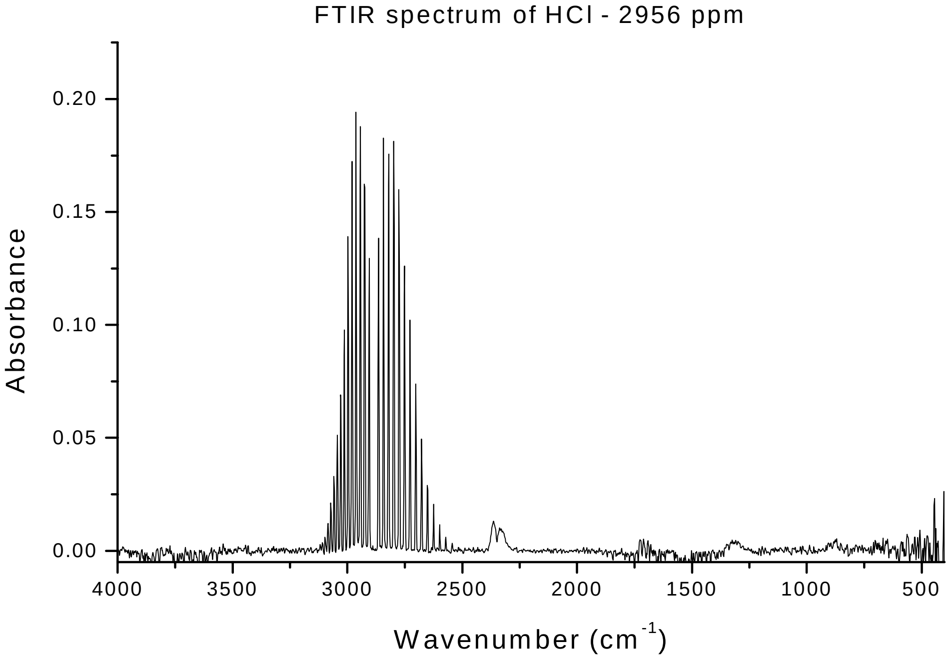


Figure 3.2 g. Reference spectrum of HCl.

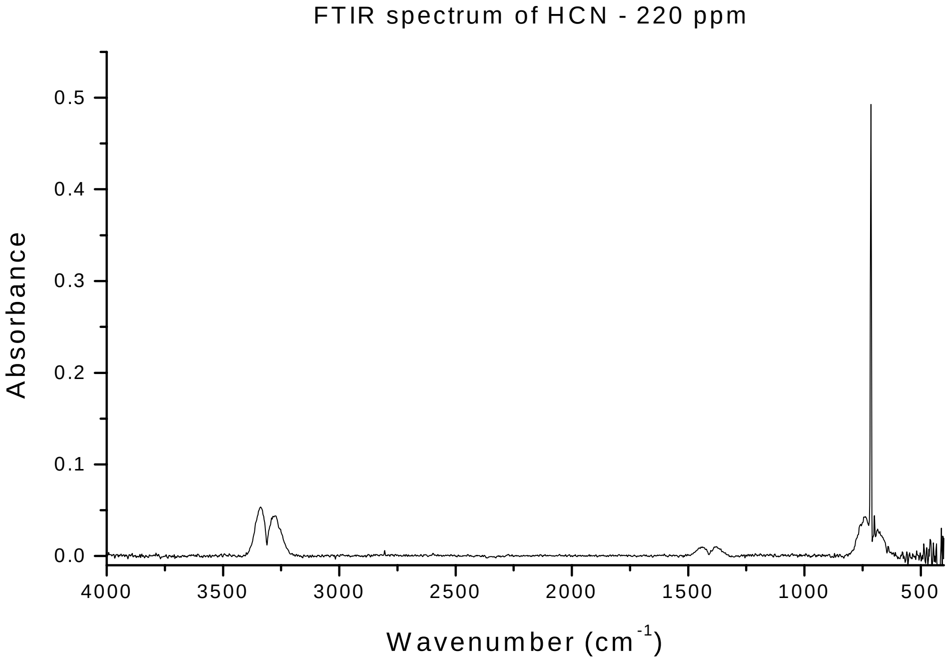


Figure 3.2 h. Reference spectrum of HCN.

As has been explained before, water vapour has a FTIR spectra which covers large parts of the FTIR wavenumber window and complicates the analysis of smoke gases. The FTIR spectrum of water is presented in Figure 3.3.

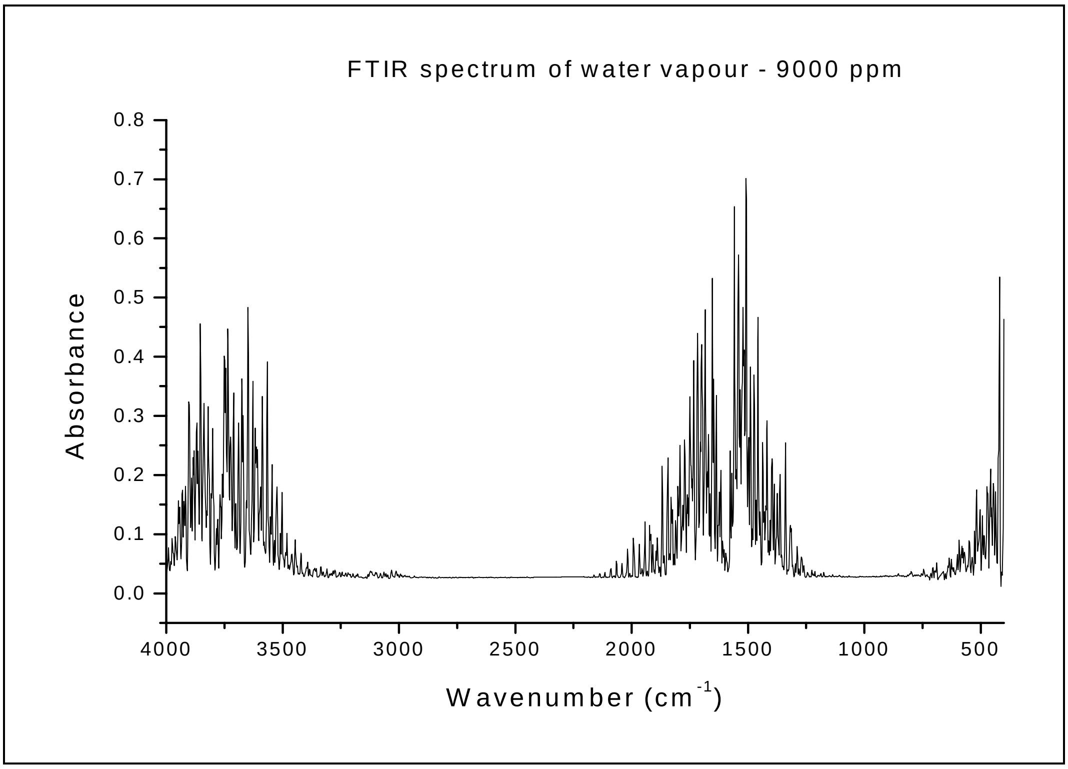


Figure 3.3. FTIR spectrum of water vapour.

3.3.2.2 Classical Chemometrical Techniques (CCT)

With Classical Chemometrical Techniques we denote techniques which are also applied in other fields of chemistry. It concerns methods such as CLS, PLS and INLR.

CLS is a well-known and proven technique for analysis of FTIR spectra. In this research, CLS was applied to analyse smoke gases. It has been shown that the technique is suitable for certain gases (SO_2 and Acrolein) which behave linearly. Because SO_2 and Acrolein are covered by water it is necessary to use gas mixture of water and the gas of interest for building the model. CLS requires that the concentration of water and the gas of interest in the reference spectra is known. PLS does not have this disadvantage. It only requires the knowledge of the concentration of the gas of interest. PLS is unfortunately also a linear technique and is only suited for linearly behaving gases such as SO_2 and Acrolein. Recently, a modified PLS strategy has been published. This INLR technique is non-linear and, as shown in this project, excellently suited for calibration of gases such as HCl, HCN, CO_2, CO, NO and NO_2. Again, the INLR technique has all the advantages of the PLS technique.

With classical chemometrical techniques it is possible to detect outliers. When an unexpected (not included in the calibration) and unknown gas component is present in the wavenumber window used for prediction, unreliable predictions will result. F-values, defined as the ratio of the unexplained information during calibration and the unexplained information during prediction, warn for these situations.

3.3.2.3 Quantitative Target Factor Analysis (QTFA)

The complexity of the calibration and modelling process is directly related to the number of interferents in the system being modelled. Even if the interferents are not of interest all the standard multivariate algorithms require that all the spectroscopically active compounds in a selected wavenumber region must be present at the time of calibration. If not, the calibration model is not representative. In such a case a good algorithm should warn the analyst that the model is incompatible with the sample and that there are outliers in the sample. If not, the results obtained will be inaccurate. However, the warning or flagging out of outliers does not solve the problem of quantifying the target gas or gases. When outlier(s) or interferences are detected it implies the whole model has to be built again in order to facilitate reliable quantification, and this can be very time consuming and in some cases impossible if the source or identity of the outlier is not known. To circumvent some of the calibration difficulties outlined above, the QTFA approach to fire gas analysis was developed. Essentially, the QTFA approach estimates the spectral profile of all possible overlapping spectra by a method of self extraction based on factor analysis (similar to Principal Component Analysis). After estimating the overlapping spectra, the target gas is quantified with a simple quadratic absorbance vs. concentration curve deduced from the calibration spectra. The QTFA is therefore an “open” model, in contract to PLS which is a “closed” model.

3.3.3 Validation

As good laboratory practice prescribes, models need to be validated regularly. There are several techniques for validating models. The easiest way is to send a reference gas down the transfer line and to predict its concentration using the model to be validated. However, better is to mix this reference gas with water vapour and to predict its concentration. In this case the model has to predict the reference gas covered by the water spectrum, which is also the case in normal testing. For some gases (for CO and CO_2) validation can also be done using the NDIR equipment available on the cone calorimeter.

3.3.4 Software

Because QTFA is a technique which is not yet commercially available and the calibration strategy of Classical Chemometrical Techniques cannot be applied without problems with a commercial software, two software programmes has been developed for the purposes of the SAFIR project. A software programme for QTFA is written in Matlab 5.0 and for the classical chemometrical techniques in Visual Basic 4.0. Both programmes are available for Windows 3.11 and Windows 95.

3.4 Recommendations

3.4.1 General recommendations

Recording reference spectra

1. Select a number of concentrations of the gas based on considerations concerning the concentration range for prediction and the behaviour of the gas (linear or non-linear). 5 to 6 concentrations for non-linear gases and 3 to 4 concentrations for linear gases is a good optimum. Buying cylinders with mixtures can be done if the gases do not have overlapping spectra.

2. Start with reliable and accurate recordings of reference gases. Record the reference spectra with the same experimental settings (path length, resolution, temperature of the transfer line, …) with which you will record real smoke gas spectra.

3. If F-values, i.e. the ratio of the unexplained information (noise) during calibration and the unexplained information during prediction, are used for detecting outliers, the noise in the spectra on which the model is built should preferably be of the same level as the noise in the real smoke gas spectra. For example, if the spectra for building a model are produced by mixing the reference spectra with water spectra obtained by burning methane, the reference spectra should be recorded with a sufficiently high number of scans. Mixing the reference spectra with the water spectra will then yield noise levels comparable with real smoke gas spectra.

3.4.2 Approach-specific recommendations

3.4.2.1 Classical Chemometrical Techniques

If classical chemometrical techniques are applied then at least some degree of familiarity with the techniques is necessary. A few excellent textbooks on chemometrics are available.

