

Transfeu WP2 Subtask 2.1.2 Development of small-scale test method for fire effluents

Step 5 : Development of calibration method

Smoke chamber test – Continuous toxic gases analysis by FTIR

Procedure for toxic gases measurement in combustion effluents of liquid during smoke chamber test (ISO 5659-2) using FTIR technique

According to DoW

► Step 5: Development of calibration method

Partners: *LSFIRE, LNE, RATP, VTT, SP, CUR*

The optimum calibration procedures will be carried out in parallel by **LSFIRE, LNE, RATP, VTT, SP** and **CUR**. These procedures will be established by checking of thermal attack and by measurements of gases, with particular attention to the quantitative measure for the expected kind of gases.

20. Forward

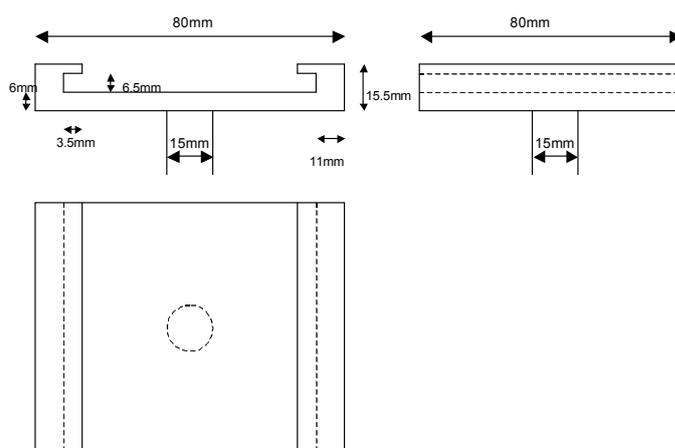
This procedure is used to validate the continuous toxic gases analysis by FTIR applied to smoke chamber fire model. The exercise shall be carried out to determine the level of repeatability and reproducibility between involved labs concerning the analysis technique in terms of detection and prediction of most gas species that shall be quantified in the future standard method. The liquid tank and sliding platform are following described and shown in this document

21. Set up of apparatus

2.1 Liquid vessel and sliding platform

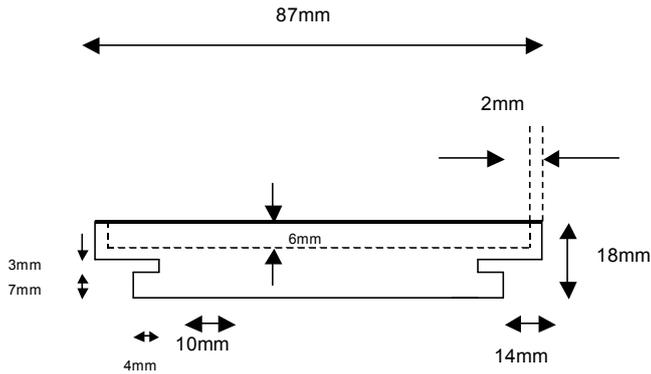
The liquids to be burned shall be put in testing vessel following described:

Sliding /guide platform - figure 1

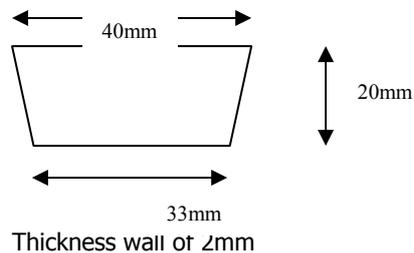


This sliding/guide platform shall be mounted as sample holder and liquid tank support.

Specimen holder sliding base - figure 2



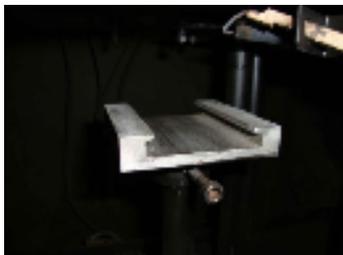
This specimen holder sliding base shall be used as base for sample frame and liquid tank.
The liquid tank consisting in a crucible porcelain small vessel having the following dimensions:



Combustible liquid vessel (to apply into specimen holder sliding base) – figure 3

This liquid vessel shall be used as combustible liquid support.

