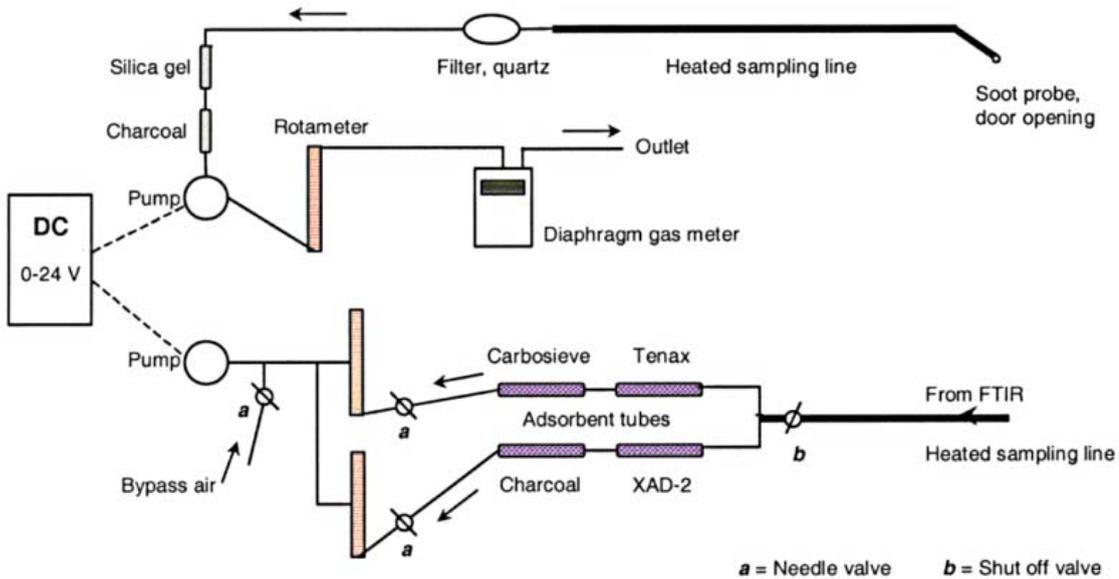


TOXFIRE - Fire Characteristics and Smoke Gas Analysis in Under-ventilated Large-scale Combustion Experiments: Adsorbents and Soot Measurements



Abstract

In the CEC project *Guidelines for the Management of Fires in Chemical Warehouse, TOXFIRE* (EV5V-CT93-0275), carried out by a consortium of seven European partners, SP Swedish National Testing and Research Institute has carried out controlled large-scale combustion experiments on amounts in the 100 kg range.

Controlled large-scale combustions were performed in two scales on materials with different chemical composition. The degree of ventilation was varied from well ventilated to under-ventilated, determined with a phi-meter measuring the amount of additional oxygen required to achieve complete combustion. Traditional fire-related parameters were measured, accompanied by extensive chemical characterization of the smoke gases.

This report gives an account of adsorbent measurements carried out to identify and quantify individual organic components in the smoke produced under different degrees of ventilation. The independent sampling and quantitation of soot formed is also accounted for, as well as attempts at an over-all characterisation of the soot in a few cases.

It has been demonstrated that it is possible to make a thorough mapping of the products of combustion formed in large-scale combustions.

Key words: combustion of chemicals, oxygen-depleted conditions, degree of ventilation, combustion products, adsorbent sampling, chemical characterization, soot sampling.

**Sveriges Provnings- och
Forskningsinstitut**
SP Rapport 1996:48
ISBN 91-7848-653-X
ISSN 0284-5172
Borås 2003

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SP Report 1996:48

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Foreword

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

We would like to thank our colleagues at the departments of Chemical Analysis and Fire Technology for their valuable assistance throughout this work. We gratefully acknowledge the special services provided by Rauno Pyykkö in complementing the equipment for the sampling process, and the friendly advice from Björn Lundgren, our head of department.

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

1 Introduction

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

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

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

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

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

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

A phi meter was used to define the degree of ventilation. In addition to the common fire test parameters mentioned previously, extensive measurements were carried out to characterise the composition of the smoke gases. On-line measurements, *e.g.* Fourier Transform InfraRed spectroscopy (FTIR), and adsorbent techniques were utilised to measure quantitatively

individual components in the smoke. Measurements of the mass loss rate allowed evaluation of yields in relation to amount of material burned for the various species in the smoke gases.

This report gives an account of the work carried out to characterise the organic components in the smoke by adsorbent sampling and subsequent analyses, and also studies of the soot formed. The over-all achievements at SP, including a brief overview of the main aims of the TOXFIRE project, are summarised in reference 1. Detailed information on the various parts of the work at SP is given in references 2 through 5.

The TOXFIRE project in its entirety is reported on in reference 6, which shows how the studies carried out by each partner in the project are linked into the risk assessment structure.

2 Design of SP combustion experiments

The aim of the work at SP was to study the fire characteristics and smoke gas composition from large-scale combustions on a set of materials representing bulk chemicals generally stored in large quantities. Of particular interest were studies of the composition of the smoke from oxygen-depleted fires, *i.e.* under-ventilated fire conditions. Some of the experiments were to be performed with the materials in a storage configuration.

2.1 Choice of substances for large-scale studies

Great care had to be exercised in the selection of compounds since they were to be used in rather large quantities indoors and combusted under poor ventilation conditions. The materials were selected such that a reasonable complexity in the smoke gas chemistry could be expected. A carbon-hydrogen (CH), a carbon-hydrogen-nitrogen (CHN), a carbon-hydrogen-nitrogen-sulfur (CHNS), a carbon-hydrogen-chlorine (CHCl) and a carbon-hydrogen-nitrogen-chlorine (CHNCl) material were chosen for the combustions (Figure 2.1).

The compounds were polypropene (PP), Nylon 66 (Ny), tetramethylthiuram monosulfide (TMTM), 4-chloro-3-nitrobenzoic acid (CNBA), and chlorobenzene (CB); two are polymers, two are crystalline compounds, and one (CB) is a fairly volatile liquid. All of them are used in industry in bulk quantities.

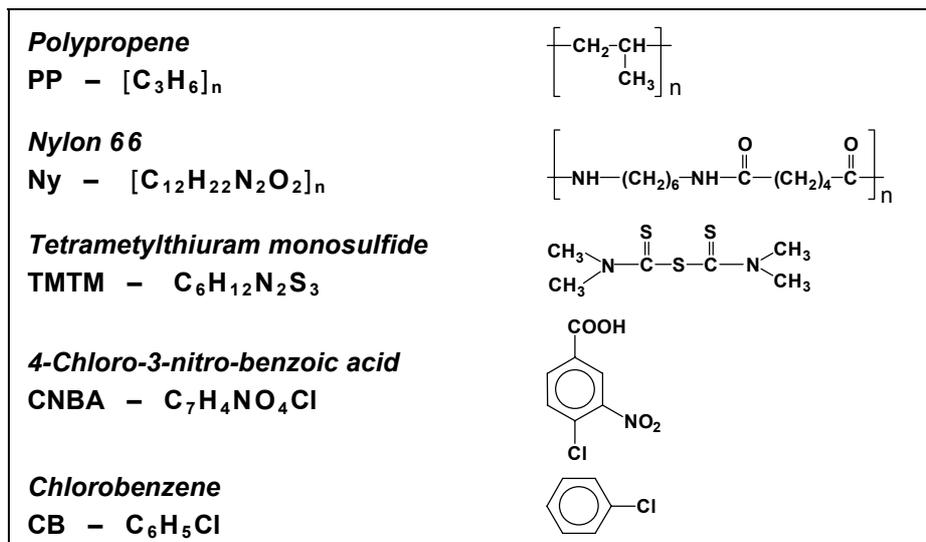


Figure 2.1 Materials selected for the fire tests.

2.2 Combustion configurations

Two types of experimental set-ups were to be used. Most of the large-scale experiments were carried out in the ISO 9705 room (20.7 m³; Figure 2.2) with the chemicals in steel pans for the combustions [2]. This test arrangement was considered to be large enough in scale to represent full-scale conditions and sufficiently controlled to provide repeatable results. As a complement to the ISO 9705 room tests, a few tests were performed in an even larger scale test enclosure (256 m³; Figure 2.3) that allowed storage configuration [3]. Hoods connected to an exhaust duct collected the combustion gases from the respective test facility.

The principal challenge for the large-scale combustions was to achieve conditions yielding under-ventilated, *i.e.* oxygen-depleted, combustions. By varying degrees of restriction of the openings of the two types of test chamber, the degree of ventilation was controlled. The ISO 9705 room has a single opening, $0.8 \times 2.0 \text{ m}^2$, centrally located on one of the short walls. To modify the ventilation conditions inside the room, non-combustible fibreboard was used to block the lower part of the opening leaving 0.89 m , 0.68 m , 0.56 m and 0.45 m , respectively, open at the top. The larger test facility had its opening along one of the long sides. The opening was kept at $0.8 \times 0.89 \text{ m}^2$ in all tests in the larger enclosure.

Thermocouples were used inside the test enclosures to measure sets of temperature required *inter alia* to calculate the mass flow through the opening [4]. The temperature profile from a smaller vertical thermocouple tree in the opening was used to define the areas of in- and out-flow through the opening. These temperatures were also needed for converting the mass flow rate to a volume flow rate.

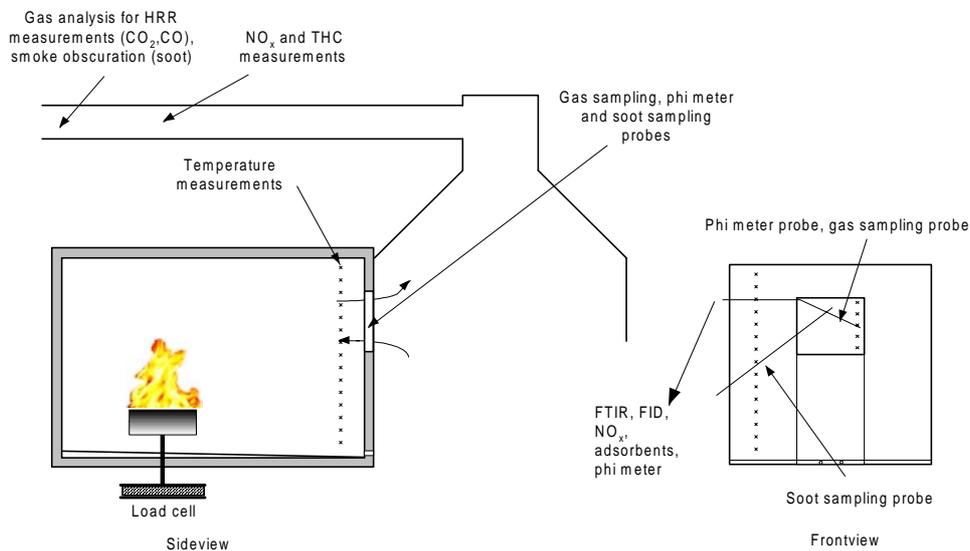


Figure 2.2 The large-scale experiment set-up including the ISO 9705 room with the dimensions $3.6 \times 2.4 \times 2.4 \text{ m}^3$ and the probe positions in the opening and in the exhaust duct to the calorimeter system.