There is a number of steps which are very important for obtaining reliable predictions. These steps are:

Preparing for calibration

1. To avoid overfitting, increase the number of reference gases up to 15 or 30. Each "synthetic" reference spectrum should have different concentration. This can be done numerically (dividing spectra by an appropriate number) starting from the recorded pure reference spectra. The concentration of this "synthetic" spectrum can be obtained by a simple area versus concentration model based on the real reference gases.

2. Several approaches can be followed for obtaining mixtures of the reference gas and water.
    - The first approach (the numerical approach) is to obtain water spectra of different concentrations and mix these spectra numerically with the reference spectra. These water spectra can be obtained by burning methane at different flow rates. If PLS or INLR is used the concentration of water in these spectra need not be known. Using these real smoke gas spectra has also another advantage: introducing noise in the models which is the same as the noise level during testing. During the burning of methane also CO_2 is generated and these spectra can by consequence not be used for a CO_2 model. In this case pure water spectra are needed.
    - Calibration gas mixtures, including water, may be purchased ready made in cylinders. Experience has shown that particularly for reactive gases the stated concentration given by the supplier may be unreliable. These calibration gases may be further mixed or diluted using suitable equipment to extend the calibration range.
    - Gas mixtures may also be made in a dynamic system using permeation or diffusion tubes to produce a range of concentrations. Gas concentrations are calculated from the weight loss of the diffusion or permeation tube. Subsequent analyses for verification may be carried out if needed.
    - A heated, pumped closed loop system attached to the FTIR cell may also be used to generate known gas concentrations for calibration. If the system is of known volume then injecting known amounts of materials will give known concentrations. After the calibration spectra has been obtained the contents of the cell and loop may be swept into an appropriate trapping medium for subsequent analysis to determine concentrations.

Building a model

1. Build your own models and do not rely on other models because models can be instrument dependent.

2. Start by selecting an appropriate wavenumber window for calibration and baseline correction. When selecting a wavenumber window for calibration consider the following:
    - Absorbance should be as high as possible but not too high (absorbance < 1).
    - Ideally only the component of interest should show up in the selected wavenumber region. In case this is not possible, select the window where the component is covered by water only.
    - If you have knowledge concerning the wavenumber regions in which unknown interferent gases occur, avoid these wavenumber windows.

3. Build CLS, PLS and INLR models and select the number of PCs (for PLS and INLR). In principle different techniques are available for selecting the number of factors (e.g. cross validation). Locating the first drastic change in the slope of the standard error of calibration is a good indication of the number of factors needed. In case there is no drastic change in slope then use INLR (if you used a linear technique) and/or reduce the concentration range. If necessary use cross validation to determine the number of factors.

4. Select models based on standard error of calibration and reference versus predicted graphs or other diagnostic tools. A standard error of calibration of 10 % of the total concentration range is acceptable.

Predictions

1. Predictions should be checked to be reliable by close examination of the F-values together with close visual examination of some spectra.

2. If you find suspicious results (e.g. large F-values) and an unknown gas is identified by visual inspection, build a new model on a different wavenumber region not containing the interferent and repeat the predictions.

3.4.2.2 QTFA

When applying QTFA, knowledge of PCA is necessary because the first step in QTFA is PCA. QTFA does not build multivariate models but, after resolving the spectra (with PCA), uses univariate quadratic calibration models to predict concentration of the identified target gas(es).

Preparing for QTFA

1. The database which is used in QTFA for the identification of the different components needs to be constructed appropriately.

2. The appropriate wavenumber window should be selected for the gas, which is to be analysed.

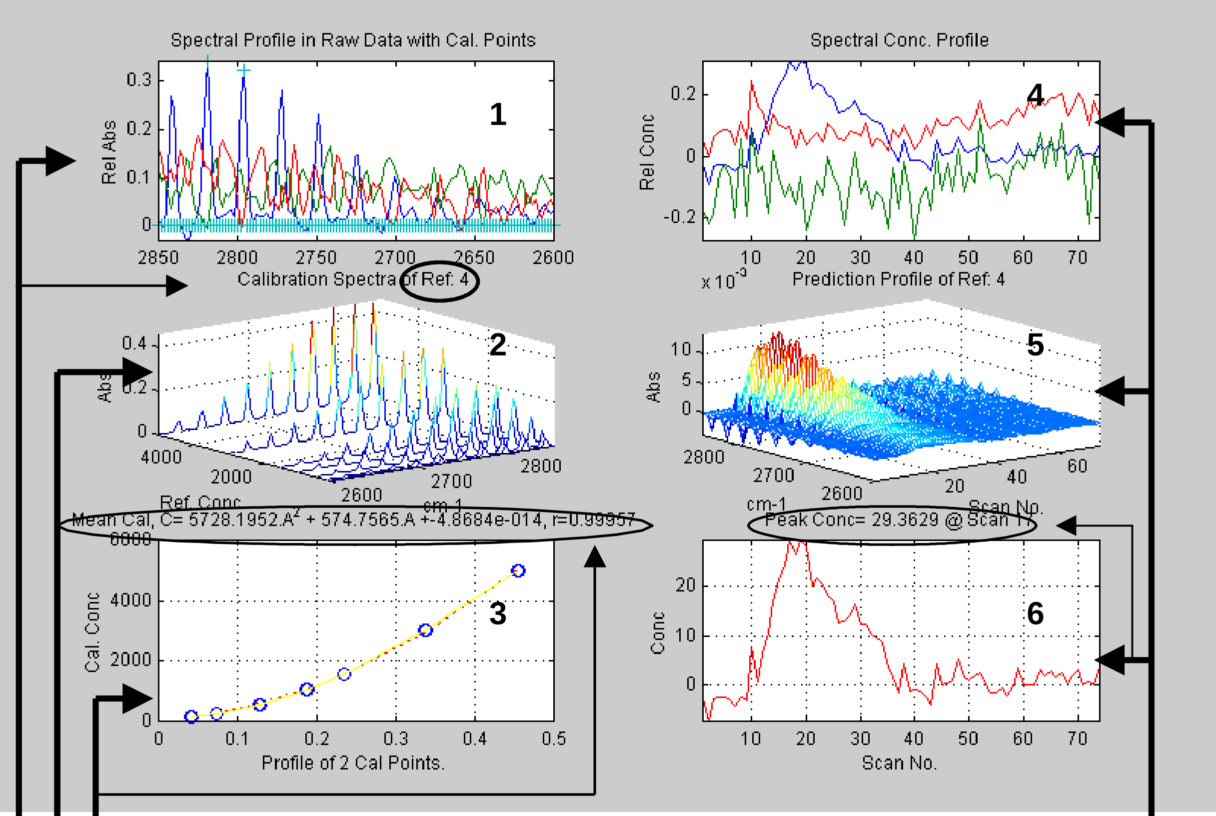
QTFA Modelling and Prediction

1. After PCA, identify the number of factors using *IND* (Factor Indicator Function), *%SL* (Percentage Significance Level) and PC plots (in time or spectral domains). For the IND, the number of factors (or PCs) is deduced from the point where the graph passes through the minimum. For %SL, the number of factors is deduced from the point where there is a drastic change in the %SL values (generally, %SL values between 0 and 5 are significant). For the graphical plots of PCs in time domain, the visual profiles with (combustion) structure are considered as significant factors. The factors with random structures are associated with noise. Combining the information from these three graphs the correct number of PCs (factors) can be deduced.

2. The number of identified PCs indicates the number of evolved gases in the selected wavenumber region. If *n* PCs are identified then there will be at least *2n-1* estimated spectra generated from which the 'KEY' *n* spectra are selected. The *n* most different spectra from the *2n-1* initial spectra should be selected either visually or automatically for the KEY.

3. If any of the KEY *n* spectra matches the predefined targets in the database then the analysis proceeds with absolute quantification of the gas(es). Else only a relative concentration profiles of the unknown *n* gases are reported.

Figures 3.4, 3.5 and 3.6 show an example of the QTFA approach. The data presented originates from a cone calorimeter test of polyurethane foam.



Graph 4. Shows the relative concentration profiles of all estimated spectra in the selected wavenumber window. 2 other gases overlaps with the target HCl and they have been quantified even though their identity are unknown.

Graph 5. Shows the fully deconvoluted HCl spectrum as it should be when the other 2 gases were not present. This graph is used to calculate the absolute concentration.

Graph 6. Shows the absolute concentration profile of the target HCl. On top of this chart are information about maximum recorded concentration and the spectral scan number for which it was recorded.

Graph 3. Shows the calibration curve generated from the reference spectra in graph 2. On top of this chart is the calibration equation.

Graph 2. Shows the spectral profile of the calibration reference files used to generate the calibration curve in graph 3.

Graph 1. Shows the spectral profiles of all the overlapping gases identified by QTFA in the selected wavenumber window. The identity of the target gas in the available reference is confirmed below the graph as 4 (i.e. HCl).

Figure 3.4. Details of HCl analysis of polyurethane foam using QTFA.