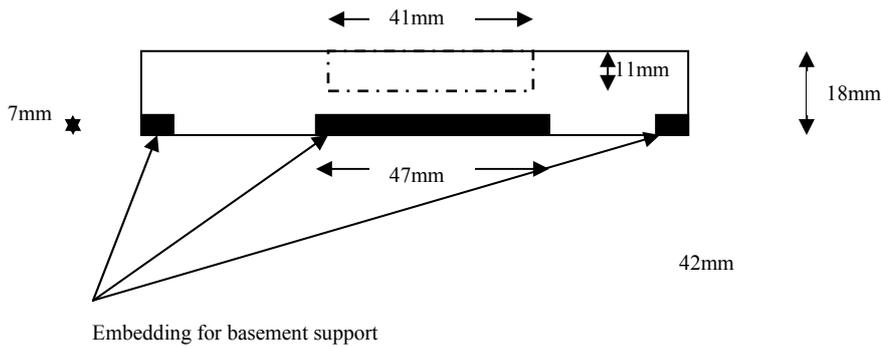
Following some picture of the above described parts:



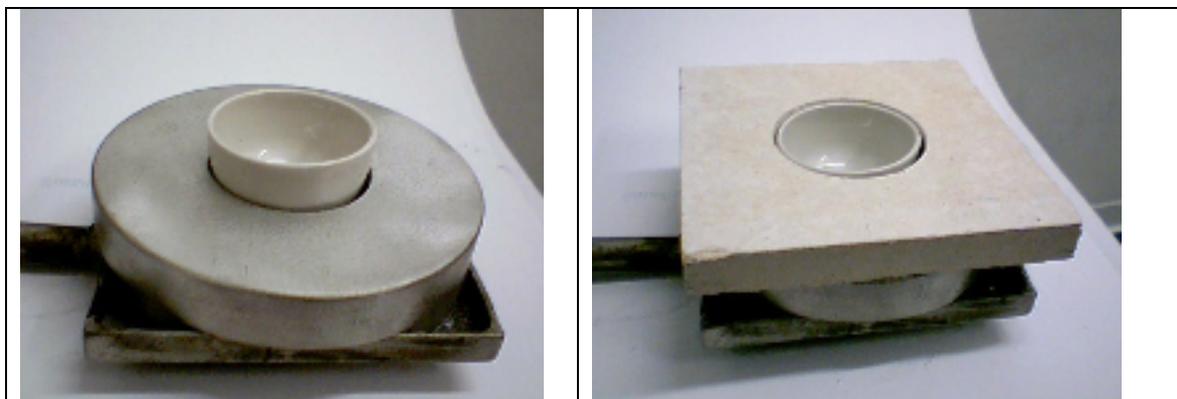
Sliding platform

The liquid tank support consisting in Al cylindrical container having a central hole of 41mm diameter and 11mm deep, where the crucible tank will be placed.

Scheme of Al cylindrical container



The small crucible tank shall be placed in the central hole and the exceeding part shall be covered by a non combustible calcium silicate pad as shown in the following picture.



Specimen holder and vessel base + liquid vessel

Before switch on the radiator cone, regulate the position of the tank above the cone basement so that the highest part of the vessel/calcium silicate pad be at 20mm from the radiator cone base.