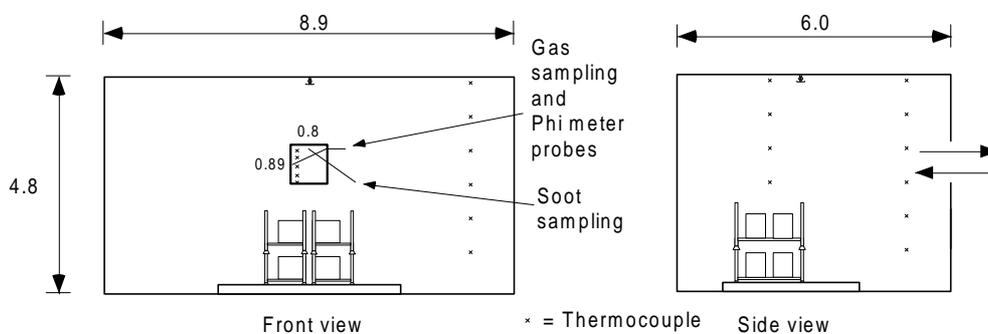


Figure 2.3 The storage configuration set-up with the test enclosure, the thermocouples and the sampling probe positions in the opening; dimensions in are in meters.

2.3 Equivalence ratio

As the degree of ventilation is a crucial parameter for characterising different types of fires, it is important, in addition to be able to control it, to have a proper measure for it. The degree of ventilation, in principle, is the ratio of *oxygen required* over *oxygen available* for complete stoichiometric combustion. This so-called equivalence ratio, ϕ , is defined as

$$\phi = \frac{(m_{\text{fuel}}/m_{\text{oxygen}})}{(m_{\text{fuel}}/m_{\text{oxygen}})_{\text{stoich.}}} \quad \phi = 1 \text{ stoichiometric conditions}$$

$\phi < 1$ signifies well-ventilated conditions, whereas $\phi > 1$ denotes under-ventilated conditions. Since the over-all combustion process is studied in this work, ϕ is defined as the equivalence ratio for the **over-all** combustion process. This is usually referred to as the *global equivalence ratio*, GER.

A phi meter was built and used for the measurement of ϕ [4]. The phi meter was originally constructed and calibrated for hydrocarbons [7], but some of the substances studied contain atoms of additional elements, namely nitrogen, sulfur and chlorine. A few limited tests were conducted to explore whether this would give rise to incorrect values of ϕ . No indication was, however, found of specific influence from the presence of these elements that would have to be specifically accounted for.

2.4 Strategy for smoke gas characterisation

As far as possible, continuous on-line measurement techniques were to be used for the characterisation of individual components in the smoke. A considerable advantage of on-line measurements is that evaluation of results can be made over time periods that do not have to be selected beforehand. Hence, as in a previous project [8, 9], a chemiluminescence instrument was utilised for the measurement of nitrogen oxides, NO_x , (NO and NO_2 , respectively). A flame ionisation detector (FID) instrument [9] was used for an overall measure of the amount of unburned hydrocarbons, THC.

The principal on-line measurements were made utilising a new Fourier Transform InfraRed (FTIR) spectrometer. The FTIR technique allows the simultaneous measurement of a large number of species in the smoke. It also facilitates subsequent identification and calibration for compounds that may not have been considered initially. But limitations in the resolution of the current instrument makes the usefulness of the FTIR limited for the identification and quantitation of individual, more or less closely related organic compounds having more than one carbon atom.

Hence, adsorbent sampling and analysis was chosen as the preferred technique for determining the composition of the smoke as regards its content of organic components. Two parallel set-ups, each with two different types of adsorbent, were selected in order to have flexibility in the choice of analysis technique and to cover a reasonable volatility range. The choice for the most volatile fraction was activated charcoal and Carbosieve/Carbotrap, respectively, and XAD-2 and Tenax, respectively, for compounds in the range of C_5/C_6 and higher, *cf.* 3.2.2 and Figure 3.1.

Sampling periods were to be limited to about 10 min for the type of adsorbent tubes and flow rates selected. The amounts determined would be integrated mean values for the sampling period. This in itself limited the duration of any one adsorbent sampling in order to be able to related adsorbent results to reasonably distinct ventilation conditions.

Sampling of smoke in the duct that collects the smoke from the actual test enclosure would have been the most convenient approach. The smoke would then be reasonably well mixed and the flow rate readily defined. However, afterburning with additional, not-controlled air oxygen was likely to occur, since the gases leaving the room would be at elevated temperatures. Such uncontrolled chemical reactions might be particularly cumbersome in the cases of under-ventilated fires. The composition of the gas in the duct might then not be representative of the reaction actually taking place in the combustion at the conditions in the room. Therefore, sampling in the duct for the measurements of ϕ and for the characterisations of the smoke gas components was considered unsuitable.

Instead, sampling was arranged for across the upper half of the respective openings in order to make sure that the smoke sampled was as close as possible in composition to that formed in the immediate fire. Stainless steel sampling probes were mounted diagonally, as shown in Figures 2.2 and 2.3, with sets of equidistant holes along the distance covering the opening; a detailed description of the different probes is given in references 2 and 3.

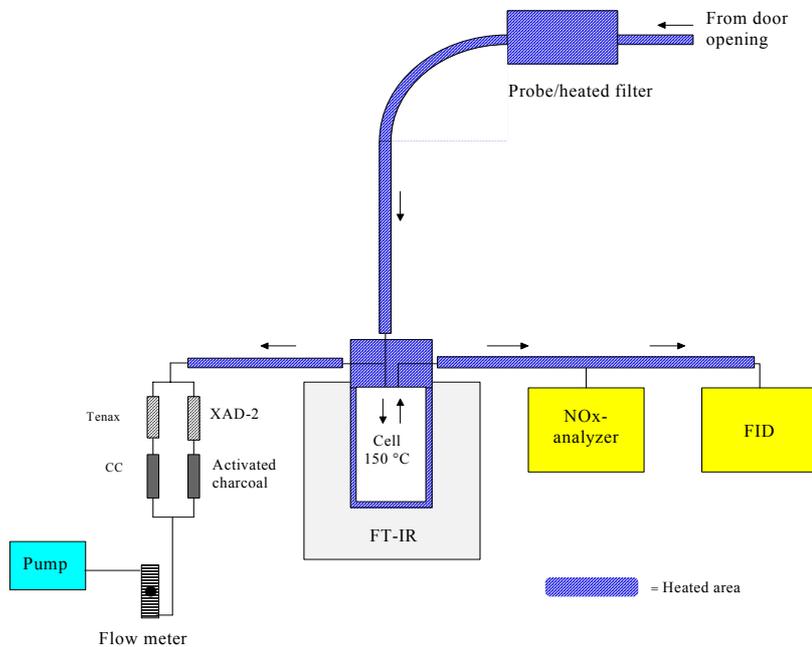


Figure 2.4 Over-all smoke gas characterisation sampling system

Gas samples were hence to be taken in the opening to the FTIR, the NO_x and the THC instruments, to the adsorption tubes, and to the phi meter. Sampling of soot particles was also performed in the opening; *cf.* Figures 2.2 through 2.4.

Hoods connected to an exhaust duct [25] collected the outflow of combustion gases from the test chambers. In the duct, gas temperature and flow rate were measured, and gas was also sampled here and transported to a further set of on-line gas analysis equipment. Concentrations measured were those of CO_2 , CO, THC (total amount of unburned hydrocarbons) and NO_x (nitrogen oxides). A lamp/photo-cell system was used to measure the light obscuration, facilitating calculation of the soot production. The production rates of CO_2 , CO, soot and THC were required for the determinations of heat release rate, HRR.

These on-line measurements and the ensuing results are dealt with elsewhere [2, 3, 5]. In the remainder of this report, the focus will primarily be on the sampling and analyses of organic compounds on adsorbents and of soot, respectively.

3 Experimental

3.1 Combustions

For the combustions in the 9705 room, the fuel was put into pans of different size, 0.5 m² to 1.4 m², aimed at generating about the same total HRR irrespective of substance. A load cell was used to measure the mass loss rate, MLR [2]. To keep the fire plume away from the opening, the pan/load cell unit was placed on the centre line, equidistant from three of the walls, two thirds of the length of the room from the opening, *cf.* Figure 2.2.

In the storage configuration tests, the material was put in cardboard boxes, positioned on steel shelves in a two-tier post pallet system as shown in Figure 2.3. The solid materials were put in paper bags, each bag containing 1.1 kg of substance [3]. The total amount of substance in the storage configuration tests was 160 kg, exclusive of the cartons. No load-cell was used in the pallet configuration tests, *cf.* Figure 2.3.

After screening tests, it was decided, for safety reasons, *not* to burn CB in polyethene bottles within boxes as was originally intended but instead in an open pan placed on a load cell. This set-up was also used in one of the two PP tests in the larger test enclosure to facilitate comparison, in this one case, of the influence from the test enclosure itself on the results. No adsorbent sampling was, however, carried out in that particular PP test.

Four individual experiments were performed in the ISO 9705 room on each of the materials. In the storage configuration test enclosure, one configured test was performed on each of the solid materials, plus the two open-pool combustions (PP; CB). An overview of the SP fire tests carried out is given in Appendix 1.

3.2 Smoke sampling

An over-view of the main system for sampling of the smoke leaving the room was outlined in Figure 2.4. Additional details on the adsorbent and the soot sampling systems are shown in Figure 3.1.

3.2.1 Probes

Smoke samples were taken diagonally across the upper half of the actual opening of the test chambers through two stainless steel probes, each having from 7 to 13 holes (3.0 mm diameter), with the suction end of the probes in the top corner [2, 3]. The probe for the phi-meter sampling had its holes inwards to include the soot with the sampled gas, whereas the other probe had the holes turned outwards to exclude the soot as far as possible. A third probe, mounted perpendicular to the opening, centred above the other two (see Figure 2.2), was used for taking soot samples and was mounted. This probe was 2 m in length, had a 10-mm diameter orifice and could be individually heated. An over-view of the main system for sampling of the smoke leaving the room was outlined in Figure 2.4, with additional details on adsorbent and soot sampling shown in Figure 3.1.