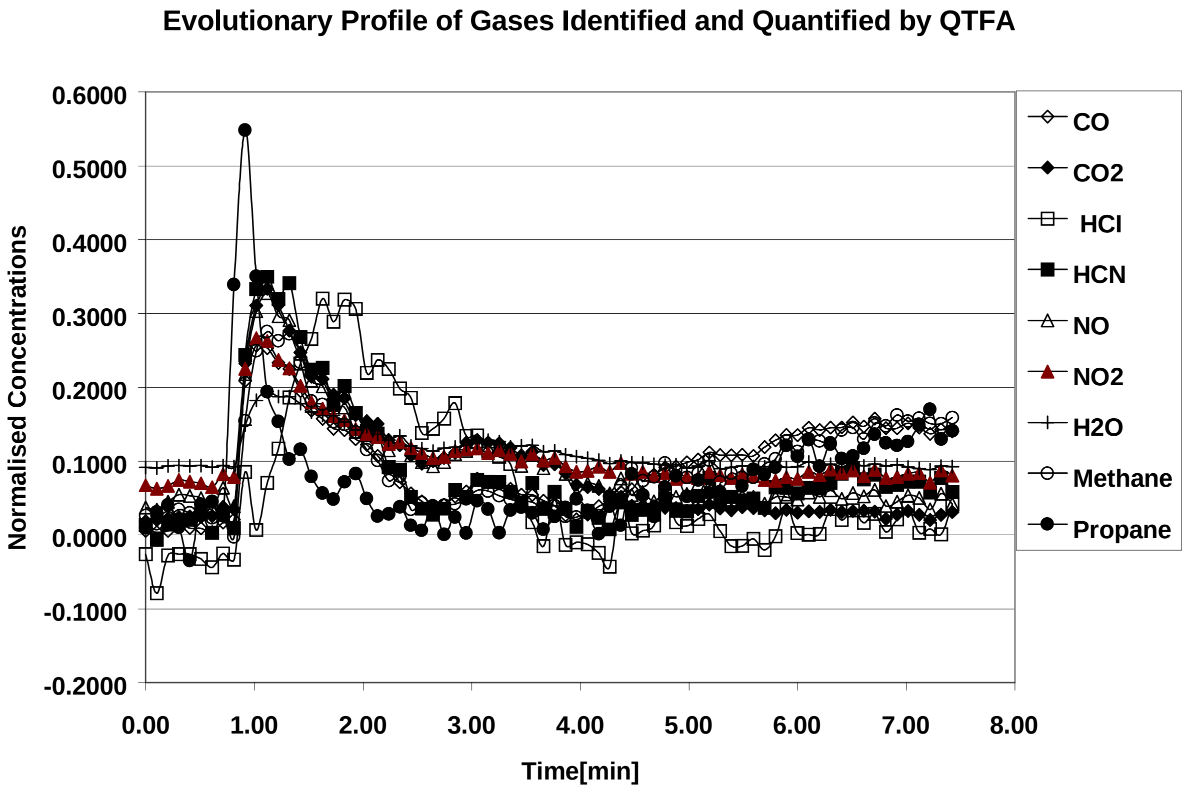
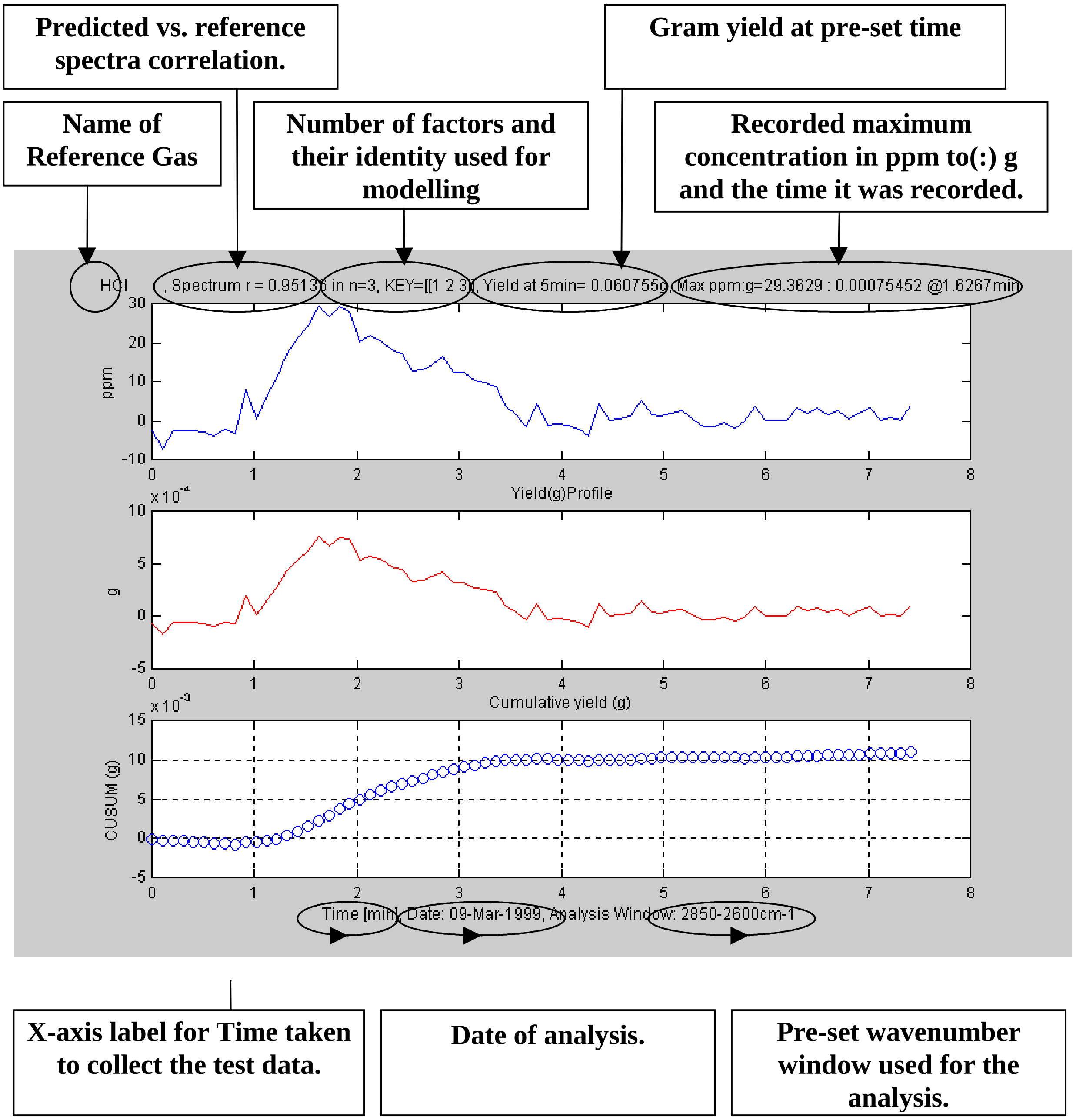


Figure 3.5. Summary profile of all identified targets in the available reference.



Predicted vs. reference spectra correlation.

Gram yield at pre-set time

Name of Reference Gas

Number of factors and their identity used for modelling

Recorded maximum concentration in ppm to(:) g and the time it was recorded.

X-axis label for Time taken to collect the test data.

Date of analysis.

Pre-set wavenumber window used for the analysis.

Figure 3.6. Profile of HCl with summary analytical information based on a configured analysis.

3.4.3 Recommended further reading

- H. Martens, T. Naes: Multivariate Calibration; J. Wiley & Sons, 1989.

- G. McClure: Computerized Quantitative Infrared Analysis; ASTM publication, 1987.
- E. R. Malinowski, Factor Analysis in Chemistry; J. Wiley & Sons, 2nd Edition, 1991.

3.5 Conclusions

The following conclusions and recommendations are given on the basis of the WP3 work:

- Not only has the model building step been studied in WP3 but also techniques for the determination of the minimum detection limit and for validation of the models have been put forward.
- To circumvent the availability of software tools for analysing smoke gases, the WP3 partners have written additional software which is used by the majority of the other partners.
- For satisfactory analysis using multivariate or univariate methods, it is essential that good reference spectra are obtained for calibration. A sufficient number of calibration spectra should be obtained to allow modelling of non-linear behaviour with reasonable precision.
- It is clear that multivariate chemometrical techniques such as CLS, PLS, INLR and QTFA are needed for the prediction of toxic components in smoke gases generated during a fire test. Also for several gases we have shown that linear techniques are inadequate and that non-linear techniques are needed.
- CLS, PLS and INLR have the advantage of being well-known techniques which are widely available. CLS and PLS are linear techniques and are thus only suited for gases behaving linearly (SO_2 and Acrolein). INLR is non-linear and is suited for the majority of the gases.
- The QTFA approach is a non-traditional multivariate method; there is no need for external calibration or mixture preparation and therefore no need for experimental design of mixtures. The method is capable of analysing samples from varied sources and types. The method will be commercially available soon.
- Extrapolation of concentrations outside the calibration range should be avoided.
- It is strongly recommended to visually inspect the data output of the multivariate models. Unexpected behaviour (e.g. non-zero baseline) should be investigated.

4. WP4 – Verification in different fire scenarios

4.1 Objectives of WP4

WP4 was tasked with verifying the results of WP1 (sampling in the small-scale) and WP2 (sampling in the large-scale) by using the recommended parameters from those WP's during sampling and analysis from small and large-scale fire tests.

A key objective was to compare quantitatively the FTIR response in each case, with the response of a comparison method, which is an alternative method for a given species, known to be capable of giving reliable results in fire gas analysis.

4.2 Participants of WP4

Seven laboratories took part in WP4. They were:

VTT	VTT Building Technology	Finland
FRS/BRE	Building Research Establishment, Fire Research Station	UK
LNE	Laboratoire National d’Essais	France
LSF SUD	L.S.F. SUD srl – Laboratorio di Studi e Ricerche sul Fuoco	Italy
RAPRA	RAPRA Technology Limited	UK
SP	Swedish National Testing and Research Institute	Sweden
RUG	Universiteit Gent	Belgium

The work package leader was FRS/BRE.

4.3 Structure of WP4

In determining the small and large-scale test methods to use in the study, the ISO definition of real fire types was used [2] and test methods chosen to represent a wide range of different fire types. The fire types are summarised in Table 4.1.

Materials for combustion (i.e. "fuels") were chosen to provide key chemical species in the combustion products, some of which had been identified in WP1 and WP2 as "problematic" in fire gas analysis. FRS arranged characterisation, purchase and delivery of all fuels to the participants for WP4, and drew up a schedule of tests for each laboratory.

Table 4.2 is a summary of the fuel types chosen for study and the key combustion products (compounds) of interest.

Table 4.1. Fire types as defined by ISO.

CLASSIFICATION OF FIRE TYPES FROM ISO TC 92 SC3 9122/1					
Fire type or stage of fire	Temperature (°C)		Fire Effluents		
	Fire	Hot layer	Oxygen to fire (%)	Oxygen from fire (%)	CO_2/CO
1. NON FLAMING					
a. Self sustaining	450 - 600	RT	21	>20	1 - 5
b. Oxidative pyrolysis	300 - 600	<50	21	>20	1 - 5
c. Non-oxidative pyrolysis	300 - 600	<50	0	0	<5
2. WELL VENTILATED FLAMING Fire size small in relation to size of compartment, flames below base of hot layer, fire size fuel controlled	>700	RT to 500	>15	5 - 21	>20[1]
3. LESS WELL VENTILATED FLAMING Fire size large in relation to size of compartment, flames partly above-base of hot layer, fire size ventilation controlled:					
a. small vitiated fires in closed compartments	>700	RT to 500	<15	0 - 12	2 - 20
b. Post flashover fires in large or open compartments.	>700	500 - 1000	<15	0 - 12	2 - 20

[1] May be lower if the burning materials contain fire retardants. (Therefore, when setting up a furnace system to obtain a particular fire type it is important to use "normally burning" materials such as wood or polypropylene which are not fire retarded). Also when studying decomposition under flaming conditions it is important that continuous flaming is observable throughout the run.

Table 4.2. Fuels used and key compounds of interest.

Fuel	**Description**	**Generated compounds of interest***
Particle board	Urea-formaldehyde glued particle board. Elemental analysis (% mass): C = 46,2; H = 6,8; N = 3,8	Acrolein, HCN, NO_x
FR flexible PU foam	CMHR foam with melamine and chlorinated phosphate fire retardant. Elemental analysis (% mass): C = 53,7; H = 9,6; N = 7,7; Cl = 1,7.	HCN, NO_x, HCl
PVC sheet	Proprietary rigid PVC sheet, 3 mm thick. Elemental analysis (% mass): C = 38; Cl = 57; H= 5.	HCl
Rubber	Sulphur cross linked rubber sheet, 3 mm thick.	SO_x, H_2S
FR polyethylene (FRPE)	Low density polyethylene with brominated FR.	HBr, HCl

* In addition to CO_2 and CO.

4.4 Work performed in subtasks

Full details of the equipment and operating parameters and protocols are provided in the respective individual laboratory reports. The comparison methods used were:

- CO_2 and CO: Non-Dispersive Infra-Red (NDIR) Spectroscopy
- HCl, HBr, HCN, SO_2: adsorbed in appropriate solutions and analysed by High Performance Ion Chromatography (HPIC)
- HCN: also photometry
- NO_x: chemiluminescence
- Acrolein: derivitised on dinitrophenylhydrazine cartridges and analysed by High Pressure Liquid Chromatography (HPLC)

Table 4.3 summarises the work actually performed by each laboratory for WP4. The last column of Table 4.3 lists the compounds which were measured successfully by FTIR but where comparison data was not available. Repeat tests have not been included here.

Table 4.3. Summary of subtasks performed in WP4.

