COMBUSTIBLE PRODUCTS:
SMOKE GAS CONCENTRATIONS, CONTINUOUS FTIR ANALYSIS

Key words: Test method, combustible products, smoke gas

1. SCOPE
This test method specifies a procedure for gas sampling and analysis to determine the smoke gas concentrations of combustible products using an on-line FTIR (Fourier Transform InfraRed) technique.

2. FIELD OF APPLICATION
2.1 The test method described is intended for combustible products which may be solids, liquids or gases.
2.2 The FTIR technique can be used to monitor gas compounds of polyatomic (more than two atoms) and heteronuclear diatomic molecules.
2.3 This gas analysis method can be used in connection with fire tests where combustion gases are collected in a representative way. Examples of these are rate of heat release tests (for instance ISO 5660 or ASTM E 1354 (Cone calorimeter), ISO 9705 or NT Fire 025 (Room/corner test) and NT Fire 032 (Furniture calorimeter), NT Fire 036 (Pipe insulation) and NT Fire 043 (Large free hanging curtains and drapery materials)).

3. REFERENCES
ISO/TR 9122 Toxicity Testing of Fire Effluents
Part 1: General, 1989
Part 2: Guidelines for Biological Assays to Determine the Acute Inhalation Toxicity of Fire Effluents (Basic Principles, Criteria and Methodology), 1990
Part 3: Analytical Methods
Part 4: The Fire Model
Part 5: Prediction of the Toxic Effects of Fire Effluents.

4. DEFINITIONS
For the purposes of this test method, the definitions given in ISO/IEC Guide 52 apply, together with the following:

4.1 Products
A basic single substance or a mixture (uniformly dispersed, layered etc.) of substances.

4.2 Specimen
A representative piece of the sample prepared to be tested.

4.3 Resolution of a FTIR spectrometer
Full width at half height of the instrument line shape function (cm⁻¹). This is the smallest spacing between absorption peaks which can be resolved.

4.4 Interferogram
The modulated component of the IR beam at the detector measured versus mirror position.

5. SYMBOLS
CO carbon monoxide
CO₂ carbon dioxide
HCN hydrogen cyanide
HCl hydrogen chloride
HBr hydrogen bromide
SO₂ sulfur dioxide
NO₂ nitrogen dioxide
C₃H₄O acrolein
O₂ oxygen
H₂O water

6. METHOD OF TEST
6.1 Principle
6.1.1 Smoke gas samples for the FTIR analysis are taken from a gas collecting system (usually exhaust duct) of a fire test method. The gas sample is drawn continuously through a heated sampling line to a heated IR absorption cell of a FTIR spectrometer. Interfered infrared beam is directed through the
The concentration-time relationship of the gases can be evaluated from successive spectra at sufficiently frequent intervals, the concentration-time relationship of the gases can be evaluated.

6.1.2 The sampling line and the IR absorption cell shall be heated ($T = 130 \pm 10 \degree \text{C}$) to keep the combustion gas composition unchanged for the analysis. At the elevated temperature of over 120 °C water is prevented from liquifying, gases soluble in water (e.g., hydrogen cyanide HCN and hydrogen chloride HCl etc.) from dissolving and light weight gases insoluble in water from precipitating.

Heating and filtering help the sampling line and the IR absorption cell with mirrors inside to keep clean.

6.1.3 The flow rate of the combustion gases drawn through the sampling line and the IR absorption cell shall be high enough and the volume of the sampling line and IR absorption cell shall be small enough for the sample in the IR absorption cell to be renewed every 10 s.

6.1.4 FTIR (Fourier Transform Infrared) is based on infrared absorption. Specific to FTIR is conversion of regular irradiance (optical path) as a function of radiation in wave numbers (number of cycles per cm).

6.1.5 Polyatomic and heteronuclear diatomic compounds have absorption in the infrared region (O2 has to be measured with other methods) and can be identified on the basis of absorbance or absorbances characteristic (at characteristic wavelengths) for the compound. Concentrations are related to intensities of absorption. Concentrations can be calculated on the basis of areas of absorbance in the spectra of the unknown and reference gas mixtures with known concentrations of gases.