3.2.2 Adsorbents

Two principally different lines of adsorbents (see Figure 3.1) were used in the sampling of the smoke from the opening of the test chambers, each line made up of adsorbents for the highly and for the less volatile organic components in the smoke, respectively.

The Carbotrap/Carbosieve S III (CC) and Tenax TA adsorbents were chosen because of the advantage *thermal desorption* offers in the subsequent gas chromatographic quantitation/-identification step. The principal advantage is that there will be neither solvent interference nor any dilution effects. A disadvantage is that the entire sample will be spent in a single analysis. For the activated charcoal– Amberlit XAD-2 adsorbents, desorption is effected by solvents that may interfere in subsequent analyses by *e.g.* gas chromatography, GC. But on the other hand this allows repeated measurements, and the use of additional analysis techniques such as liquid chromatography, *e.g.* high-pressure liquid chromatography, HPLC.

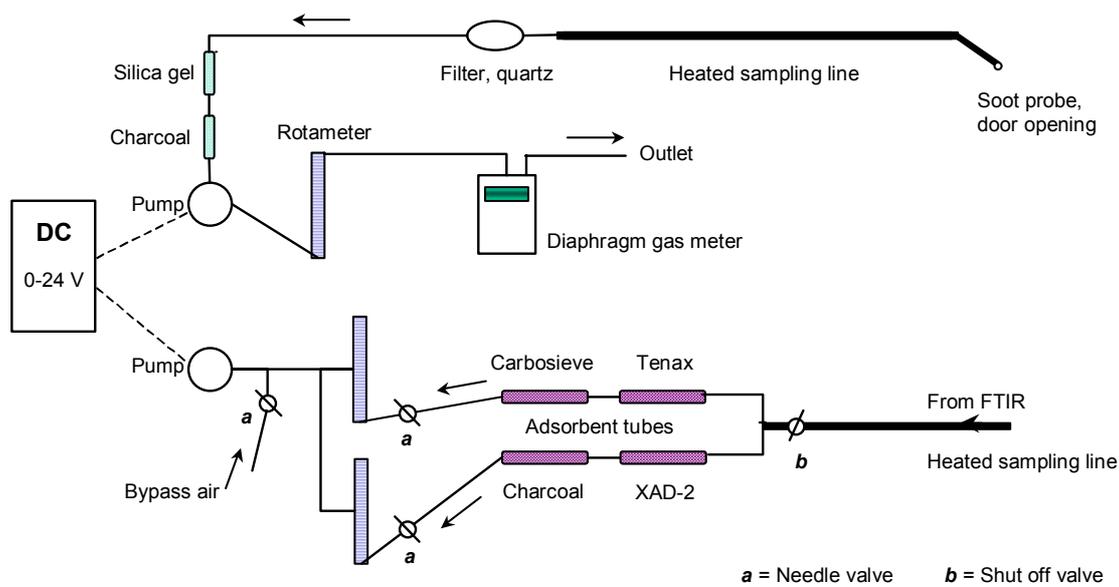


Figure 3.1 Sampling system for the characterisation of organic compounds on adsorbents and of soot, respectively.

Compounds with boiling points around that of benzene and above are more or less completely retained on Tenax as long as the recommended sampling volume is not exceeded. The more volatile components in the smoke largely pass through the Tenax adsorbent, but are retained on the CC adsorbent, or retained in varying proportions on both adsorbents. The CC adsorbent, in addition, is more suitable for adsorption/desorption of polar compounds. Although not shown in Figure 3.1, two parallel CC–Tenax adsorbent lines were utilised, the intention being to sample a smaller amount for identification of components by mass spectrometry (MS), and to use the second set with approximately 5 times larger amounts adsorbed for quantification utilising a flame ionisation detector (FID). The principal make up of the different adsorbents used is identified in Table 3.1.

Table 3.1 Identification of adsorbent tubes for the TOXFIRE measurements.

Sampling tube	Adsorbent	Amount /mg	Volume /L
Glass, d_o ~10 mm	Amberlit XAD-2 *	(600 + 300)	10 – 0.4
Glass, d_o ~10 mm	Charcoal *	(800 + 200)	10 – 0.4
Stainless steel, d_o ~6 mm	Tenax TA	200	1.0
Stainless steel, d_o ~6 mm	Carbotrap/Carbosieve S III	200 /200	1.0
Glass, d_o ~6 mm	Tenax TA	100	0.2
Glass, d_o ~6 mm	Carbotrap/Carbosieve S III	100 /200	0.2

* Two layers; 2nd layer as back up.

3.2.3 Adsorbent sampling

The smoke-characterisation gas-sampling probe in the opening was connected to a heated (180 °C) stainless steel filtering unit with a ceramic filter of 2- μ m porosity to remove particles [2]. Via 7 m of heated flexible 6 mm inner diameter Teflon tubing (200 °C), gas samples were drawn through the adsorbent tubes by a set of Brey pumps. Needle valves ahead of the rotameters were utilized to balance the ratio of the flows through the individual adsorbent lines (see Figure 3.1). The bypass air needle valve ahead of the pump was used for adjustment of the total flow through the adsorbent tubes. The actual flow rates through the adsorbent lines were measured individually using rotameters calibrated against a Gilian Primary Flow Calibrator, a soap-film type flow meter. The volume of gas sampled was calculated from the flow rate and sampling time.

It is essential that the temperature of the sampled gas is just high enough to avoid condensation of smoke components without causing decomposition/pyrolysis to occur. However, adsorption is less efficient at higher temperatures, which means that the temperature of the gas has to be significantly lowered upon entry into the adsorption tubes.

The adsorbent sampling periods were close to ten minutes in most cases with flow rates from 0.4 L/min (XAD-2) down to 0.015 L/min for the smaller CC/Tenax set, where larger amounts adsorbed on the charcoal/XAD-2 are intended as a compensation for the dilution effect by subsequent desorption with a solvent.

The beginning of the sampling period was decided on beforehand, or alternatively sampling was initiated when a steady-state period of the fire appeared to be approaching. The adsorbent sampling periods are indicated in graphs of HRR versus time in Appendix 2, together with values of the integrated mean, and the minimum and maximum values of ϕ . Although sampling was not performed at a constant degree of ventilation, the difference between the mean value of ϕ and the average of the *max* and *min* value is only of the order of 0,1 or less, with the exception of the results for TMTM. For CNBA4 the difference is 0,6, but this is caused by anomalous combustion behaviour, most likely from instability/decomposition of the CNBA.

3.2.4 Sampling of soot

Soot was sampled through the dedicated heated probe in the door opening as shown in Figures 2.2, 2.3 and 3.1, respectively. The probe was heated to between 180 °C and 200 °C. The soot was retained on previously conditioned and weighed quartz sock filters. Sampling periods were generally the same as for the adsorbents with flow rates between 5 L/min and 8 L/min corresponding to a velocity of 1.1 m/s to 1.7 m/s in the opening. The accumulated volumes of gas sampled were measured using a calibrated diaphragm gas meter and were mostly of the order of from 60 L to slightly above 100 L. In some cases, soot accumulation on the filter gave rise to an increased pressure drop across the filter and a decrease in flow rate.

Ideally, flow rates for sampling of particles should be such that the sampling flow is the same as the main flow, isokinetic sampling. However, the intended on-line evaluation of the flow out of the room could not be realized as planned and hence no reference value was available. The flow rates applied were not far from isokinetic and since the amounts of soot were not used to determine total amounts this deficiency was not considered a serious one.

3.3 Analyses

3.3.1 Gas chromatographic analyses

Two set-ups of a Hewlett Packard HP-5890 GC with auto injector HP 7673A were used for the identification and quantitation of smoke gas components. One was fitted with a Perkin Elmer ATD 400 for thermal desorption of the Tenax and the CC adsorbents, respectively, and with a flame ionisation detector, FID, and a mass selective detector, MSD HP 5972, in parallel. The other GC was used with a single FID and used for liquid samples.

Extensive exploratory GC measurements were made on the solutions obtained from treating the XAD-2 and the charcoal adsorbents with, respectively, diethyl ether and carbon disulfide in sealed ampoules. Retention times were utilised for identification of a few individual components, but primarily these results were used for a measure of the total amounts of volatile organic compounds, TVOC, adsorbed during sampling. TVOC then served as a guide for setting the injection split conditions for the thermal desorption measurements of the Tenax and the CC adsorbents.

For the thermal desorption, a balance must be achieved between the temperature and the time selected for desorption and the spectrum of compounds to be desorbed. The adsorbent itself sets a limit for the maximum temperature, but an unnecessarily high temperature may cause decomposition or isomerisation of species adsorbed, whereas with lower desorption temperatures considerably less than the total amount of the less volatile components may be eluted. Both the Tenax and the CC adsorbents used in this work were desorbed at 275 °C for 7 min with a flow of helium at 100 mL/min through the tubes. For the Tenax, compounds containing up to 18 carbon atoms are expected to elute quantitatively under these conditions. The cold trap collecting the desorbed matter was kept at -30 °C. As an aid to efficiently trap the most volatile components from the CC adsorbent, the cold trap in that case contained a minute amount of Carbotrap adsorbent.

For the Tenax and the XAD-2 measurements, the GC columns used were non-polar HP1 fused silica capillary columns (bonded and cross-linked methyl silicon, d_i 0.32 μm , 100 m or 50 m, respectively, for the separation of components. For the CC measurements an $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT (porous layer open tubular) column was used, 50 m, d_i 0.32 μm , 5 μm phase thickness.

All initial quantifications of individual components were made from the FID peaks, with detector response calibrated against toluene. Portions of 2 μL of an ether solution with known amounts of toluene, decane, xylene and octadecane were injected via a stream of clean air onto Tenax tubes, which were then used daily to check the FID response and the desorption efficiency. In a few rare cases where the FID did not work properly in the beginning of a run, the MSD could be used to give a reasonable estimate of the amount of the main components. – Results for TVOC were expressed in terms of toluene equivalents, and should hence be comparable with the on-line THC (FID) results; *cf.* 2.4.

The principal advantage of the FID is its large dynamic range and response linearity over several powers of ten in amounts measured. The FID, in principle, is a carbon counter. Its specific response to different organic compounds is generally predictable and allows calculation of response factors with reasonable accuracy, particularly useful in a project such as this one. Response factors can, of course, be checked against measurements of established amounts when regarded significant/necessary. If strictly comparable to the adsorbent measurements, such checks may to some extent compensate for deficiencies in desorption.