LAB.	TEST METHOD	FUEL	ISO FIRE TYPE	SPECIES MEASURED WITH DEVIATION ESTIMATE	SPECIES MEASURED WITH NO DEVIATION ESTIMATE
FRS	Purser furnace	PU foam	1c, 2, 3b	CO_2, CO, HCN	H_2O, HCl
FRS	SBI	Rubber, PVC	2	HCl	CO_2, CO, HCN, H_2O, HCl, SO_2
VTT	Cone calorimeter (vitiated)	Particle board	3a	CO_2, CO, NO	-
VTT	Cone calorimeter (vitiated)	Rubber	3a	CO_2, CO	SO_2
LNE	Cone calorimeter	Particle board	2	CO_2, CO	NO, NH_3, acrolein, NO_2, HCN
LNE	Cone calorimeter	PVC	2	CO_2, CO, HCl	-
RAPRA	Purser furnace	Particle board	1c,3a	CO_2, CO, acrolein, formaldehyde	HBr, HCN, NO, NO_2, NH_3
RAPRA	Cone calorimeter	Fire retarded polyethylene	3b	CO_2, CO	HBr
LSF/SUD	Cum. Smk. Cbr. ISO 5659.2	Particle board	2	CO_2, CO	HCN
SP	Room/corner test ISO 9705	Particle board	2	CO_2, CO, HCN, NO, NO_2	-
SP	Room/corner test ISO 9705	PU foam	2	CO_2, CO, HCl, HCN, NO, NO_2	-
RUG	SBI	Particle board	2	CO_2, CO	
RUG	SBI	PVC	2	CO_2, CO, HCl,	Acrolein

4.5 Results of WP4

In general, the shapes of the concentration vs. time curves measured by FTIR were reasonable considering the fire characteristics of the tests. FTIR gave good peak response, even in the case of rapid concentration changes. Figures 4.1 and 4.2 show some example curves measured in WP4 tests.

To compare the FTIR results with the comparison measurements, “FTIR deviation” is defined as follows:

$$\text{FTIR deviation (\%)} = \frac{\text{FTIR result - Comparison method result}}{\text{Comparison method result}} \times 100\ \%$$

The deviations were calculated for either total yields or maximum concentrations, depending on the participating laboratory’s report.

There was no evidence to suggest that there was any influence of the concentration level of the gases on the deviation of the FTIR results from the comparison method.

The FTIR deviations of the WP4 tests for CO_2 and CO are collected to Figures 4.3 and 4.4, respectively. The results of the participating laboratories are presented anonymously with randomly assigned laboratory numbers. It is emphasised that all tests of WP4 are included in these graphs. Thus, Figures 4.3 and 4.4 present the worst case.

For other compounds (HCl, HCN, NO, NO_2), less data was available but the results were mostly similar to those of CO_2 and CO.

In most cases of large deviations, it was possible to trace the reason for the difference between the results of FTIR and the comparison method. For instance, different locations of sampling points for the two methods could cause notable discrepancies. When the concentration levels measured were low (near to the minimum detection limit), the relative deviation was often exceptionally high. In some experiments, the problems were related to the comparison method rather than to the FTIR measurements.

When results from several laboratories were available for a compound, the sign of the deviation seemed to be laboratory dependent. This suggests that the difference between the results of the methods is due to the measurement procedure of each laboratory, related either to FTIR or the comparison method. Systematic positive or negative deviations in all laboratories related to the compound measured or the fire model used were not observed showing that FTIR is a valid method for fire gas analysis over a wide range of fire test and operating conditions.

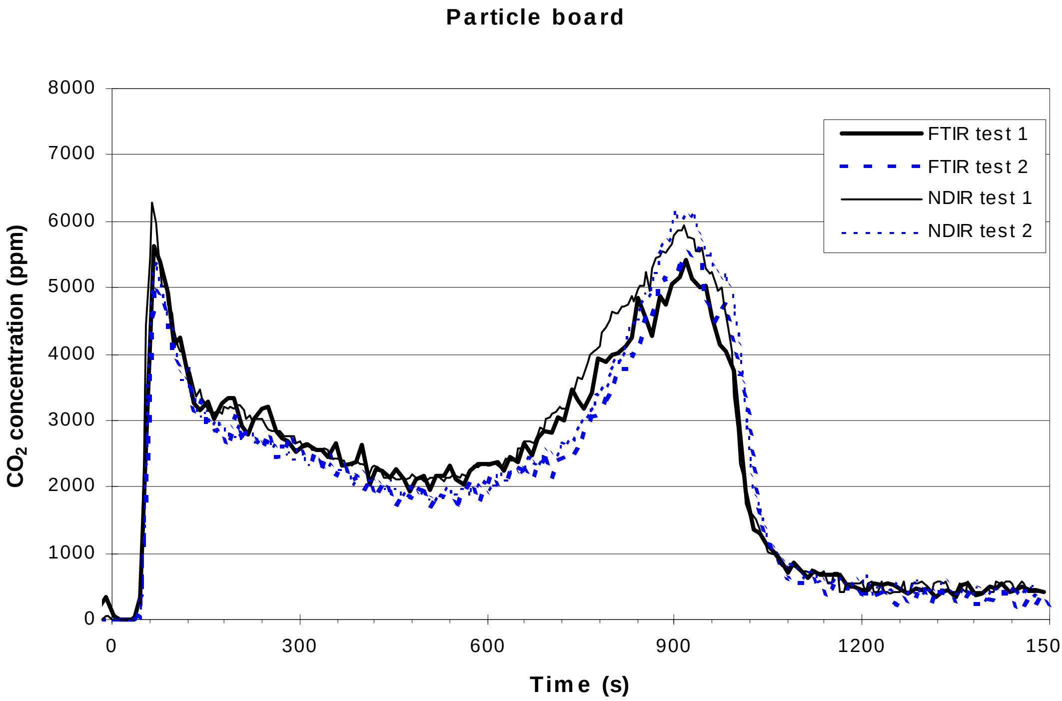


Figure 4.1. CO_2 concentration measured by FTIR and comparison method (NDIR) in cone calorimeter tests of particle board at 50 kW/m^2.

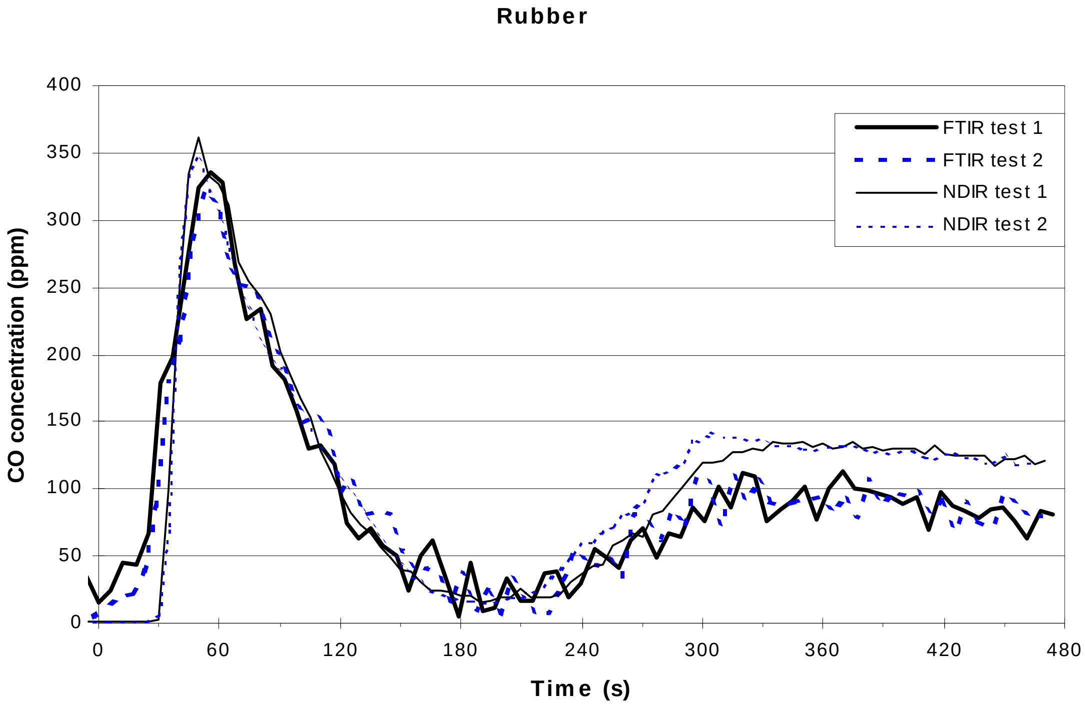


Figure 4.2. CO concentration measured by FTIR and comparison method (NDIR) in cone calorimeter tests of rubber at 50 kW/m^2.

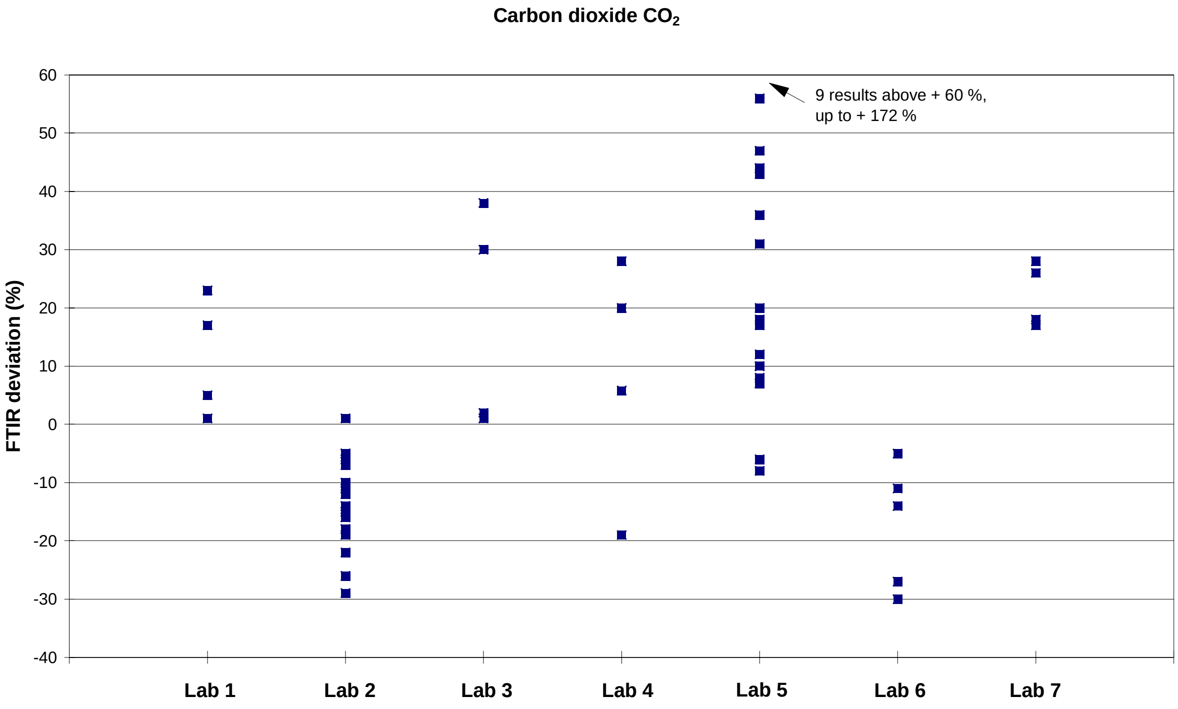


Figure 4.3. FTIR deviations for CO_2.