2.2 Set up of apparatus for toxic gases measurement

All the parts needed for toxic gases measurement shall be set as the following scheme:

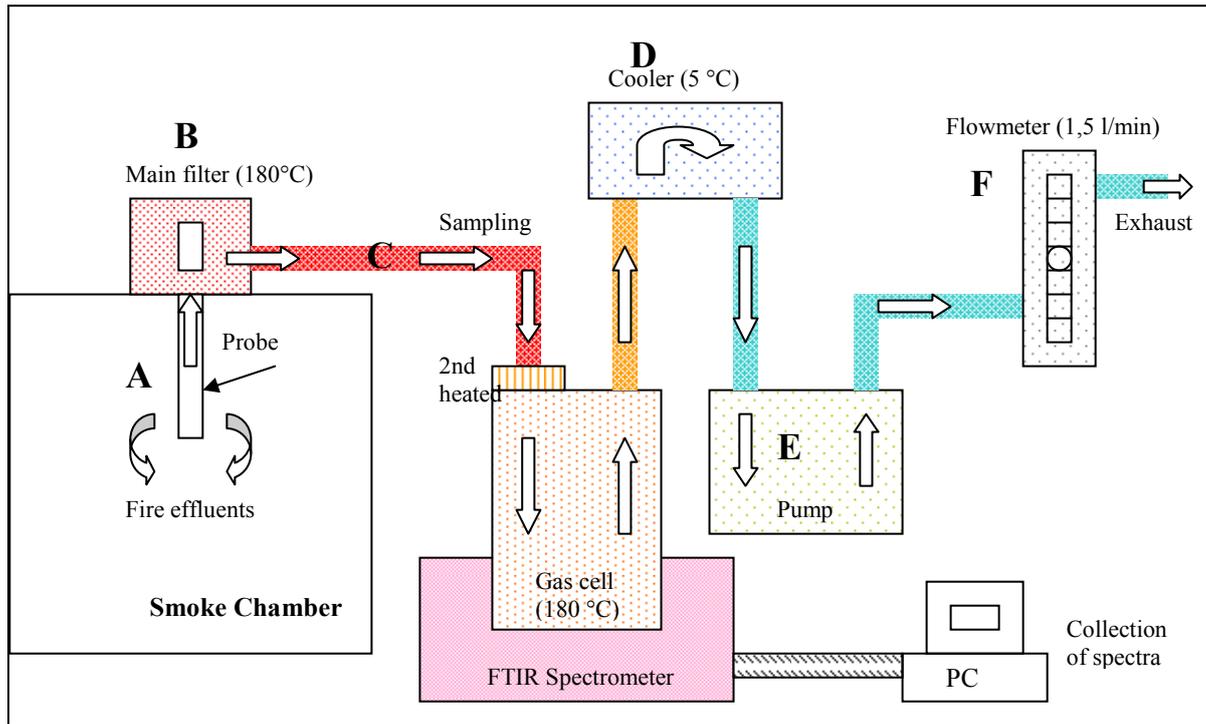


Figure 4 – Scheme of FTIR sampling

2.2.1 Internal probe

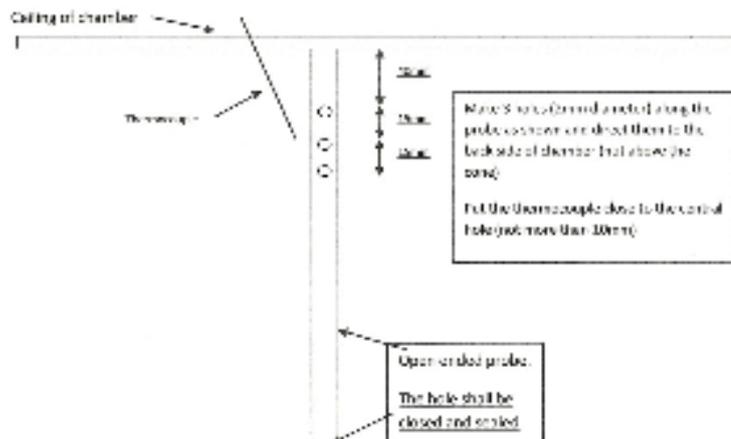
The internal probe shall consist in a SS closed ended tube having 4mm internal diameter and 30 cm long. It shall be fixed in the central point of chamber roof.

The tube shall provide 3 holes (2mm diameter) along the probe as shown and direct them to the back side of chamber (not above the cone).

The holes shall be (center) respectively at 40mm, 55mm and 70mm from the internal ceiling of the chamber.