Table 3.2 Relative response factors, $m(\text{compound})/m(\text{toluene})$ in g/g, for selected substances.

Compound	Molar mass	Molar carbon	Response factor	Compound	Molar mass	Molar carbon	Response factor
Acetaldehyde	44.05	24.02	1.67	Chloroform	119.38	12.01	9.1
Acetic acid	60.05	24.02	3.9	Chlorophenol	128.56	72.07	1.74
Acetonitrile	41.05	24.02	2.60	Cyclohexanone	98.15	72.07	1.24
Benzaldehyde	106.12	84.08	1.30	Cyclopentanone	84.12	60.06	1.28
Benzonitrile	103.12	84.08	1.26	2-Cyclopentenone	82.10	60.06	1.55
Butane	58.12	48.04	1.10	Dichlorobenzene	147.00	72.07	1.86
Butanol	74.12	48.04	1.56	Dichloromethane	84.93	12.01	6.4
Butene	56.11	48.04	1.07	Isothiocyanatomethane	73.12	24.02	4.6
Butyraldehyde	72.11	48.04	1.71	Propene	42.08	36.03	1.07
Carbon disulphide	76.14	12.01	5.8	Propene nitrile (acrylonitrile)	53.06	36.03	1.83
Carbon tetrachloride	153.82	12.01	11.7	Propenoic acid	72.06	36.03	1.82
Chlorobenzene	112.56	72.07	1.43	Thiophene	84.14	48.04	1.68
Chlorobenzonitrile	137.57	84.08	1.68	Trichlorobenzene	181.45	72.07	2.30
Chloroethynylbenzene	136.58	96.09	1.30				

In this project, response factors were calculated based on published data, *e.g.* in references 10, 11. Via molar responses based on functional group increments, the g/g responses for individual compounds were evaluated relative to that for toluene (basis for determining FID response), which is set to 1.00. Table 3.2 lists response factors deviating significantly from unity. For acenaphthene, anthracene, benzene, biphenyl, butadiene, ethynylbenzene, indene, naphthalene, styrene, butenyne, and propyne the relative response is between 0.97 and 1.03.

Identifications were based on the MSD measurements. Comparisons were made with spectra in a reference library, the NBS75K containing 70 000 spectra, complemented with spectra from previous in-house identification measurements. In addition, retention times are considered as a further check on the credibility of the identifications.

3.3.2 Soot measurements

In addition to measuring the amount of soot, it was considered of interest to study what might be adsorbed on the soot particles that might considerably aggravate the health hazard associated with particles. As only a limited study could be undertaken in this particular project, adsorbed matter on the CB soot was focused on. Elemental analysis (C, H, N) indicated that the carbon content of the soot was only 82 % by mass for soot from CB4 and 94 % for the CB6 soot. Both HCl and the parent compound CB can be expected to adsorb on the soot particles. A check was considered worthwhile.

0.5 g portions of the soot were washed with 10 mL of water. The amount of HCl was determined by ion chromatography (CI). Two portions of 100 mg of the dried remainder of the soot were combusted in a calorimetric combustion bomb in pure high-pressure oxygen together with halogen-free paraffin oil. The combustion converts the chlorine in CB, and any additional organochlorine substances, to HCl, which is then readily quantified by ion chromatography.

3.4 Yields

From the adsorbent measurements, the amounts of individual components are measured for the volume of smoke sampled. Concentrations are then easily calculated from amount divided by volume. However, concentrations depend on various dilution factors and are not suitable in comparisons of results obtained under different conditions such as *e.g.* different scale. Yields, *i.e.* the amounts of individual components formed in relation to the amount of material combusted at a defined period of time, are more invariant character. Yield is therefore the more relevant parameter for comparison of results for species found in the smoke.

Total amounts formed during the sampling periods were obtained from adsorbent amounts multiplied by the volume ratios between the total volumes of smoke for the sampling period versus the sampled volumes. For that, a measure is required for the flow versus time through the opening where the sampling is performed.

Using velocity and temperature sensors in the plane of the opening to establish mass flow rates is difficult. Means other than direct measurement techniques had to be used to assess the flow in the opening. The model chosen for calculating the flow has been described by Babrauskas [12] and assumes a well-stirred uniform-temperature compartment, with uniform density inside. The calculations are based on temperature measurements only and assume that outflow and inflow are equal. This model was refined to include the MLR [4]. The mass flow can then be converted to volume flow.

Finally, yields are evaluated from the total amounts calculated and the mass of material combusted during the adsorbent sampling period.

4 Results

Sets of detailed results from the individual combustion experiments are given in Appendix 1 of references 2 and 3, respectively. In addition, graphs are shown [2] of yields in the opening of the ISO room as functions of ϕ or temperature, respectively, for the individual materials studied. For PP, Ny and TMTM, the results are comprehensive ones. The CNBA did not burn at a reasonable rate by itself in the ISO room, but had to be boosted by polypropene making the interpretation of the results less straightforward. The large proportion of soot from combustion of CB clogged the sampling lines, making the sampling deficient in some of the CB tests. A listing of the individual SP combustion tests is given in Appendix 1.

4.1 Ventilation conditions – equivalence ratios

The estimates for the choice of different openings in the ISO 9705 room aimed at attaining steady-state periods of equivalence ratios around 0.5, 1.0, 1.5 and 2.0, respectively [2]. This was based on the assumption that the total HRR would remain rather constant independently of the size of the opening. But the ventilation conditions affected the total HRR and this in turn affected the equivalence ratio. Only a few tests had pro-longed steady-state periods with constant values of the equivalence ratio, and in those cases ϕ was rather low.

In the ISO 9705 room, almost all the tests had a short steady-state period in the beginning with equivalence ratios between 0.5 and 0.8. The development after that varied considerably between the different substances. Some tests never reached ϕ values higher than 0.8, but those reaching equivalence ratios in excess of 1, all had a very fast increase through ϕ equal to 1.0. For $\phi > 1$, there were clear differences. In tests with TMTM, the fast increase continued until the fire was manually extinguished, while in other tests ϕ reached a second plateau with an almost constant ϕ value between 1.0 and 1.5. The ϕ values for CB are somewhat uncertain, as they had to be calculated from the MLR curve and substantial turbulence inside the room made the MLR signal exceptionally noisy in these tests.

4.2 Adsorbent yields

The individual yields reported here were derived from GC analysis of the larger-amount Tenax and CC adsorbent tubes (*cf.* 3.4.2). Adjustment of the split ratio was made to suit the amounts sampled, as determined on the ether extracts of the corresponding XAD-2 adsorbents. Yields were calculated from the amount of the individual components determined using the FID, from the volume of gas sampled and the total flow of smoke through the opening during the sampling period and from the corresponding mass loss of the material burned. The component identifications were based on the MSD measurements performed simultaneously in parallel. Comprehensive, semi quantitative lists of identified individual substances in the smoke are given in Appendix 3.

The combined yields of the highest-concentration components obtained from the Tenax plus the CC adsorbent measurements are listed in Tables 4.1 through 4.5. Generally, the five principal components from the Tenax were taken into account together with those from the CC with comparable amounts.

The Tenax analyses were in general all successfully performed. For PP3 the yields are significantly lower than those for the other PP tests. Most likely this is caused by some undetected sampling error, not only an effect of the 3.6 L sampled (24 min) instead of the intended 1.0 L (10 min); *cf.* graphs in Appendix 2.

The most difficult part in the utilisation of the CC adsorbent was the trapping of the most volatile components such as methane, ethane and propane during sampling and, in addition, subsequently retaining them in the cold trap after thermal desorption before injection on to the GC column. This means that the yields quoted for species such as *e.g.* propene are likely to be too low. Compounds such as methane, ethane, *etc* were identified at low levels but surely not representative of their true amounts in the smoke. Quantification of methane from the FTIR measurements [5] would, if required, be reasonably straightforward and there is similarly potential for another few of the lower hydrocarbons. From a toxicity hazard point of view, only the unsaturated species are considered of importance here.

The CC adsorbent capability, which is of considerably greater importance, is the sampling/-desorption of more polar compounds such as the lower aldehydes and nitriles. These types of compound do indeed present more of a hazard in terms of their inherent toxicity.

One conclusion has been [1] that although the measured values of ϕ for the larger test facility (storage configuration) indicate cases of well-ventilated fires, the bulk of the results generally indicate that locally under-ventilated combustions have taken place. This effect is most noticeable for the PP and TMTM materials. The packaging/packaging material is also expected to have some effect on the pattern of combustion products in the storage configuration tests.

Table 4.1 Yields of individual organic components in the smoke from combustions of polypropene, PP.

Yield / (g/kg)							
$\phi = 0.74$		$\phi = 0.99$		$\phi = 1.03$		$\phi = 1.09$	
Substance	PP9*	Substance	PP3	Substance	PP6	Substance	PP5
Benzene	7.14	Benzene	0.512	Benzene	15.5	Benzene	10.8
Naphthalene	0.909	Naphthalene	0.118	Naphthalene	7.85	Naphthalene	3.50
Toluene	0.529	Acenaphthene	0.035	Toluene	4.43	Styrene	0.456
Propyne	0.187	Toluene	0.012	Butenes	4.17	Toluene	0.450
Styrene	0.184	Ethynyl-benzene	0.011	Propene	2.49	Ethynyl-benzene	0.252
Benzaldehyde	0.133			Styrene	1.86	1,3-Butadiene	0.031
1,3-Butadiene	0.086			Ethynyl-benzene	0.97	1-Buten-3yn	0.016
Butene	0.013						

* Storage configuration test.

For the PP, in total four experiments could be formally evaluated in full (Table 4.1). The yields of PP3 are suspiciously low, very likely because of some sampling error. The adsorbent results for PP4 are more in line with what one would expect. However, because of malfunctioning of the system data logger about $\frac{1}{4}$ into the adsorbent sampling period (*cf.* Appendix 2) no total flow/volume could be evaluated and hence no yields could be calculated for PP4. Unfortunately, there is not really much of a variation in the degree of ventilation in the PP tests.

Table 4.2 Yields of individual organic components in the smoke from combustions of Nylon 66, Ny.