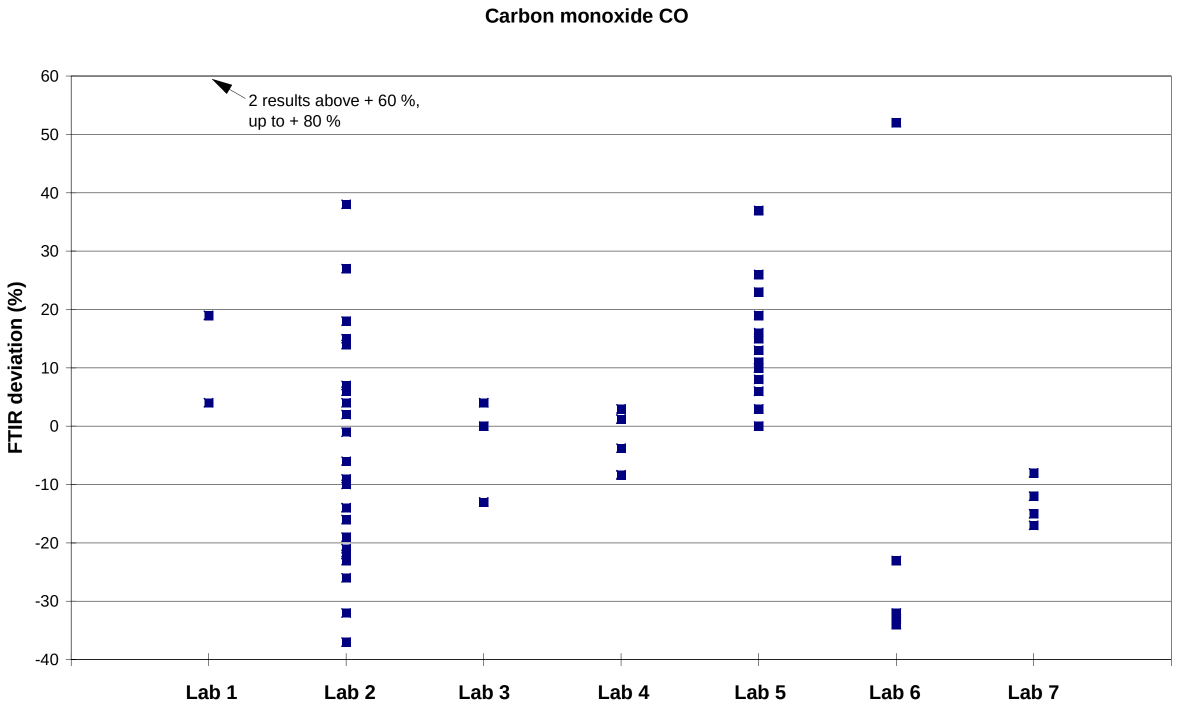


Figure 4.4. FTIR deviations for CO.

In WP5, an interlaboratory trial using the cone calorimeter, CO_2 and CO concentrations were measured with both FTIR and NDIR. The WP5 FTIR deviations shown in Table 4.4 were obtained from the mean values resulting from the statistical analysis. Therefore, these values may not reflect the FTIR deviation for each laboratory. Generally there appeared to be an overall improvement in deviations for CO_2 and CO from WP4 to WP5.

Table 4.4. FTIR deviations of CO_2 and CO results in WP5.

Quantity / Material	Particle board	FR PVC	PUR foam panel
$CO_{2,max}$	+4,8 %	+8,5 %	+7,4 %
CO_2 yield	-0,5 %	-0,6 %	-1,2 %
CO_{max}	+8,9 %	-14,1 %	-1,1 %
CO yield	+16,7 %	-7,8 %	+9,3 %

Within the spread of the data achieved in WP4 and WP5 there does not seem to be any particular trend associated with a particular software package. The scattering of the data presented includes the possible effects of data analysis methods, e.g. those of the IR spectral regions used in the analyses.

The following sections present a summary of the conclusions for each compound measured in the WP4 study. In each case, the number of laboratories providing information is given, followed by a conclusion for that compound.

4.5.1 Carbon dioxide

(i) All laboratories provided deviation results.

(ii) Good agreement generally but deviation appears to be laboratory dependant (either positive or negative). With PVC results there is a bias towards positive deviation values. This may be due to a compound absorbing IR, in the same window as used for the CO_2 measurement.

4.5.2 Carbon monoxide

(i) All laboratories provided deviation results.

(ii) Good agreement generally but deviation appears to be laboratory dependent (either positive or negative).

4.5.3 Hydrogen chloride

(i) Four laboratories provided deviation results.

(ii) Three laboratories show high positive deviation values but this may be due to difficulties in sampling in the verification method. The fourth laboratory obtained good agreement.

4.5.4 Hydrogen cyanide

(i) Four laboratories provided deviation results.

(ii) The two laboratories that had sufficient HCN concentrations to perform a deviation estimate, showed results of approximately +50 % positive. Where zero or trace levels were reported, FTIR did not give a false positive result.

4.5.5 Nitric oxide

(i) Two laboratories provided deviation results.

(ii) Reasonable agreement within about ±20 %.

4.5.6 Nitrogen dioxide

(i) One laboratory provided verification results.

(ii) Deviation approximately ±50 %, but the presence of an interfering compound in both FTIR and the verification method, make this judgement very uncertain.

4.5.7 Acrolein

(i) One laboratory provided verification results.

(ii) Deviation -40% but with only one laboratory and two tests, result needs refining.

4.6 General conclusions of WP4

(1) The recommendations from WP1 (Sampling in small scale) and WP2 (Sampling in large scale) were verified.

(2) FTIR is capable of making time resolved measurements on many species simultaneously.

(3) Concentration/time profiles are generally very good and realistic and follow the same shape as the comparison method and the expected profile from the fire model. FTIR gives a good peak response. FTIR deviation is variable, but mostly within acceptable limits for fire gas analysis.

(4) Cell pressure will influence results. Where not measured and allowed for, results will have some uncertainty.

(5) Concentrations will be influenced by water vapour. NDIR measurements are with dried gas. Other comparison measurements are mainly taken at room temperature i.e. at a low water vapour pressure. Not allowing for water vapour will tend to make FTIR measurements lower than the comparison method. Some laboratories have reported correction for water.

(6) When comparison data were not available, the FTIR concentration/time profile was consistent with the course of the combustion as observed/monitored by other methods and the FTIR method followed rapid changes in concentrations.

5. WP5 – Interlaboratory trial

5.1 Objective of WP5

The objective of the interlaboratory trial (WP5) is to gain international acceptance for the FTIR analysis of smoke gases by determining the repeatability and reproducibility of the method according to the ISO 5725 principles.

5.2 Participants of WP5

The responsible partner of WP5 was VTT. All SAFIR partners participated in WP5.

The experimental work was performed by VTT, Centexbel, GRL, FRS/BRE, LNE, LSF SUD, RAPRA, SP, and RUG. Centexbel and University of Greenwich gave guidance and assistance in the data analysis and software issues. VTT was responsible for the statistical analysis of the results.

5.3 Structure of WP5

To reach the goals of WP5 with minimum resources, the following starting points were defined for the study:

- number of participating laboratories at least 8
- minimised number of replicate tests (3)
- minimised number of materials tested (3)

The interlaboratory trial was carried out in two steps:

- Step 1: Preliminary checks with one material
- Step 2: Interlaboratory trial with 3 materials

5.4 Work performed in WP5

The experience gained in earlier work packages offered a sound basis for the interlaboratory trial. The FTIR test procedure of WP5 was based on the results of WP1 and WP4. The software packages produced in WP3 were recommended to be used in the spectral analysis.

5.4.1 Test procedure

To obtain the repeatability and reproducibility of the FTIR method in connection with real fire test smoke gas measurements, the WP5 tests were carried out using the cone calorimeter method which is a well-defined small scale fire test. The cone calorimeter tests were performed in the horizontal orientation according to the ISO 5660-1 standard [3]. The heat flux level of 50 kW/m^2 was used in all tests.

The materials tested in WP5 were the following:

1. Particle board, thickness 12 mm, density 700 kg/m^3,
2. Fire-retarded (FR) PVC, thickness 3 mm, density 1180 kg/m^3,
3. PUR foam panel, thickness 35 mm, density 40 kg/m^3.

The specimens of were acquired and disseminated by VTT. Before the tests, the specimens were conditioned to constant mass at a temperature of (23 ± 2)°C, and a relative humidity of (50 ± 5) % in accordance with ISO 554 [4]. All specimens were tested with a retainer frame. In addition, a wire grid (included in the specimen delivery) was used for FR PVC to reduce the intumescence of the material towards the cone heater.

The work in WP5 was divided to two steps. In step 1, two replicate tests were carried out for particle board to detect and correct possible major differences between the cone calorimeter test procedures of the partners. In step 2, all three materials (particle board, FR PVC, and PUR foam panel) were tested in three replicates.

The NDIR analyser of the cone calorimeter equipment, or an additional NDIR analyser, was used for comparison of CO_2 and CO results measured by the FTIR spectrometer. The gas sample for the NDIR analyser was taken as close as possible to the gas sampling point of the FTIR spectrometer.

5.4.1.1 FTIR procedure

In the composition of the FTIR sampling device, the recommendations resulting from WP1 were taken into account. In addition, the following points in the FTIR test procedure were emphasised:

- The normal FTIR practice and parameters of each laboratory were used as far as possible (unless contradictory to WP5 special instructions).
- Before the test series of each material, the sampling line was flushed with air flow for at least an hour.
- The background spectrum was measured using nitrogen (note: this recommendation was not followed by all laboratories).
- The wavenumber resolution was 4 cm^{-1} or less.

- The FTIR time resolution was selected by each participant. However, spectrum collection intervals longer than 10 seconds were not recommended.
- Data was collected over a pre-defined time period in each test (see Table 5.1).
- Possible changes in the sampling line flow rate and/or the FTIR cell pressure (e.g. due to filter clogging) were reported with occurrence time.
- Planar filters: the filter was replaced after each test. Cylindrical filters: the filter was replaced or cleaned at least after each material tested.
- Filter analysis for acidic gases after the test was recommended.

5.4.1.2 FTIR analysis

The software packages produced by Centexbel (CCT) and University of Greenwich (QTFA) were strongly recommended to be used in the analysis of the FTIR spectra measured in WP5 tests. Due to the tight schedule and some incompatibility problems, however, also the “traditional” analysis procedures of the participants were accepted. In all cases, the model building parameters were reported using a questionnaire form prepared by Centexbel.

5.4.1.3 Reporting

The quantities reported were the following:

1) Cone calorimeter:
    - time to ignition, t_{ig} (s)
    - maximum rate of heat release, RHR_{max} (kW/m^2)
    - total heat release, THR (MJ/m^2)
    - total smoke production, TSP (m^2)
    - total mass loss, TML (g)
    - effective heat of combustion, $\Delta h_{c,eff}$ (MJ/kg)

2) FTIR
    - maximum concentrations of relevant gases (ppm) with their occurrence times (s)
    - total yields of relevant gases (g)
    - graphs of concentrations vs. time

3) NDIR
    - maximum concentrations of CO_2 and CO (ppm) with their occurrence times (s)
    - total yields of CO_2 and CO (g)
    - graphs of concentrations vs. time

The total yields were obtained by

$$m_{gas} = \left(\frac{P_{amb} M_{gas}}{R} \right) \int_{t_0}^{t_{end}} \left(\frac{c_{gas}(t') \dot{V}_{exhaust}(t')}{T_{exhaust}(t')} \right) dt' \approx \left(\frac{P_{amb} M_{gas}}{R} \right) \sum_{i=0}^{N-1} \left(\frac{c_{gas,i} \dot{V}_{exhaust,i}}{T_{exhaust,i}} \right) \Delta t_i \qquad (4)$$

in which P_{amb} is the ambient pressure, M_{gas} is the molecular weight of the particular gas, R is the gas constant (8,3143 $\mathrm{Jmol^{-1}K^{-1}}$), c_{gas} is the volumetric concentration of the gas determined from the FTIR spectra, $\dot{V}_{exhaust}$ is the volumetric flow in the exhaust duct, $T_{exhaust}$ is the gas temperature in the exhaust duct, and Δt is the time step.