Close to the central hole (55mm) and at max 10mm from it, a thermocouple shall be placed to measure the temperature of sampling.

Scheme of internal sampling probe





2.2.2 Main filter

The main filtering system shall be a cylindrical PTFE cartridge of 30mm diameter and 75mm length with a porosity of 2 microns into a heating housing having a temperature controller set to 170 ± 10 °C.

The use of PTFE was previously decided because HF may be reactive with fiber glass and ceramic may absorb HCl also at high temperature.

2.2.3 Sampling line

A heated PTFE sampling line shall be used to join the main filter to FTIR gas cell and the temperature was set to 170 ± 10 °C.

2.2.4 Gas cell

A FTIR gas cell of a volume from 0.2l to 0.4l and a pathlength from 2m up to 5m shall be used for fire effluent sampling and in order to increase the level of safeguard of internal mirrors a small circular planar filter (47mm diameter) with a PTFE membrane of 1 micron porosity shall be placed in the way in of the cell (2nd filter).

The gas cell was heated at 170 ± 10 °C. The cell safeguard filter shall be heated at least of 130 ± 5 °C. The gas cell shall provide a pressure transmitter which should be able to real time read the cell absolute pressure output values with a sensitivity of mbar unit (working range from vacuum to 3bar absolute press.). Its sensor shall not be a extension probe with a volume not more than 2% of the gas cell volume. It shall be able to working at temperature ≤ 200 °C.

2.2.5 Way out of the cell

The sampling line after the cell shall be connect to a cooler system to decrease the temperature of sampling flow at less than 30 °C to improve the flow measurement and increase the stability of it before to go in the pump. The pump was then collected to a flow meter which was used to set and check the sampling flow. The pump should be able to keep the constant exhaust flow rate of 1.5 ± 0.1 l/min.

2.2.6 Sampling flow rate

The sampling flow rate shall be kept at 1.5 ± 0.1 l/min for 3 different technical reasons.

The first one is that as the VTT study on modeling demonstrated, no influences in smoke measurement if the gas sampling flow is set between 1 and 2 l/min.

The second is concern the response time of the cell which shall be short enough to permit at least 4 readings per minute. It means an interval time between toxicity measurement less or equal to 15s. This condition shall be reached with a gas cell of limited volume between 0.2l to 0.4l which require a flow rate at max of 1.5 ± 0.1 l/min.

A third reason is limiting the volume drawn out of the chamber during 20min test period in order to avoid any under-pressure effects inside the smoke chamber. This can be respected only working with a sampling flow rate less than or equal 1.5 ± 0.1 l/min.

Finally, the sampling flow rate shall be the same used for calibration of FTIR using standard mixture bottles.

A complete set of example picture is shown in annex 1 of this document.

2.3 Set up of Smoke chamber

The internal walls of the chamber shall be cleaned from residues of previous tests. The condition for testing shall be set to 50 kW/m² of irradiance level with pilot flame. The length of the flame shall be regulated to 30mm horizontal and at 5mm from the highest part of the small tank.

22. Test condition and nr. of tests

The test condition to set for these exercises shall be 50 kW/m² in presence of pilot flame. 5 replicates shall be carried out and the 3 central repeatable tests data will be reported.

23. Liquids – Type, Sampling and maintenance

4.1 Type

The following reference liquid mixture shall be tested under above conditions.

46,5% of 4,4 Isocyanate
46,5% of Chlorinated paraffin
7,0 % of Tetramethyl sulphone

4.2 Sampling

Just before starting of test the following quantity of liquids shall be put in the small tank:

5,0±0.1 g

4.3 Manteinance

The liquid mixture shall be maintained at a minimum temperature of 35-40°C (max 60°C) before the use because has a melting point around 28°C.