Yield / (g/kg)									
$\phi = 0.48$		$\phi = 0.56$		$\phi = 0.73$		$\phi = 0.87$		$\phi = 0.99$	
Substance	Ny6*	Substance	Ny2	Substance	Ny4	Substance	Ny3	Substance	Ny5
Propene	0,350	Benzene	0,114	Benzene	0,362	Benzene	3,20	Benzene	2,78
Benzene	0,231	Naphthalene	0,029	Naphthalene	0,090	Naphthalene	0,815	Naphthalene	0,782
Toluene	0,110	Acenaphthene	0,028	Benzonitrile	0,063	Benzonitrile	0,480	Benzonitrile	0,668
Cyclopentanone	0,053	Benzonitrile	0,018	Ethynylbenzene	0,010	2-Propene nitrile	0,321	2-Propene nitrile	0,595
Benzonitrile	0,042	Anthracene	0,014	2-Propene nitrile	0,010	Propene	0,214	Toluene	0,325
2-Propene nitrile	0,040			Acetonitrile	0,005	Ethynylbenzene	0,160	Propene	0,157

* Storage configuration test.

For the Ny tests it has been possible to evaluate all of the tests performed (Table 4.2). Again, the variation in the degree of ventilation is limited. In particular, none of the ϕ values are >1 , *i.e.* no average under-ventilated conditions were achieved. But it should be noted, that for tests Ny3 and Ny5 the ϕ_{\max} values are well in excess of unity (*cf.* Appendix 2) signifying that under-ventilated conditions pertained during part of those sampling periods. That does appear to be reflected in the levels of the yields obtained

Table 4.3 Yields of individual organic components in the smoke from combustions of tetramethylthiuram monosulfide, TMTM.

Yield / (g/kg)									
$\phi = 0.83$		$\phi = 0.84$		$\phi = 0.96$		$\phi = 1.06$		$\phi = 1.33$	
Substance	TMTM6*	Substance	TMTM2	Substance	TMTM4	Substance	TMTM5	Substance	TMTM3
Propene	0.170	Propene	0.488	Acetonitrile	0.247	Isothiocyanatomethane	0.844	Acetonitrile	1.42
Acetonitrile	0.102	Carbon disulfide	0.251	Acetic acid	0.138	Acetonitrile	0.723	Acetic acid	0.920
Benzonitrile	0.040	Acetonitrile	0.141	Thiophene	0.113	Acetic acid	0.469	Isothiocyanatomethane	0.310
Benzene	0.037	Benzene	0.116	2-Propene nitrile	0.113	2-Propene nitrile	0.126	Propene	0.269
2-Propene nitrile	0.029	Thiophene	0.091	Benzene	0.073	Thiophene	0.097	2-Propene nitrile	0.107
Thiophene	0.026	Benzonitrile	0.060	Benzonitrile	0.049	Benzene	0.058	Thiophene	0.106
Carbon disulfide	0.011	2-Propene nitrile	0.025	Carbon disulfide	0.004	Benzonitrile		Benzonitrile	0.090
				2-Propenoic acid	0.002			Benzene	0.056

* Storage configuration test.

TMTM burned without hardly any noticeable formation of soot. This may indeed have had a favourable influence on the adsorbent sampling process. Comprehensive evaluations of all of the TMTM tests have been carried out quite successfully. The adsorbent results for TMTM show a rational trend with the degree of ventilation, as do all of the on-line results,

presented in detail in references 2, 3 and 5. It is worth noting that for the TMTM there were hardly any steady state periods of combustion. As evidenced by the ϕ_{\max} values under-ventilated conditions ($\phi > 1$) occurred during parts of all of the ISO 9705 room TMTM combustions; *cf.* Appendix 2.

In the case of carbon disulfide, the yields may be expected to deviate from their true values because of the low boiling point (high volatility) of that compound, likely to cause deficiencies in the sampling as well as during analyses. The anomalous result obtained for the FID response factor for CS_2 in an experimental determination of its value, is another indication of that same problem. This would in part explain the seemingly irrational behaviour of the carbon disulfide yields. – The value for the CS_2 FID response factor used in the evaluations was that calculated from group increments. The uncertainty of that value may be larger than that for the other compounds, but it may be noted that the response factor calculated from group increments for carbon tetrachloride agreed surprisingly well with values given in the literature.

Attempts to identify and quantify CS_2 by FTIR [5] were not successful, whereas carbon oxysulfide, COS, was detected for the under-ventilated parts of the TMTM tests.

Table 4.4 Yields of individual organic components in the smoke from combustions of 4-chloro-3-nitro-benzoic acid, CNBA.

Yield / (g/kg)							
$\phi = 0.17$		$\phi = 0.19$		$\phi = 0.51$		$\phi = 0.63$	
Substance	CNBA1	Substance	CNBA3	Substance	CNBA2	Substance	CNBA5*
Chloro-benzene	19.8	Chloro-benzene	8.42	Chloro-benzene	0.672	Chloro-benzene	6.33
Dichloro-benzene	8.80	Dichloro-benzene	3.10	Benzene	0.411	Dichloro-benzene	3.55
Chlorobenzo-nitriles	1.67	Benzene	0.469	Chlorobenzo-nitriles	0.140	Propene	2.13
Benzene	0.568	Chlorobenzo-nitriles	0.393	Naphthalene	0.114	Chlorobenzo-nitriles	0.479
Benzonitrile	0.495	Benzonitrile	0.258	Benzonitrile	0.089	Benzene	0.234
Propene	0.137	Propene	0.123	Acetonitrile	0.017	Benzonitrile	0.220
				2-Propene nitrile	0.007	Ethane	0.142

* Storage configuration test.

The principal problem in the CNBA tests was to make the compound burn at an acceptable rate. The HCl formed tends to act as an extinguisher and quench the fire. Only in CNBA1 did the CNBA burn all by itself; for the rest of the ISO 9705 room CNBA tests, layers of non-woven polypropene were mixed in to increase the temperature and the combustion rate (*cf.* Appendix 1); complicating the interpretation of the results. An additional problem was the substantial production of smoke blocking the sampling lines.

Adsorbent results for CNBA4 have not been included in the listing of results in Table 4.4, mainly because of the twin-peak behaviour (“bottom effect” at the end of the test) during the adsorbent sampling period [2] resulting in very low yields. Unexpectedly low yields were obtained also for CNBA2.

Sampling problems caused by the substantial amount of soot formed were even more severe in the combustions of CB. In the CB5 test, adsorbent sampling lasted only 1 min due to clogging of the sampling lines. The results for CB4 indicated that significant clogging occurred already in that test. A complete renovation of the sampling set-up was made prior to the CB6 test. Results for CB4 and CB5 had to be ignored.

Table 4.5 Yields of individual organic components in the smoke from combustions of chlorobenzene, CB

Yield / g/kg					
$\phi = 0.17$		$\phi = 0.39$		$\phi = 1.88$	
Substance	CB7*	Substance	CB3	Substance	CB6
Chlorobenzene	106	Chlorobenzene	171	Chlorobenzene	11.7
Benzene	2.94	Benzene	4.82	Benzene	5.61
Naphthalene	0.84	Naphthalene	1.37	Naphthalene	1.73
Chloro-4-ethynylbenzene	0.45	Chloro-4-ethynylbenzene	0.82	Ethynylbenzene	0.24
Ethynylbenzene	0.37	Ethynylbenzene	0.59	Biphenyl	0.21

* Pool fire in the larger scale test facility; cf. Figure 2.3.

Adsorbent results for the CB combustion tests are presented in Table 4.5. CC adsorbent MSD measurements were performed only for CB4, the major component being HCl. Further CC MSD analyses were not considered worthwhile, as the adsorption of organic components had most likely been hampered by the large amount of HCl formed in the combustions.

The rather high yields for chlorobenzene in the CB3 and the CB7 tests may to a large extent be caused by evaporated CB in the rooms prior to ignition of the material. In both cases, the sampling periods were in the early phase of the tests, with only moderate HRR levels attained. For CB6, the sampling took place later in the experiment at a considerably higher HRR level with the possibility that most of the prior-to-ignition evaporated CB had been consumed by then. CB6 is, in fact, a nice example of a steady-state under-ventilated fire.

Of considerable interest in connection with fires in chemicals (in particular fires in pesticides) is the so-called survival fraction, the portion of the original compound that escapes the fire unaltered as one of the components of the smoke. Even though CB can be labelled *survival fraction*, it is in itself not a particularly interesting concept in this case. Adsorption of the high-yield CB on the soot formed may, however, be of more concern from a health hazard point of view.

More comprehensive, semi quantitative lists of identified individual substances in the smoke are given in Appendix 3.

4.3 Soot

In Table 4.6 the results are listed for the soot sampled in the respective door opening. In addition to yields as given for the adsorbents, the amounts per volume of gas sampled (density) are presented.

Table 4.6 Soot sampled in the openings.

Test Id.	ϕ	Soot		Test Id.	ϕ	Soot	
		Amount mg m ⁻³	Yield g kg ⁻¹			Amount mg m ⁻³	Yield g kg ⁻¹
PP9*	0.74	0.54	0.005	CNBA1	0.17	8.9	0.130
PP4	0.99	0.93	– **	CNBA2	0.51	1.7	0.020
PP6	1.02	1.02	0.010	CNBA5*	0.63	3.0	0.014
PP5	1.09	7.3	0.073	CNBA4	0.74	3.0	0.068
Ny6*	0.48	<0.01	<0.001	CB7*	0.24	2.0	0.050
Ny2	0.56	0.85	0.012	CB3	0.39	6.4	0.24
Ny4	0.73	2.1	0.021	CB4	1.4	40	0.90
Ny3	0.87	2.5	0.019	CB6	1.88	35	0.177
Ny5	0.99	1.23	0.008	CB5	3.40	8.9	0.011
TMTM6*	0.83	0.32	0.002				
TMTM2	0.84	2.4	0.016				
TMTM4	0.96	1.26	0.007				
TMTM5	1.06	0.55	0.002				
TMTM3	1.33	6.7	0.028				

* Test carried out in the storage configuration test facility.

** No data available for total volume and mass of material burned, respectively; *cf.* Appendix 2.

Values are missing for tests PP3 and CNBA3 due to errors in the sample volume. Since soot was sampled independently of the FTIR sampling line (*cf.* Figure 3.1), the clogging problems were of no consequence. Even so, the amount of soot for CB5 appears lower than expected in relation to the ϕ value, possibly an effect of the considerably larger than normal uncertainty in this ϕ value because of the way it was evaluated [2].

Soot samples from the CB4 ($\phi = 1.40$) and the CB6 ($\phi = 1.88$) tests were analysed for their inorganic and organic chlorine content, respectively, as outlined in 3.3.2. The results show a chlorine content in terms of HCl of 5.9 mass % and 1.0 mass %, respectively, for the CB4 and the CB6 soot samples. As it has not been possible to detect free chlorine in any of the combustions performed, inorganic chlorine should principally mean that in HCl.