All integral values (THR, TSP, TML, total yields of gases) were calculated from the beginning of the cone calorimeter test (i.e. the start of the heat exposure) to the time defined in Table 5.1. The data acquisition continued at least for 1 minute after this time period to ensure the sufficiency of the data considering all sampling delays. The species analysed and the duration of the test for each material are summarised in Table 5.1.

Table 5.1. Species analysed and duration of tests.

Material	CO_2	CO	NO	HCl	HCN	Duration of test (min)*⁾
Particle board	x	x	x			15 + 1
FR PVC	x	x		x		10 + 1
PUR foam panel	x	x		x	x	5 + 1

*⁾ time for data analysis + 1 minute extra

5.4.2 Statistical analysis of interlaboratory tests

The statistical evaluation of results obtained in interlaboratory tests is described in the ISO 5725 standard. The first version of the standard was issued 1986 [5], and the second enlarged version in six parts was published 1994 [6].

Repeatability describes the precision of test results measured in a single laboratory with a particular specimen. Reproducibility is defined as the precision of test results obtained in different laboratories when testing the same specimen. They are expressed by the repeatability standard deviation σ_r and the reproducibility standard deviation σ_R. In practice, σ_r and σ_R are estimated as the standard deviation estimates s_r and s_R calculated from the test data using the procedures defined in the ISO 5725 standard.

The ISO 5725 standard defines two types of observations which can be considered to lie beyond the valid range of values: stragglers and outliers. Their identification is based on the probability of occurrence, P, as compared to critical reference values. Stragglers are entries with a probability of occurrence of $1\ \% < P \leq 5\ \%$, and outliers are entries with $P \leq 1\ \%$. According to the ISO 5725, only outliers are discarded.

In the present version of the standard, Cochran's test is used to determine outliers in the observations of each laboratory, *i.e.* outliers with respect to repeatability. Grubbs' test can be used in two cases: to find outlying observation from the average values from the different laboratories at each level, or to single out observations of a specific laboratory where the Cochran's test has shown that the standard deviation may be susceptible.

5.4.3 Results of step 1

All nine laboratories participating in the experimental work reported test results (at least partially) in step 1. The statistical analysis was performed for 12 quantities related to the cone calorimeter, FTIR measurements, and comparative CO_2 and CO measurements by NDIR. Quantities with an inadequate number of consistent observations were excluded from the statistical analysis.

On the basis of the quantities reported, the questionable results of each participant were reviewed. Possible reasons for the discrepancies were suggested, and the points of special attention in the step 2 tests were listed.

In step 1, the relative repeatabilities (s_r/m) varied from 1,5 to 12,4 % with an average of 6,4 %. The relative reproducibilities (s_R/m) of step 1 tests were in the range of 11,7 - 31,4 % with an average of 22,7 %.

In general, the results of the statistical analysis of the SAFIR WP5 step 1 data were promising. Especially the repeatabilities were good, both for the cone calorimeter data and the FTIR results. In respect of reproducibility, however, the cone calorimeter quantities were typically superior to the FTIR data. As a whole, the results of step 1 can be considered satisfactory.

In step 1, only two repeat tests for one material were performed in each laboratory. Thus, more data was needed to reliably evaluate the repeatability and reproducibility of the FTIR method.

5.4.4 Results of step 2

Test results of step 2 were reported by eight participating laboratories. The statistical analysis was performed for the following 17 quantities:

- time to ignition; t_{ig} (s)
- maximum rate of heat release; RHR_{max} (kW/m^2)
- total heat release; THR (MJ/m^2)
- total smoke production; TSP (m^2)
- effective heat of combustion; $\Delta h_{c,eff}$ (MJ/kg)
- maximum concentrations and total yields of CO_2 and CO measured by NDIR; NDIR $CO_{2,max}$ (ppm), NDIR CO_2 yield (g), NDIR CO_{max} (ppm), and NDIR CO yield (g)
- maximum concentrations and total yields of CO_2 and CO measured by FTIR; FTIR $CO_{2,max}$ (ppm), FTIR CO_2 yield (g), FTIR CO_{max} (ppm), and FTIR CO yield (g)
- maximum concentration and total yield of HCl measured by FTIR for FR PVC; FTIR HCl_{max} (ppm) and FTIR HCl yield (g)
- maximum concentration and total yield of HCN measured by FTIR for PUR foam panel; FTIR HCN_{max} (ppm) and FTIR HCN yield (g)

Due to the different volume flow settings of the laboratories (0,020 - 0,027 m^3/s), the maximum values of the gas concentrations reported by the participants were scaled with the ratio of the average volume flow of each laboratory to the nominal value of ISO 5660-1 (0,024 m^3/s).

Examples of time-concentration curves measured by FTIR for the materials tested are presented in Figures 5.1 - 5.4. The curves shown for each material result from a single test selected randomly. The shapes of the curves are typical for the tests of each material, but the concentration levels shown do not necessarily represent the average.

The general burning behaviour of each material can be seen from the gas concentration curves measured. The flaming period of particle board consisted of intense peaks in the beginning and in the end, and a plateau between the maxima. The smouldering period was characterised by continuous increase of CO concentration. The burning of FR PVC went typically through 2 - 3 cycles of ignition and self-extinction. The production of HCl, however, was continuous throughout the test. Ignition immediately after the start of the heat exposure and an intensive early stage of burning were typical for PUR foam panel. A smaller local maximum was seen before the end of the flaming period. During smouldering, increasing concentrations of CO and HCN were observed.

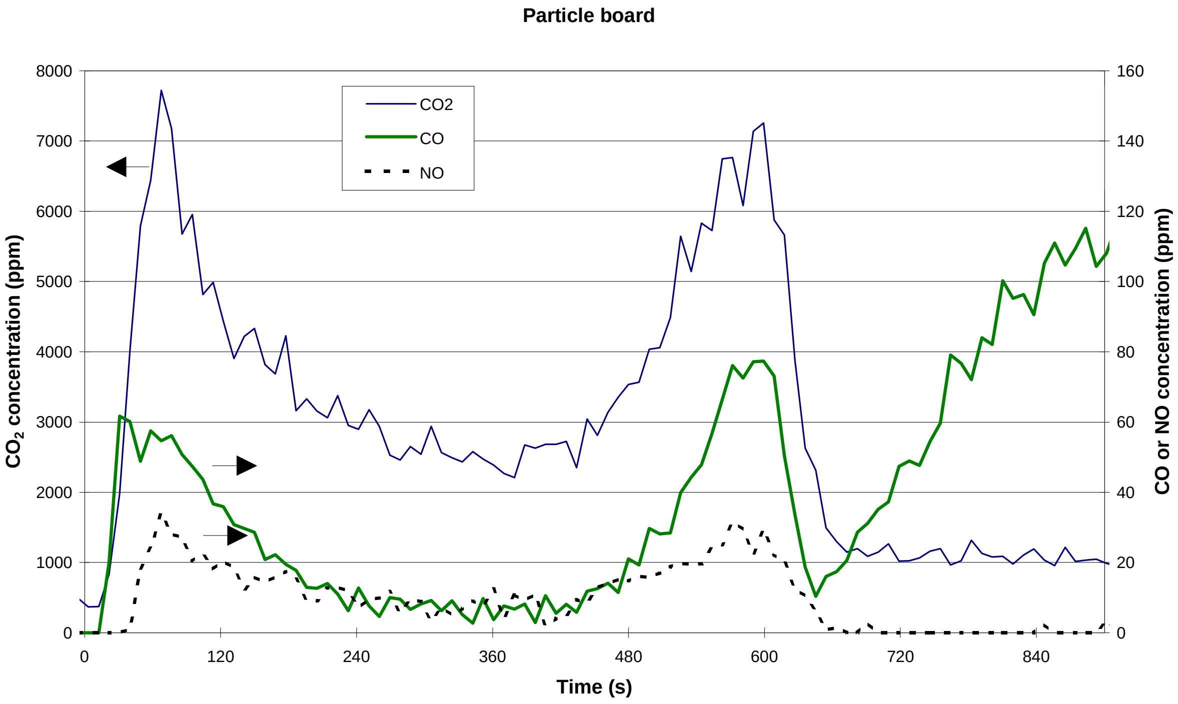


Figure 5.1. Gas concentrations produced by particle board. The arrows show the vertical axis to be used for each curve.

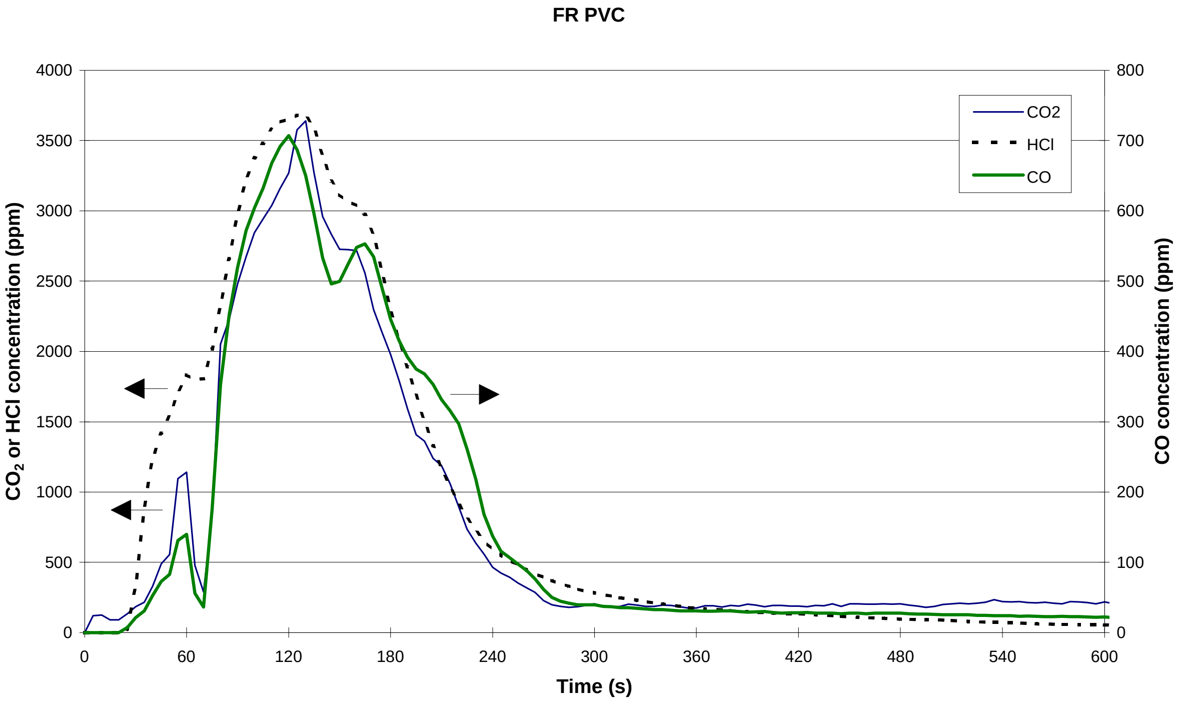


Figure 5.2. Gas concentrations produced by FR PVC. The arrows show the vertical axis to be used for each curve.