6.1.6 Concentrations of combustion gases as a function of time can be calculated from successive measurements of sufficient frequency (at intervals not exceeding 5-10 s).

6.2 Apparatus

6.2.1 The apparatus of the fire test is described in the relevant standard. This section describes the gas sampling technique and the FTIR instrument specifications needed for the analysis of combustion gas concentrations. A schematic view of gas sampling is given in Annex 1.

6.2.2 Gas samples are taken from an exhaust duct or other relevant gas collecting system of a fire test method, where the gases are not yet cooled and gases with boiling points below about 100 °C are not yet condensed. In the case of non-uniformly mixed gases, in order to get a representative sample, the gas samples shall be taken at several points over the cross section of the gas collecting system of the fire test method. A flow rate of 7-20 l/min is adequate in the sampling line specified in 6.2.3.

6.2.3 Glass fiber filters shall be used at the junction of the exhaust duct and sampling line. Two fold filters of about 50 mm diameter are effective enough for safe use and they are heated only by the hot gases flowing through the filters. The sampling line shall be made of non-reactive material, e.g. teflon to withstand temperatures of at least 130 °C. A sampling line of 4-10 mm inside diameter and 5 m or less in length is recommended for short delay time. The delay time (flow through the sampling line) shall be less than 5 s.

6.2.4 The volume of the gas cell shall be small enough for a response time of less than 20 s (the time to renew the gas content of the cell) at the sample gas flow rate used. On the other hand the path length of the IR beam shall be long enough for adequate sensitivity of the lowest detection limits of ppm level. A longer path length than the gas sample cell is therefore usually needed, which is achieved by several reflections from mirrors at both ends of the gas sample cell. For instance a gas sample cell volume of about 0.5 l and an optical path length of 5-10 m meet these criteria.

6.2.5 Throughput of the intensity of the IR beam shall be high enough e.g. over 10 % or according to the instructions of the instrument. In order to achieve this the mirrors shall be well aligned and the mirrors and potassium bromide KBr windows shall be clean and in good condition. The elevated temperature in the gas sample cell usually keeps the mirrors clean and uncorroded. Hydrogen fluoride which may cause corrosion also at elevated temperatures is an exception. The normal cleaning procedure consists of purging the heated gas sampling line and the gas cell with nitrogen N2 or air. If the mirrors accidentally get dirty they can be cleaned by rinsing with ethyl alcohol, and polishing mirrors if within reach with a soft tissue and drying the gas cell by heating and nitrogen or air flow.

6.2.6 FTIR instrument specifications: High intensity and temperature stabilized IR-source, continuous scan Michelson interferometer, resolution 2-4 cm$^{-1}$ is recommended, wave number range 4500-500 cm$^{-1}$, wave number precision 0.01 cm$^{-1}$ with an internal HeNe laser, high speed detector (e.g. deuterated triglycine sulfate (DTGS) is suitable), sensitivity: peak to peak signal to noise ratio of 1000 to 1 measured at 2000 cm$^{-1}$, scanning time less than 10 s, time interval between spectra not exceeding 10 s, the lowest detection limits around 1-15 ppm.

6.2.7 Microcomputer and software recommendations: Microcomputer type 386 or more powerful, software including instrumental control and data acquisition, spectral display, x and y axes expansion, peak find, interference subtraction, baseline correction, quantitative analysis and plotting capability.

6.2.8 Combustion gases from the FTIR gas cell can be led back to the exhaust duct of the fire test instrument at a location which does not disturb any other measurements.
6.2.9 The test environment of the fire test shall be according to the relevant standard.

The FTIR apparatus shall be located in a draught-free environment in an atmosphere of up to 55 % relative humidity and temperature between 15 and 30 °C.

6.3 Calibration

6.3.1 Gas mixtures of known concentrations shall be used as reference gases in calibration. Usually they are single or two gas mixtures in nitrogen. Mixtures of several gases would be preferred, if obtainable.