The organically bonded chlorine content was 0.59 mass % and 0.70 mass %, respectively, in the soot from CB4 and CB6. Assuming that most of the organochlorine was present as chlorobenzene, the amount of that compound adsorbed on the soot was 1.9 mass % and 2.2 mass %, respectively.

5 Discussion and conclusions

In this project it has been demonstrated that it is possible to make a thorough mapping of the products of combustion from controlled large-scale fires. In particular, it has been shown that adsorbent measurements can yield detailed information about species formed in fires of various degrees of ventilation.

For the adsorbent measurements, the results obtained were mean values over the entire sampling periods, pre-selected for the individual combustion experiments. Hence only one set of results was obtained from each combustion experiment, referring to the integrated ϕ value for the sampling period. Unfortunately, the range of ϕ values from one sampling to the other is limited for most of the materials studied. Although most of the adsorbent sampling periods include sub-periods with $\phi > 1.0$, TMTM and CB were the only materials having adsorbent results that formally refer to under-ventilated conditions. For the storage configuration tests, no attempt could really be made to design the experiments such that pre-determined values for the degree of ventilation might be achieved.

Results for the TVOC yields from adsorbent measurements have not been presented in this report. Values for TVOC can only be given in terms of FID toluene equivalents (3.3.1). That would not be very useful information here where the amounts of the different components have been calculated using individual FID response factors.

From the components tables in chapter 4 and from the listings in Appendix 3, it is clear that benzene is one of the principal components in the smoke from all of the experiments performed. TMTM is the only material that does not yield benzene or substituted benzene as the highest-yield organic species among those identified in the adsorbent measurements.

TMTM and CNBA were materials where survival fractions might be of interest as potential hazards. CNBA is, however, not very stable thermally and hence not likely to escape as such from a fire. Survival fractions of TMTM were looked for by HPLC on extracts from XAD-2 but in no case were amounts found that would allow proper identification.

A closer examination of soot properties would have been desirable, in particular identification and quantitation of adsorbed species. The independent soot sampling performed could have been used for such a purpose but more rigorous handling of filters to prevent losses in storage would have been required. Suitable technique(s) would have had to be developed and qualified.

It has not been possible identify whether or to what degree the adsorbent sampling may have been flawed by losses due to adsorption on soot collected on the heated ceramic filter in the FTIR sampling line. The necessity of protecting the ISO 9705 test room itself from damage made it inevitable that components would adhere to the wall coverings. In a previous project [8], where sampling took place in the duct, a routine was devised for cleaning of the hood/-duct facility between tests. Such precautions were, unfortunately, not feasible in the TOXFIRE project.

Similarly, condensation on the walls in the storage test facility is likely to have been magnified by an increase in resident time for the smoke components. The higher the boiling point, the more extensive the loss caused by condensation. In cases of slow burning, *e.g.* CNBA, particles are more likely to precipitate in the test room and not escape with the smoke. A certain level of turbulence of the smoke produced is required to facilitate proper mixing and representativeness of the sampling.

A specific problem encountered for the adsorption of the most volatile components on the CC adsorbent was that carbon dioxide and water, the principal products of combustion, compete such that adsorption of the less abundant organics becomes less efficient. Subsequent analyses are also unfavourable affected; *cf.* the effects of HCl on the CC adsorbent in the CB tests (4.2).

Extensive work was undertaken to ascertain the quality of the results, in particular the suitability of the sampling as performed. Different layers of XAD-2 adsorbent were analysed *e.g.* to prove that no break-through had occurred during sampling for the conditions selected. Studies suggested for the future include checks on the desorption efficiency for individual components.

Even though available funding called for all of the TOXFIRE tests to be carried out during a single period in time, the results are satisfactory. The know-how acquired is now a good starting point for the choice of selective conditions of adsorbent sampling and analysis in order to set the focus on potentially toxic or otherwise hazardous species formed in fires involving chemicals.

6 References

- [1] Månsson, M., Lönnemark, A., Blomqvist, P., Persson, H., Babrauskas, V. "TOXFIRE – Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments", SP Report 1996:44, ISBN 91-7848-649-1.
- [2] Lönnemark, A., Blomqvist, P., Månsson, M., Persson, H. "TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments: Tests in the ISO 9705 Room", SP Report 1996: 45, ISBN 91-7848-650-5.
- [3] Lönnemark, A., Blomqvist, P., Månsson, M., Persson, H. "TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments: Storage Configuration Tests", SP Report 1996:46, ISBN 91-7848-651-3.
- [4] Lönnemark, A., Babrauskas, V. "TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments: Theoretical Background and Calculations", SP Report 1996:49, ISBN 91-7848-654-8.
- [5] Blomqvist, P., Lindberg, P., Månsson, M. "TOXFIRE - Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments: FTIR Measurements", SP Report 1996:47, ISBN 91-7848-652-1.
- [6] Pedersen, K.E., Markert, F. "Assessment of Fires in Chemical Warehouses – An Overview of the TOXFIRE Project", Risø-R-932(EN), Risø National Laboratory, Roskilde Denmark, 1997, ISBN 87-550-2232-4.
- [7] Babrauskas, V., Parker, W. J., Mulholland, G., Twilley, W. H. "The phi Meter: A Simple, Fuel-independent Instrument for Monitoring Combustion Equivalence Ratio", Rev. Sci. Instrum. 65(7), July 1994.
- [8] Månsson, M., Dahlberg, M., Blomqvist, P., Ryderman, A. "Combustion of Chemical Substances – Fire Characteristics and Smoke Gas Components in Large-scale Experiments", SP Report 1994:28, ISBN 91-7848-487-1.
- [9] Månsson, M., Blomqvist, P., Isaksson, I., Rosell, R. "Sampling and Analysis of Smoke Gas Components from the SP Industry Calorimeter", SP Report 1994:35, ISBN 91-7848-494-4.
- [10] Dietz, W.A. "Response factors for gas chromatographic analyses", J. Gas Chromatography 5 (1967) 68.
- [11] Anderson, D.G. "The use of Kovats retention indices and response factors for the analysis of coating solvents", J. Paint Technology 40 (1968) 549.
- [12] Babrauskas, V. "Fire Endurance in Buildings", Fire Research Group, University of California, Berkeley, Report no UCB FRG 76-16, Nov. 1976.

Appendix 1 Identification of the SP TOXFIRE experiments

Table A.1 ISO 9705 room combustion experiments

Opening height/m	Fuel designation	Pool size/m ² / Fuel mass/kg	Fuel designation	Pool size/m ² / Fuel mass/kg	Fuel designation	Pool size/m ² / Fuel mass/kg	Fuel designation	Pool size/m ² / Fuel mass/kg	Fuel designation	Pool size/m ² / Fuel mass/kg
0.89	Polypropene		Nylon 66		Thiuram monosulfide		Chloronitrobenzoic acid		Chlorobenzene	
0.89	PP3	1.2 / 60	Ny2	1.4 / 75	TMTM2	1.2 / 60	CNBA1/2/3	1.4 / ^{a,b}	CB3/4	^c
0.68	PP5	1.2 / 60	Ny4	1.4 / 75	TMTM4	1.2 / 60			CB6	0.8 / 50
0.56	PP4	1.2 / 60	Ny3	1.4 / 55	TMTM3	1.2 / 60.5				
0.45	PP6	1.2 / 60	Ny5	1.4 / 75	TMTM5	1.2 / 60.5	CNBA4	1.4 / 60 ^b	CB5	0.8 / 50.5

^a CNBA1 74.5 kg; CNBA2 60 kg; CNBA3 40 kg

^b CNBA2, CNBA3 and CNBA4: CNBA mixed with PP [1]

^c CB3 0.5 m² / 45 kg; CB4 0.8 m² / 51 kg

Table A.2 Storage configuration room tests

Opening height/m	Fuel designation	Configuration
0.89	PP8	Pool 1.2 m ² / 42.5 kg
0.89	PP9	Bags in boxes / 160 kg
0.89	Ny6	Bags in boxes / 160 kg
0.89	TMTMT6	Bags in boxes / 160 kg
0.89	CNBA5	Bags in boxes / 160 kg
0.89	CB7	Pool 0.8 m ² / 39.5 kg

For more details, see reference 2.

Appendix 2 Adsorbent and soot sampling periods

In this Appendix, sampling periods are indicated in graphs of heat release rate, HRR, for all of the large-scale combustion experiments in the ISO 9705 room and in the storage configuration facility, respectively.

Values are given for the integrated mean of the degree of ventilation, ϕ . In addition, ϕ_{\max} and ϕ_{\min} values are provided to indicate whether the variation in ϕ was linear, or had more of a non-linear progression, over the period of sampling. For the tests in the storage configuration facility, only mean values of ϕ are available.

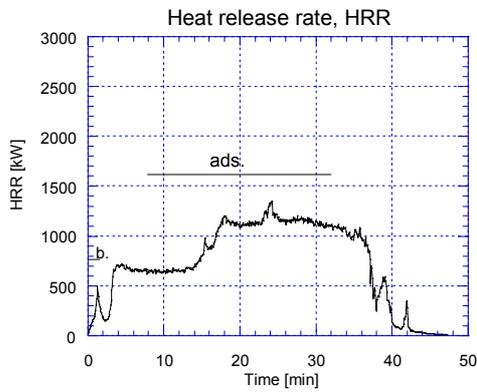
The periods for sampling of soot were, with a few exceptions (indicated), the same as those for the adsorbent sampling.