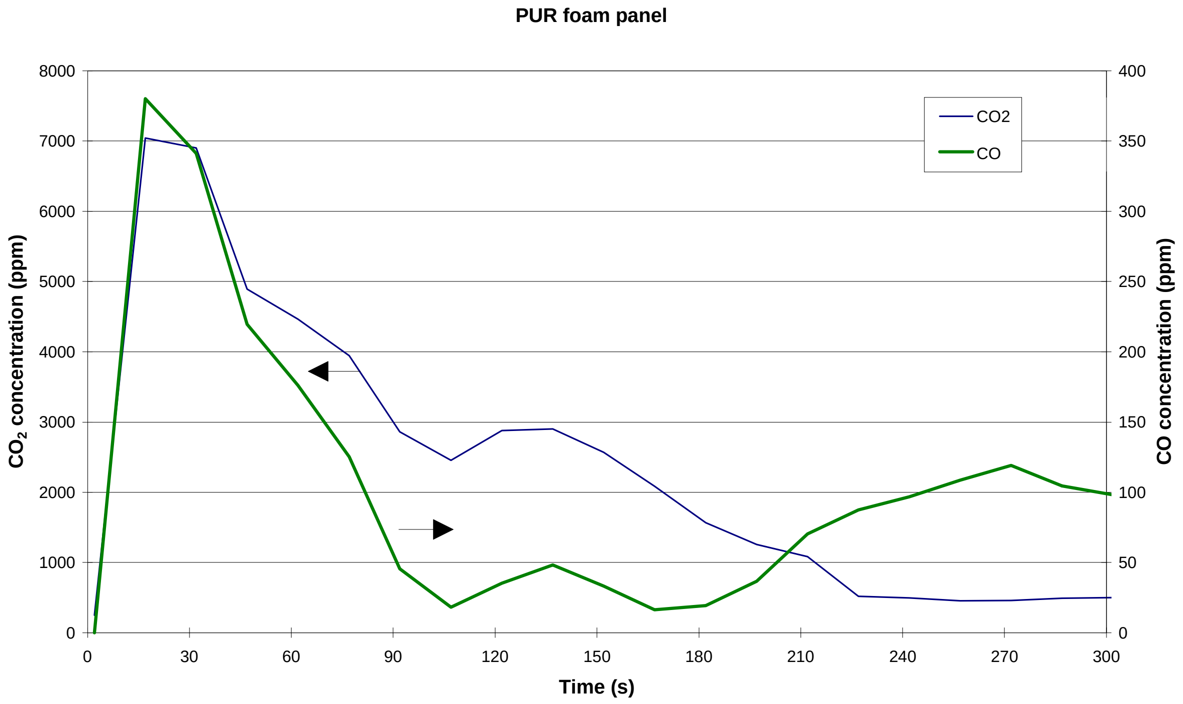


Figure 5.3. CO_2 and CO concentrations produced by PUR foam panel. The arrows show the vertical axis to be used for each curve.

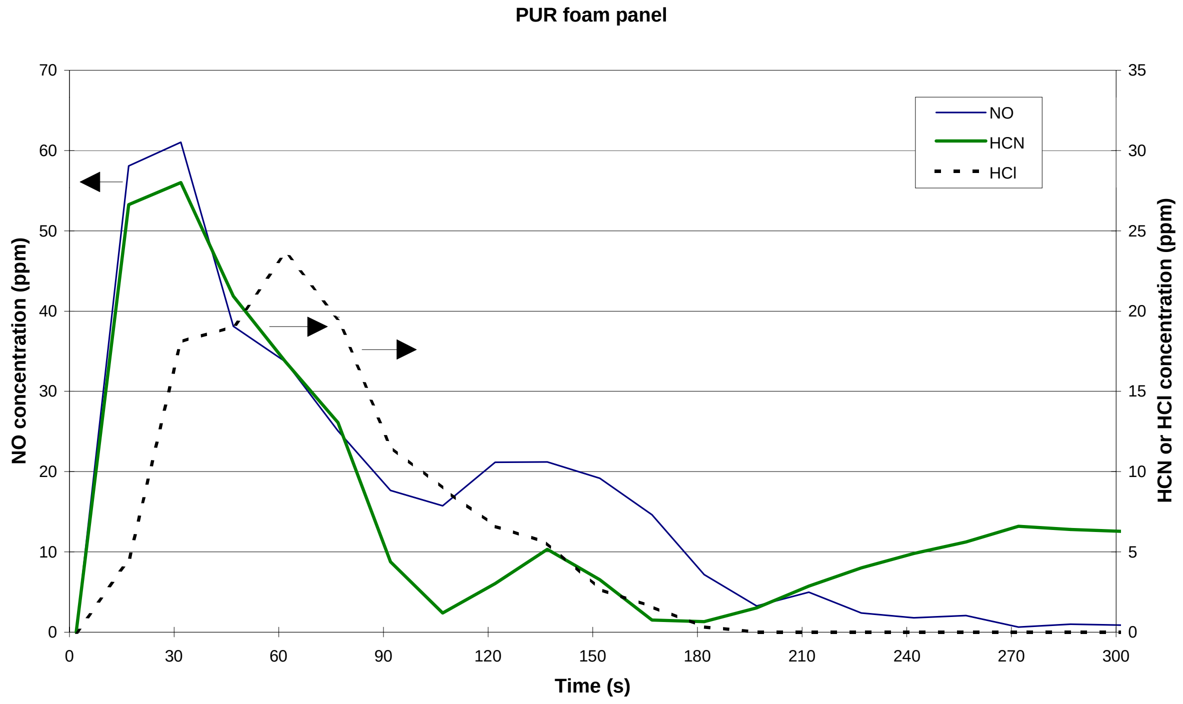


Figure 5.4. NO, HCN and HCl concentrations produced by PUR foam panel. The arrows show the vertical axis to be used for each curve.

5.4.4.1 Cone calorimeter quantities

The relative repeatability and reproducibility standard deviations (s_r/m and s_R/m, respectively) of the cone calorimeter quantities are summarised in Table 5.2.

Table 5.2. Ranges and average values of relative repeatability and reproducibility standard deviations for cone calorimeter quantities.

Quantity	s_r/m		s_R/m	
	Range (%)	Average (%)	Range (%)	Average (%)
t_{ig}	7,3 - 17,7	12,0	19,0 - 68,3	36,3
RHR_{max}	3,9 - 15,5	8,1	14,3 - 34,4	22,3
THR	5,6 - 14,7	8,7	10,2 - 25,7	16,3
TSP	3,6 - 14,0	8,7	8,5 - 17,9	13,1
$\Delta h_{c,eff}$	2,4 - 13,0	6,1	6,2 - 33,2	16,5

Most of these repeatability and reproducibility values can be considered satisfactory. The main exception is the ignition time of PUR foam panel. It must be noted, however, that the mean value of the ignition time for this material was very small (only 2,6 seconds), leading to rather high s_r/m and s_R/m values. The absolute values of s_r and s_R for the ignition time of PUR foam panel are very low, less than 2 seconds.

In conclusion, the repeatability and reproducibility of the cone calorimeter results were satisfactory. Thus, the effect of the variability of the cone calorimeter procedures on the scattering of the FTIR results in this interlaboratory trial can be considered typical for well-defined fire tests.

5.4.4.2 FTIR quantities

The relative repeatability and reproducibility standard deviations (s_r/m and s_R/m, respectively) of the FTIR results are summarised in Table 5.3.

Calculated over all materials and gases included in the statistical analysis, the averages of s_r/m and s_R/m for FTIR results are 11,7 and 25,4 % for the maximum concentration values, and 10,3 and 30,4 % for the yields, respectively.

The FTIR results clearly deviating from the typical magnitude of the values in Table 5.3 are the relative reproducibilities of CO yield and HCN_{max}. In the statistical analysis of the CO yields, no outliers or even stragglers were detected. However, if the results of the laboratory with the greatest deviation from the mean value were excluded for each material (not the same laboratory in all cases), the average s_R/m of CO yield would be reduced to 30,7 %.The high s_R/m value of HCN_{max} can be explained by the relatively low mean value, 40 ppm.

The CO yield calculations for particle board and PUR foam panel were repeated over shorter time periods (0 - 7 min for particle board and 0 - 3 min for PUR foam panel) excluding the smouldering phase of the test. However, this did not improve the average reproducibility of CO yield. In case of particle board, s_R/m got worse as a result of the low mean value. The improvement for PUR foam panel was insignificant.

Table 5.3. Ranges and average values of relative repeatability and reproducibility standard deviations for FTIR results.

Quantity	s_r/m		s_R/m	
	Range (%)	Average (%)	Range (%)	Average (%)
$CO_{2,max}$	4,9 - 16,2	9,2	14,9 - 23,8	19,7
CO_2 yield	3,8 - 15,6	8,3	15,6 - 39,1	24,2
CO_{max}	9,9 - 16,5	13,8	19,8 - 29,8	25,3
CO yield	5,7 - 17,0	12,2	34,0 - 46,7	38,8
HCl_{max} *)	–	13,0	–	28,5
HCl yield *)	–	8,6	–	26,0
HCN_{max} *)	–	11,7	–	39,3
HCN yield *)	–	12,2	–	28,7

*) Statistical analysis of HCl and HCN results was performed only for one material. These single repeatability and reproducibility values are reported in the “Average” column for HCl and HCN.

Comparing the results presented in Tables 5.2 and 5.3 it can be seen that the repeatability and reproducibility values of the cone calorimeter are better than those of the FTIR method. The difference between the cone calorimeter and FTIR method is typically about 2 - 3 % (absolute) for repeatability and about 7 - 10 % (absolute) for reproducibility. The repeatability and reproducibility of fire gas measurements are worse than those of the main fire test parameters because fire gas generation is more complex and includes a secondary stage. In addition, the scattering of the fire test is unavoidably summed up with the scattering of the FTIR method when the measurements are carried out in a real fire test situation.

5.4.4.3 Comparison of quantities measured by FTIR and NDIR

FTIR deviation

The quantities measured by FTIR and NDIR can be compared using the “FTIR deviation”, defined as follows:

$$\text{FTIR deviation (\%)} = \frac{\text{FTIR result - NDIR result}}{\text{NDIR result}} \times 100\ \%$$

The FTIR deviations of the mean values of the maximum concentrations and yields of CO_2 and CO are presented in Table 5.4. It is emphasised that these numbers are calculated from the mean values resulting from the statistical analysis, not from the results reported by individual participants.

Table 5.4. FTIR deviations of CO_2 and CO results.

Quantity / Material	Particle board	FR PVC	PUR foam panel
$CO_{2,max}$	+4,8 %	+8,5 %	+7,4 %
CO_2 yield	-0,5 %	-0,6 %	-1,2 %
CO_{max}	+8,9 %	-14,1 %	-1,1 %
CO yield	+16,7 %	-7,8 %	+9,3 %

In the comparison of FTIR and NDIR results, it must be noted that differences are also known to occur between other analytical methods.

As seen from Table 5.4, the $CO_{2,max}$ values of FTIR are slightly higher than those of NDIR, but the difference is balanced when the yields are calculated. The differences in CO results are more random, but the FTIR deviation is within ± 17 % in all cases. Excluding the results of the laboratory deviating most from the mean value (as described in 5.4.4.2) would improve the FTIR deviations of CO yield to values better than ± 1 % for all materials!

The difference between the CO_2 maximum concentrations measured by NDIR and FTIR can be explained by the difference in the time response of the analysers. The work performed in WP1 revealed that the response times of NDIR analysers are generally longer than those of FTIR spectrometers. As a result, the time variation of CO_2 concentration measured by NDIR tends to be smoothed. Therefore, the maximum concentration value decreases, especially for materials like PU foam panel exhibiting peaks of short duration.