6.3.2 Before a calibration, the sampling line and gas sampling cell are heated to a temperature of 130 ± 10 °C. A new filter (two pieces of glass fiber filter) is inserted. The throughput value of the IR beam is checked. A reference spectrum of nitrogen flow is obtained before each calibration in the same conditions as the calibration gas mixture (specified in 6.3.3).

6.3.3 In calibration the reference gas is drawn through the IR absorption cell at the same flow rate and pressure as the sample gas during a fire test and an absorbance spectrum is obtained. The reference gas should flow a long enough time (at least one minute) to ensure that there is no air or other gases left in the sampling line or IR absorption cell, which can be seen in the spectrum.

6.3.4 It is recommended to use three or more different concentrations of each compound. In the case of non-linear relationship between the area of absorbance and the concentration, the region calibrated with five calibration gases shall be concentrated in the non-linear part (concentrations of the five calibration gases shall also be close enough to each other) so that the non-linear curve can be reliably defined. Reliable gas concentrations of the sample are calculated when the results are between 0.8 x lowest and 1.2 x highest concentration calibrated. A note on choosing calibration gases is given in Annex 2.

6.3.5 If there are any changes in the spectrometer, for example changes in the mirrors inside the IR absorption cell, changes in the path length of the IR beam or the windows of the gas cell are changed, new calibrations shall be made.

6.4 Test specimens

The size of a test specimen in the fire test shall be according to the relevant standard, the amount of the specimen material shall however be such that it burns at least 20 s.

Test specimens shall be conditioned to equilibrium at a temperature of 23 ± 3 °C and a relative humidity of 50 ± 5 % or according to the relevant fire test standard.

6.5 Test procedure

6.5.1 Before a test, the sampling line and gas sampling cell are heated to a temperature of 130 ± 10 °C. A new filter (two pieces of glass fiber filter) is inserted. The throughput value of the IR beam is checked. A reference spectrum of air flow is obtained. At the start of the fire test a computer program is started which acquires absorption spectra at preset (10 s or less for short tests) intervals. Spectra will be acquired until the end of the fire test (taking into account the delay time).

6.6 Analysis procedure

6.6.1 The general principle of the analysis is shown in the figure in Annex 3. The integrated areas (shaded areas) are used to calculate the sample gas concentration. This example also shows the base line correction. The calculation routine should be formulated so that if other gases overlap only the non-overlapping part is used.

When absorption bands to be analysed are totally overlapped, interference can be removed by subtracting the absorbance of an interfering compound by using a reference spectrum. An example of spectral subtraction is shown in Annex 4.

The height of absorption bands used for the analysis shall be inside the linear region (e.g. < 5) according to the instrument used.

Table 1 shows regions of absorbance for 8 gases, of which interference free parts are used for analysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Region cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2143-2000, (2212-2143)</td>
</tr>
<tr>
<td>CO₂</td>
<td>3763-3500, 665-570¹</td>
</tr>
<tr>
<td>HCN</td>
<td>723-708</td>
</tr>
<tr>
<td>HCl</td>
<td>3090-2587</td>
</tr>
<tr>
<td>HBr</td>
<td>2726-2322</td>
</tr>
<tr>
<td>SO₂</td>
<td>1412-1294</td>
</tr>
<tr>
<td>NO₂</td>
<td>1665-1528</td>
</tr>
<tr>
<td>C₃H₄O</td>
<td>1750-1653</td>
</tr>
</tbody>
</table>

¹) This region can be used only for concentrations < 2.5 % in the linear region.

6.6.2 One spectrum corresponds to concentrations at one single time. When the measuring times of each spectrum are recorded the time-concentration curve can be determined.

6.7 Expression of results

Calculated concentrations are expressed in ppm (parts per million of the volume) and can be presented as:

- time dependence curve
- average concentration during 60 s at highest concentration or/and average concentration during the main burning period or any other specified times.