Events indicated in the graphs are:

- b. Ignition burner on
- ads. Sampling periods for adsorbents and soot
- soot Soot sampling period, when different from that for adsorbent sampling

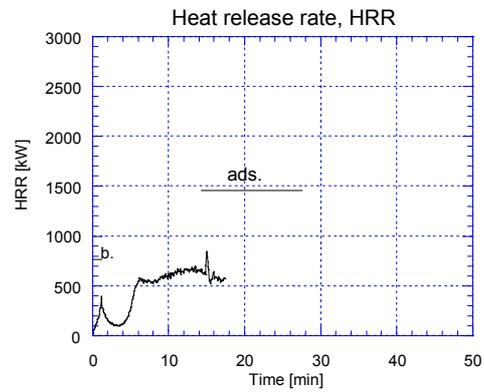
Adsorbent sampling periods – Polypropene

PP3



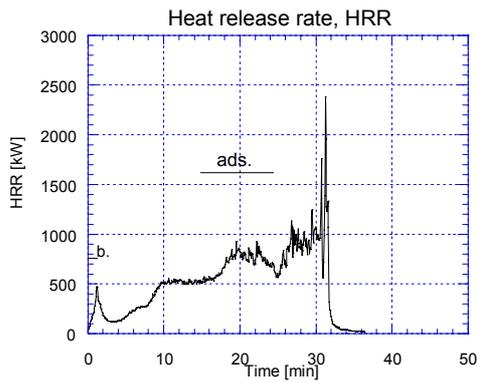
$$\phi = 0.99 \quad \phi_{\max} = 1.37; \phi_{\min} = 0.50$$

PP4



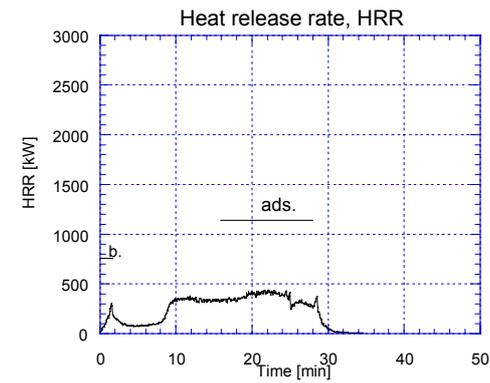
$$\phi = 0.99^1$$

PP5



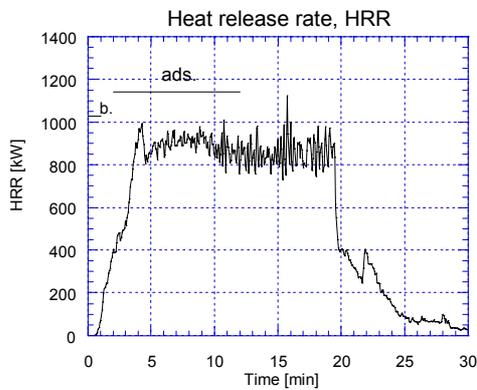
$$\phi = 1.09 \quad \phi_{\max} = 1.45; \phi_{\min} = 0.60$$

PP6



$$\phi = 1.02 \quad \phi_{\max} = 1.36; \phi_{\min} = 0.73$$

PP9

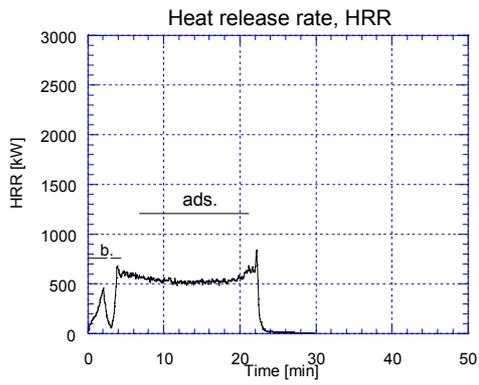


$$\phi = 0.74$$

Adsorbent sampling periods – Nylon 66

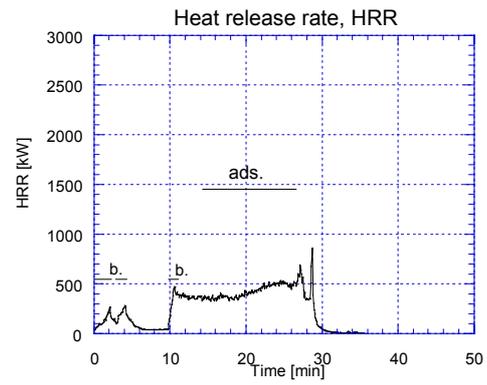
¹ Data beyond 20 min lost due to malfunctioning of data logger.

Ny2



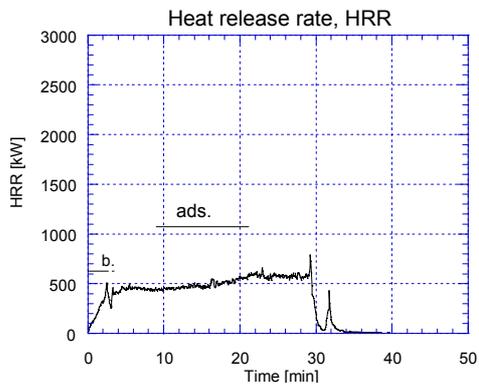
$$\phi = 0.56 \quad \phi_{\max} = 0.69; \quad \phi_{\min} = 0.50$$

Ny3



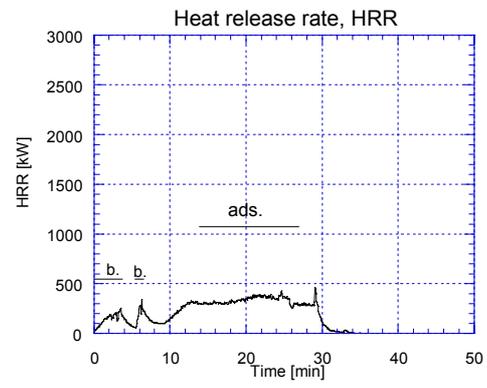
$$\phi = 0.87 \quad \phi_{\max} = 1.32; \quad \phi_{\min} = 0.63$$

Ny4



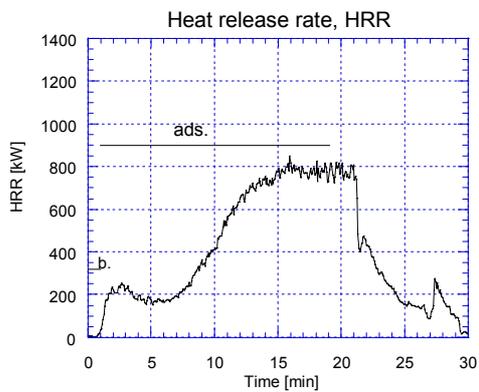
$$\phi = 0.73 \quad \phi_{\max} = 1.04; \quad \phi_{\min} = 0.56$$

Ny5



$$\phi = 0.99 \quad \phi_{\max} = 1.28; \quad \phi_{\min} = 0.79$$

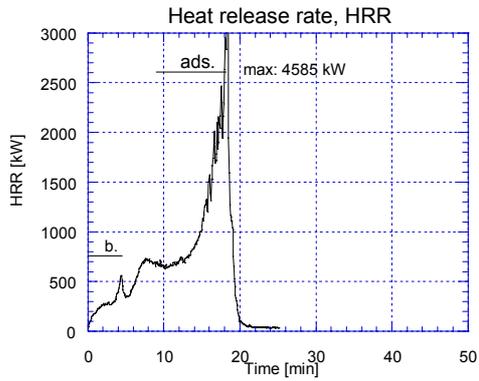
Ny6



$$\phi = 0.48$$

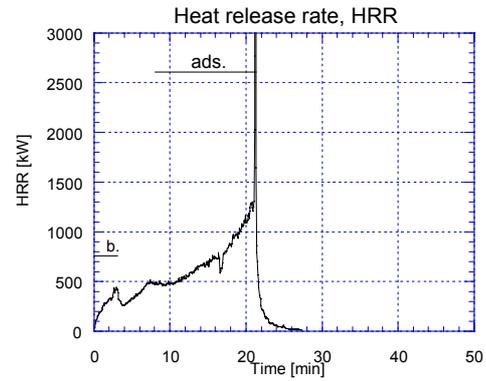
Adsorbent sampling periods – Tetramethylthiuram monosulfide

TMTM2



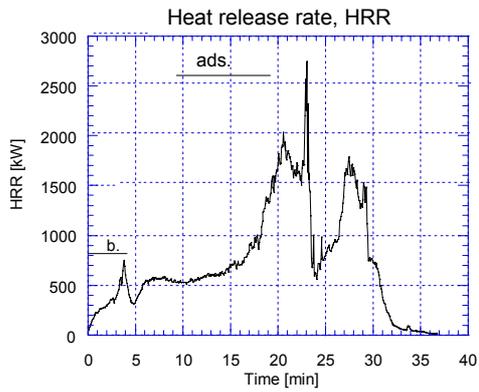
$$\phi = 0.84 \quad \phi_{\max} = 1.93; \quad \phi_{\min} = 0.58$$

TMTM3



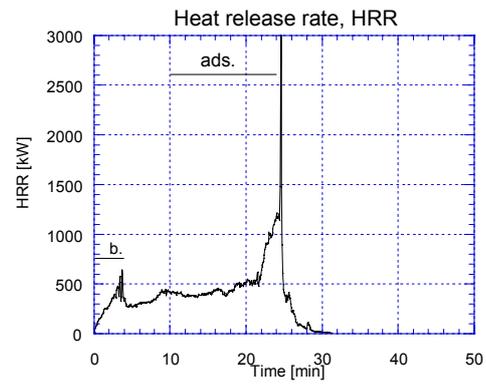
$$\phi = 1.33 \quad \phi_{\max} = 2.68; \quad \phi_{\min} = 0.72$$

TMTM4



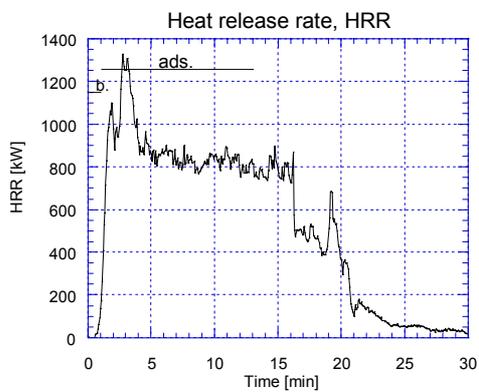
$$\phi = 0.96 \quad \phi_{\max} = 1.88; \quad \phi_{\min} = 0.67$$

TMTM5



$$\phi = 1.06 \quad \phi_{\max} = 2.64; \quad \phi_{\min} = 0.71$$

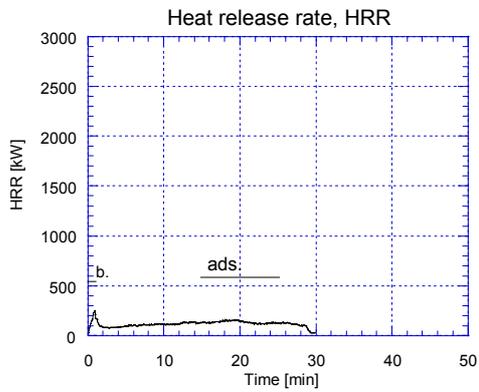
TMTM6



$$\phi = 0.83$$

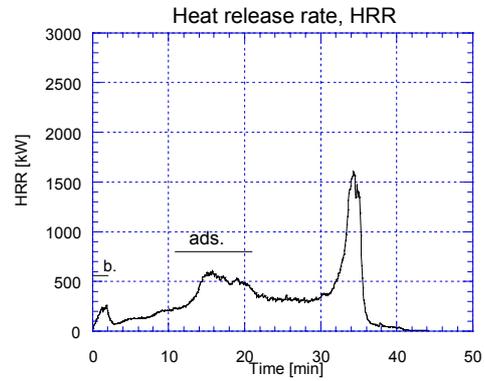
Adsorbent sampling periods – 4-Chloro-3-nitrobenzoic acid