In this study, the yields were calculated over a pre-determined time period beginning from the start of the heat exposure. The substantial production of CO in the end of the test (i.e. after the flaming combustion) for particle board and PUR foam panel makes the CO yield results of these materials sensitive to the end point of the calculation. In such cases, even a relatively small asynchronism of the time scales of FTIR and NDIR can contribute significantly to the difference between the results. This kind of time difference could arise e.g. from different sampling delays of the methods.

Repeatability and reproducibility of the methods

The repeatability and reproducibility values for CO_2 and CO are summarised in Table 5.5.

Table 5.5. Repeatability and reproducibility for CO_2 and CO measurements by FTIR and NDIR.

Quantity	Average s_r/m (%)		Average s_R/m (%)	
	NDIR	FTIR	NDIR	FTIR
$CO_{2,max}$	9,8	9,2	23,1	19,7
CO_2 yield	9,4	8,3	20,4	24,2
CO_{max}	10,6	13,8	24,0	25,3
CO yield	11,5	12,2	24,0	38,8

The repeatability and reproducibility of the FTIR and NDIR results are of the same order, excluding the reproducibility of CO yield which is better for the NDIR method (see possible reasons above).

5.4.4.4 FTIR quantities excluded from statistical analysis

In addition to the gases discussed above, some FTIR findings of other compounds were reported. The number of observations was insufficient for reliable statistical analyses. However, the statistical calculations for these quantities gave indications of the same levels of repeatability and reproducibility as for the FTIR quantities subject to full analysis with larger number of consistent observations.

As seen from Table 5.1, also NO results from particle board tests and HCl results from PUR foam panel tests were expected. In step 2, these gases were detected only by four laboratories. In addition, four participants reported NO production from PUR foam panel.

NO production of particle board

The production of NO seemed to be very sensitive to the conditions prevailing during the combustion. It is known that NO production is critically affected by factors such as temperature and O_2 availability. Thus, the results obtained in a single laboratory can vary in the long run, not to mention the differences between different laboratories.

The NO concentrations produced during the combustion of particle board were relatively low. The mean value of the detected maximum NO concentrations was 31 ppm which is near to the typical MDL of FTIR spectrometers with a DTGS detector.

The interference of water can additionally mask low levels of NO. Consequently, the NO production could not be detected by all participants in this test series.

NO production of PUR foam panel

For PUR foam panel, the mean value of the detected maximum NO concentrations was 54 ppm. Also in this case, the sensitivity of the NO production to the ambient conditions and the concentration level near the MDL can contribute to the limited number of laboratories reporting the results. Another reason is probably the fact that the analysis of NO from PUR foam panel was not included in the list of gases to be reported.

HCl production of PUR foam panel

The mean value of the detected maximum HCl concentrations from PUR foam panel was 32 ppm (on the basis of results from three laboratories; the fourth laboratory excluded as an outlier). This is also a relatively small value, even though the MDLs of HCl are typically lower than those of NO.

Data about the condition sensitivity of HCl production of PUR foam panel is not available. However, the effect of the ambient conditions on the burning process cannot be directly excluded.

5.4.4.5 Accuracy factors of FTIR measurements

Uncertainty of calibration gas concentrations

The uncertainty of the calibration gases is generally in the range of 0,5 - 5 % (relative).

Minimum detection limits

Typical MDLs of the gases of interest for MCT and DTGS detectors are summarised in Table 5.6. The values are based on the WP3 report of minimum detection limits and the data reported by the participants in connection with WP5.

Table 5.6. Typical MDLs for MCT and DTGS detectors.

Gas	MCT detector	DTGS detector
CO	≈ 1 ppm	10 - 30 ppm
CO_2	≈ 1 ppm	< 10 ppm
HCl	≈ 1 ppm	2 - 25 ppm
HCN	< 1 ppm	≤ 3 ppm
NO	2 - 3 ppm	8 - 55 ppm

Adsorption of acidic gases

The adsorption of acidic gases (e.g. HCl) onto the filter and sampling line is a well-known problem in all gas analysis techniques. Due to the trapping effects, the amount of certain gases reaching the analyser is reduced compared to the amount actually produced in the fire test in many cases. The relative significance of the adsorption increases with decreasing gas yields.

In WP5 step 2, the amount of HCl accumulated on the filters was determined after the FR PVC and/or PUR foam panel tests by several participants. Compared to the HCl yields measured by, the amounts adsorbed on the filter were relatively small, about 0,1 % at maximum. It must be noted, however, that the HCl adsorption on the inner walls of the sampling line was not analysed in these tests.

Considering the differences of the adsorbed HCl on the filter (and the sampling line) in different laboratories, the possibility that the adsorption could cause some variation to the FTIR results of the partners cannot be excluded, at least in the case of PUR foam panel. However, the effect is probably minor to other sources of inaccuracy.

Analysis techniques

The participants used different analysis techniques and software packages in the spectral analyses of the WP5 tests. The scattering of the results due to the different analysis methods is included in the repeatability and reproducibility reported.

5.5 Conclusions

In this interlaboratory trial, statistical analysis according to the ISO 5725 principles was performed for 17 quantities related to the cone calorimeter, NDIR measurements and FTIR analysis.

For the cone calorimeter quantities, the relative repeatability and reproducibility standard deviations varied in the ranges of 2,4 - 17,7 % and 6,2 - 68,3 %, with averages of 8,7 % and 20,9 %, respectively. Thus, the scattering of the cone calorimeter results can be considered normal. Consequently, the effect of the variability of the cone calorimeter procedures on the scattering of the FTIR results in this interlaboratory trial can be considered typical for well-defined fire tests.

The repeatability and reproducibility values of gas concentrations and gas yields are best comparable with those of heat release/total heat release measurements. To give an indication for the interpretation of the data of this study, results from previous interlaboratory trials are reviewed. Table 5.7 summarises the comparisons with the results of the SBI and cone calorimeter methods.

Table 5.7. Comparison of accuracy data of test methods.

Method / parameters	Repeatability standard deviation s_r/m	Reproducibility standard deviation s_R/m
SBI, 1997		
RHR_{max} , THR	5 - 41 %	7 - 60 %
Smoke production	7 - 78 %	19 - 114 %
Cone calorimeter,		
ISO TC92/SC1, 1997		
RHR_{max} , THR	3 - 55 %	4 - 87 %
Cone calorimeter,		
ISO TC92 SC1/WG5, 1991-1992		
Smoke production	6 - 60 %	16 - 100 %
This study		
Max. gas concentration	4 - 17 %	15 - 47 %
and gas yield (FTIR) *)	(11,0 % in average)	(27,9 % in average)
RHR_{max} , THR	4 - 16 %	10 - 34 %
Ignition	7 - 18 %	19 - 68 % **)
Smoke production	4 - 14 %	9 - 18 %

*) Including results for CO_2, CO, HCl and HCN.

**) The high maximum value of s_R/m (68 %) is due to the short ignition time of PUR foam panel.

The following conclusions can be made on the basis of the results of Table 5.7:

- repeatability standard deviation values for FTIR measurements are similar to those of RHR_{max} and THR measurements;
- reproducibility standard deviation values are larger for FTIR measurements than for RHR_{max} and THR measurements because of the scatter in ignition and burning processes in the test method.

Considering the effect of the scattering of the fire test method included in the FTIR variation, the repeatability and reproducibility of the FTIR analysis of smoke gases can be regarded as satisfactory.

6. Summary

FTIR spectrometers offer a continuous monitoring technique of many gases simultaneously in smoke gas analysis. Using FTIR, it is possible to set up a calibration and prediction method for each gas showing a characteristic spectral band in the infra-red region of the spectrum. The main problem in the measurements is to have a representative sample of fire gases analysed.

The SAFIR project included the following tasks: small scale and large scale sampling (WP1 and WP2, respectively); analysis, calibration and software techniques (WP3); the verification of the method (WP4); and an interlaboratory trial (WP5).

The principle in defining an optimum sampling system for FTIR was to transfer the fire effluents through the sampling device as quickly as possible and keep them unaltered during the passage. To ensure the representative smoke gas samples for the analysis, the following recommendations applicable to both small and large scale should be taken into account:

- A multi-hole probe made of stainless steel with minimum hole diameter of 3 mm is recommended. The holes shall be oriented downstream from the fire gases.
- Both circular (glass fibre except for HF) and cylindrical (e.g. ceramic) filters can be used. The initial amount of Cl and Br in the filters shall be checked.
- A gas sampling line made of PTFE with inner diameter of 3 - 4 mm offers the best performance. The line should be as short as possible; lengths up to 4 m are found acceptable.
- The flow rate shall be as high as possible; at least 3,5 l/min.
- The temperature of the sampling device shall be as high as possible with minimum of 150°C and practical maximum of 190°C. To avoid cold points where condensation could appear, the temperatures of the different parts should be as close to each other as possible. If the same temperature cannot be maintained in all parts of the sampling system, the temperature shall preferable increase towards the end of the device.
- When acidic gases are analysed by FTIR, it is recommended to wash the different parts of the sampling device especially when the concentrations determined are low. The washing solution can be analysed by an appropriate analytical method to evaluate the total amount of the gas produced by the combustion.
- The pressure in the gas cell must be monitored during the experiments because the variation of the pressure inside the sampling configuration leads to a variation in the measured concentrations of gaseous products.

There are some features of the measuring system that are specific for large scale testing. Making measurements e.g. in the door of a fire room places extra constraints on the measuring system:

- When measuring gases that are not well mixed the multi-hole probe sampling from the fire gases should have holes that are graded in size according to where they are on the probe.
- Due to the size of the testing facilities it can sometimes be difficult to keep the sampling line short. In cases where the sampling line is very long and acid gases are being studied it is advisable to wash the line to check for adsorbed acids.

The findings of this project concerning sampling techniques are most relevant for all other methods used for defining fire gases.

Quantitative calibration and prediction methods have been constructed for different components present in smoke gases. Recommendations on how to deal with interferents, non-linearities and outliers have been provided and a verification method for the spectrometer for unexpected variations and for the different models have been described. To circumvent the availability of software tools for analysing smoke, additional software has been written.

The following conclusions and recommendations are given related to data analysis, calibration and software:

- Multivariate chemometrical techniques such as CLS, PLS, INLR and QTFA are needed for the prediction of toxic components in smoke gases generated during a fire test. For several gases, linear techniques are inadequate and non-linear techniques are needed.
- For satisfactory analysis using multivariate or univariate methods, it is essential that good reference spectra are obtained for calibration. A sufficient number of calibration spectra should be obtained to allow modelling of non-linear behaviour with reasonable precision.
- Extrapolation of concentrations outside the calibration range should be avoided.
- It is strongly recommended to visually inspect the data output of the multivariate models. Unexpected behaviour (e.g. non-zero baseline) should be investigated.

For the verification of the FTIR results, FTIR measurement procedures in different fire test scenarios have been studied using the recommendations of this project for measurement techniques and analysis, and real precision values for specific test scenarios have been estimated. A proposal for draft standard of the FTIR method for smoke gas analysis has been prepared.

As a results of the verification study, the following conclusions have been made:

- FTIR is capable of making time resolved measurements on many species simultaneously.
- Concentration/time profiles are realistic and follow the shape of the profiles from comparison methods and fire test characteristics. FTIR gives a good peak response.
- Cell pressure shall be monitored due to its influence on the concentration results.
- Concentrations will be influenced by water vapour, i.e. the FTIR results can be different from the comparison method results obtained with dried gas sample.

An interlaboratory trial was carried out using the cone calorimeter method testing three materials in three replicates. The FTIR method of measuring smoke gases was found repeatable and reproducible when analysed statistically according to the ISO 5725 principles and compared with corresponding data of well-known fire test methods.

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