Yields can be calculated when the specimen burning rate (g/s) and flow rate are known and are expressed in kg/kg.
6.8 Accuracy

Examples of practical detection limits determined on the basis of signal to noise ratio in reference spectra (interference free) in one scan of the calibration gas mixtures are given in Table 2.

Table 2. The lowest detection limits.

<table>
<thead>
<tr>
<th>Compound</th>
<th>The lowest detectable concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>15</td>
</tr>
<tr>
<td>HCN</td>
<td>1</td>
</tr>
<tr>
<td>HCl</td>
<td>10</td>
</tr>
<tr>
<td>HBr</td>
<td>15</td>
</tr>
<tr>
<td>SO₂</td>
<td>1</td>
</tr>
<tr>
<td>NO₂</td>
<td>1</td>
</tr>
<tr>
<td>C₃H₄O</td>
<td>5</td>
</tr>
</tbody>
</table>

In spectral subtraction of interfering water, noise is increased and detection limits of the compounds overlapping with water become higher e.g. 10 ppm for SO₂ and NO₂ and 40 ppm for acrolein or less depending on the concentration of water. Subtraction of CO₂ does not increase the noise around the region of HCN absorption by very much and the detection limit of HCN is 2-5 ppm after the subtraction.

It must be noted that variations in gas concentration results of fire effluents are caused by variations both in the burning process and in the chemical analysis plus gas sampling.

Average standard deviation values in triplicate testing found in a cone calorimeter study (14 products) were as follows: CO 10.3 %, CO₂ 11.7 %, HCN 4.2 % and HCl 7.3 %. The standard deviation of rate of heat release results was 11.0 % for the same products.

6.9 Test report

The test report shall include relevant items from the following list:

a) Name and address of the testing laboratory
b) Identification number of the test report
c) Name and address of the organisation or person who ordered the test
d) Purpose of the test
e) Method of sampling and other circumstances (date and person responsible for the sampling)
f) Name and address of manufacturer or supplier of the tested product
g) Name or other identification marks of the tested product
h) Description of the tested product
i) Date of supply of the tested product
j) Date of the test
k) Test methods including fire test and chemical analysis
l) Conditioning of the test specimens, environmental data during the test (temperature, pressure, RH, etc.)
m) Identification of the test equipment and instruments used
n) Any deviation from the test method
o) Test results (use SI units)
p) Inaccuracy or uncertainty of the test results
q) Date and signature
SCHEMATIC VIEW OF GAS SAMPLING AND IR MEASUREMENT
# NOTE ON CHOOSING CALIBRATION GASES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linearity</th>
<th>Calibration region ppm</th>
<th>Suggested number of different concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>non-linear</td>
<td>500 - 50000</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>non-linear</td>
<td>50 - 5000</td>
<td>5</td>
</tr>
<tr>
<td>HCN</td>
<td>non-linear</td>
<td>50 - 500</td>
<td>4</td>
</tr>
<tr>
<td>HCl</td>
<td>non-linear</td>
<td>100 - 5000</td>
<td>5</td>
</tr>
<tr>
<td>HBr</td>
<td>non-linear</td>
<td>50 - 2000</td>
<td>4</td>
</tr>
<tr>
<td>SO₂</td>
<td>almost linear</td>
<td>50 - 500</td>
<td>3</td>
</tr>
<tr>
<td>NO₂</td>
<td>linear</td>
<td>50 - 1000</td>
<td>3</td>
</tr>
<tr>
<td>C₂H₄O</td>
<td>linear</td>
<td>50 - 300</td>
<td>3</td>
</tr>
</tbody>
</table>
EXAMPLE OF THE ANALYSIS

Wavenumbers (cm$^{-1}$)

Absorbance

PVC hard

HCl reference

Flexible PU foam with CO$_2$ subtracted

HCN

HCN reference
AN EXAMPLE OF SPECTRAL SUBTRACTION

Flexible PU foam

Flexible PU foam with CO\textsubscript{2} subtracted

Wavenumbers (cm\textsuperscript{-1})