CNBA1



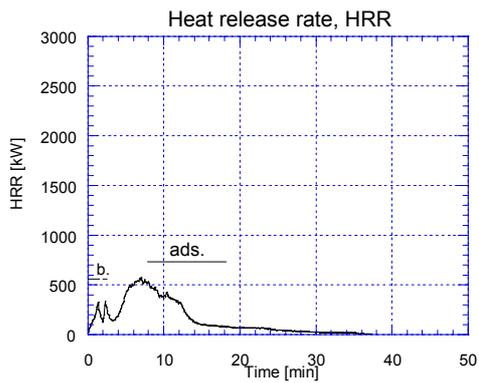
$$\phi = 0.17 \quad \phi_{\max} = 0.20; \phi_{\min} = 0.11$$

CNBA2



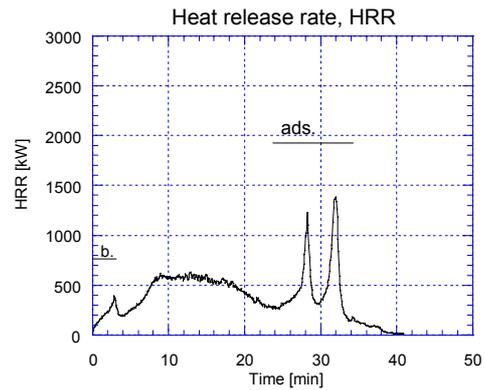
$$\phi = 0.51 \quad \phi_{\max} = 0.69; \phi_{\min} = 0.29$$

CNBA3



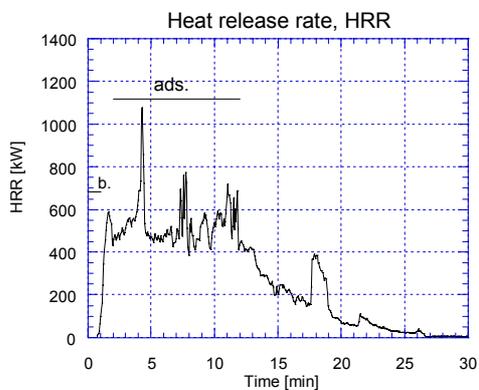
$$\phi = 0.19 \quad \phi_{\max} = 0.42; \phi_{\min} < 0.01$$

CNBA4



$$\phi = 0.74 \quad \phi_{\max} = 2.64; \phi_{\min} = 0.13$$

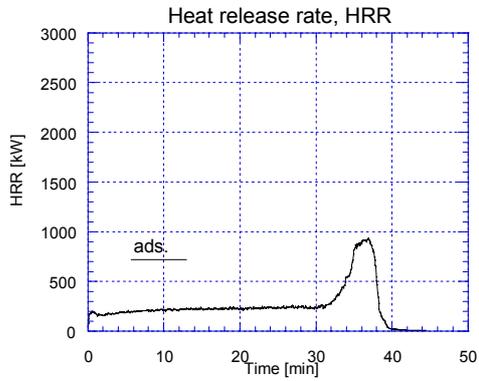
CNBA5



$$\phi = 0.63$$

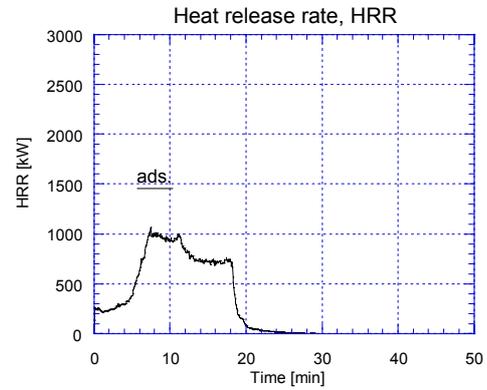
Adsorbent sampling periods – Chlorobenzene

CB3



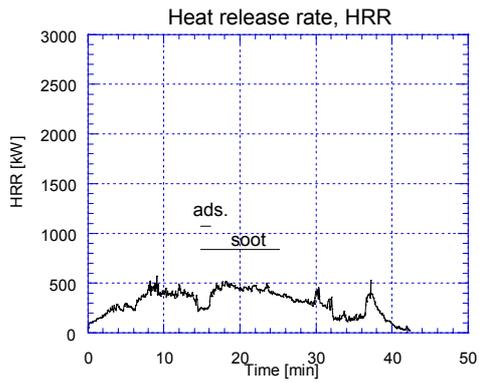
$$\phi = 0.39 \quad \phi_{\max} = 0.43; \phi_{\min} = 0.35$$

CB4



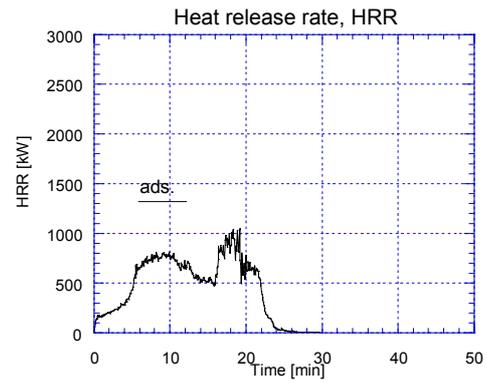
$$\phi = 1.40 \quad \phi_{\max} = 1.85; \phi_{\min} = 0.93$$

CB5



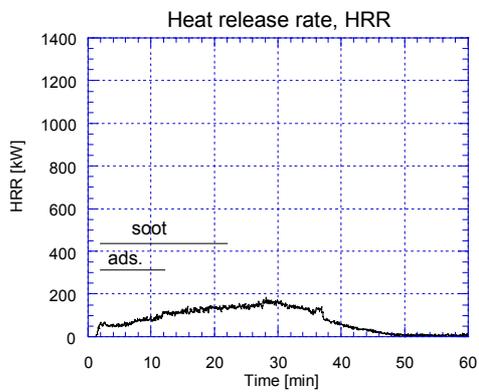
$$\phi = 3.4^2 \quad \phi_{\max} = 10.4; \phi_{\min} = 0.9$$

CB6



$$\phi = 1.88 \quad \phi_{\max} = 2.53; \phi_{\min} = 1.22$$

CB7



$$\phi_{\text{ads}} = 0.17 \quad \phi_{\text{soot}} = 0.24$$

² ϕ values given refer to soot sampling; adsorbent sampling **off** after 1.0 min due to clogging in the adsorbent sampling line.

Appendix 3 Smoke gas components

In the listing below, a more extensive account is given of species identified in the smoke by the adsorbent analyses. Although no direct quantitative information on yields is provided, the listings show semi quantitatively the relative abundance of the components. Substances shown in **bold** are the major ones, whereas those given in *italics* are the minor components in terms of yields or concentration.

PP	Ny	TMTM
Acenaphthene	Acenaphthene	Acetic acid
Anthracene	Acetonitrile	Acetonitrile
Benzaldehyde	Anthracene	Anthracene
Benzene	Benzaldehyde	Benzene
Benzfuran	Benzene	Benzonitrile
Benzonitrile	Benzfuran	Benzothiophene
Biphenyl	Benzonitrile	Butene nitriles
1,3-butadiene	Biphenyl	Carbon disulfide
Butenes	2,3-Butadione	<i>Dimethylsulfide</i>
1-Buten-3-yn	2-Butenal	Dimethyldisulfide
Ethane	Butene nitriles	Formic acid
Ethylbenzene	3-Buten-2-one	Isocyanatomethane
Ethynylbenzene	Cyclopentanone	Isocyanomethane
Indene	2-Cyclopenten-1-one	2-Methylpropane nitrile
<i>1-Methyl-1,3-cyclopentadiene</i>	Ethane	Methylthiophene
2-Methylpropenal	Ethene	Naphthalene
2-Methyl-1-propene	Ethynylbenzene	3-Penten-1-yne
<i>Methylindene</i>	Ethenylpyridine	Propene
Methylnaphthalenes	Indene	2-propene nitrile
<i>Methylstyrene</i>	Isocyanomethane	2-propenoic acid
Naphthalene	Methylbenzonitrile	<i>Styrene</i>
3-Penten-1-yne	Methylnaphthalenes	Tetramethylthiourea
Phenol	Methylpyridine	<i>Tetramethylurea</i>
<i>2-Propenal</i>	Naphthalene	Thiophene
Propene	3-Penten-1-yne	Toluene
Propyne	<i>2-Propenal</i>	
Styrene	Propene	
Toluene	2-propene nitrile	
Xylene	Pyridine	
	Quinoline	
	Styrene	
	Toluene	

CNBA	CB
Acenaphthene Acetonitrile <i>Benzaldehyde</i> Benzene Benzfuran Benzonitrile Biphenyl Chlorobenzene Chlorobenzonitriles <i>Chlorobenzoic acid</i> Chloronaphthalenes 2-Chlorophenol 2-Chloro-2-propene nitrile <i>4-Cyclopenten-1,3-dione</i> Dibenzofuran Dichlorobenzene Dichlorobenzonitriles Dichloromethane Ethane Ethynylbenzene Naphthalene <i>Phenol</i> Propene <i>2-propene nitrile</i> Styrene Tetrachloroethene Tetramethylurea <i>Trichlorobenzene</i> Trichloroethene Trichloromethane	Benzene <i>Benzfuran</i> Benzonitrile Biphenyl Chlorobenzene Chlorobenzonitriles Chlorobiphenyl 2-Chloro-1-buten-3-yne 1-Chloro-4-ethynylbenzene Chloronaphthalenes 2-Chlorophenol <i>2-Chlorostyrene</i> <i>Dibenzofuran</i> Dichlorobenzene Ethynylbenzene <i>Indene</i> Naphthalene <i>Phenol</i> <i>Propene</i> <i>Styrene</i> <i>Tetrachloroethene</i> Toluene <i>Trichlorobenzene</i> <i>Trichloroethene</i>

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SP Chemical Analysis
 SP REPORT 1996:48
 ISBN 91-7848-653-X
 ISSN 0284-5172



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