Before to put the liquid in the tank for testing, the bottle shall be previously put in a hot water vessel and kept for at least 3 minutes (temperature of water shall be 55-60 °C)

24. Calibrations

The FTIR calibration shall be in accordance with the document "Transfeu WP2 subtask 2.1.2 step 5 - FTIR analyser calibration using standard gas bottles procedure V1 - Draft 1"

The cone radiator calibration shall be in accordance with the document "Transfeu WP2 subtask 2.1.2 step 5 - Cone radiator calibration procedure V2 - Draft 1".



The Chamber leakage test shall be previously performed according to the document "Transfeu WP2 subtask 2.1.2 step 5 - Chamber leakage test procedure V1 - Draft 1"

The calibration of smoke measurement system shall be in accordance with the document "Transfeu WP2 subtask 2.1.2 step 5 - Smoke opacity calibration procedure V2 - by LSF glass filters - Draft 1".

25. Test procedure

6.1 Before the test

- A. Before each test, check very carefully the internal walls condition of the test chamber and eventually clean them removing all dirty layers/particles. The same operation shall be done on the surface of the internal probe for FTIR sampling.
- B. Set the test condition in accordance with paragraph 3.
- C. The temperature of the chamber wall shall be $55 \pm 5^\circ\text{C}$.
- D. The inlet of the probe shall be cleaned.
- E. The filter element of main filter shall be cleaned or changed prior to the start of the test.
- F. The filter element of safeguard cell filter shall be cleaned or changed prior to the start of the test.
- G. Before of each test flush the sampling line and cell with nitrogen for at least 2 min.
- H. Start the pump and let the air (chamber atmosphere) flow through the sampling line for at least 10 minutes to flush the line and set the pre-established operative sampling flow rate. During this operation ensure that the pressure in the sampling line and the gas cell remain constant and close to the ambient pressure (pressure transmitter monitoring) and that the temperature of the air in the sampling line remains within $170 \pm 10^\circ\text{C}$ for at least 10 minutes prior the test.
 - I.
- J. Close the chamber door, and regulate the 0% - 100% trasmittance values of smoke density measuring system.
- K. Collect the background reference spectrum with the sampling line and cell flushed with nitrogen gas (N_2) at working sampling flow rate .

6.2 Testing

- a) After Background spectrum recording and 0-100% trasmittance setting, start the following data collection at least 1 minute before introduce the sample:
 - L.
 - Sampling point temperature (T_s) with 15s time interval between data
 - Pressure transmitter with 15s time interval between data
 - FTIR spectra continuous collection with a minimum interval time of 15s between spectra.
 - M.
 - N. All above measurements shall be carried out until the end of the test.
 - O.

Note1: The starting of spectra data collection shall be done one minute prior the beginning of the test in order to allow for detection of any significant contaminants and the test can be aborted if such contaminants are discovered. Ambient CO_2 and contaminants other significant is measured quantitatively (during pre-measurement period) and can be subtracted from reported values.
 - P.
 - Q.

Note2: Response Time shall be previously measured according to the procedure described in ISO 19702 Standard.. The toxicity curves shall be time shifted taking into consideration this delay time.

- R.
- b) After 1 minute, open the chamber door and introduce the sample previously prepared in accordance with paragraph 9, start the clock and close the chamber door within 5s.
- S.
- c) Start the following data collection in the same time:
- T.
- Smoke density measurement with a 5s time interval between data
- U.
- d) The collection of all vector data shall be done for 20min (duration of the test)
- V.
- e) During the test shall be noted Ignition time and end flame.

6.3 Toxic gas species analysis correction

W.

Concentration vector data of the gases detected according to the following list and corrected in accordance with paragraph 6.3.1

Carbon monoxide
 Carbon dioxide
 Hydrogen chloride
 Hydrogen Bromide
 Hydrogen Fluoride
 Hydrogen cyanide
 Sulfur dioxide
 Nitrogen monoxide
 Nitrogen dioxide
 Acrolein
 Formaldehyde
 Ammonia

Gas analysis shall be carried out in accordance with ISO 19702.

6.3.1 Calculation of corrected concentration

Each value of concentration vector data (for each gas species) shall be corrected looking to pressure transmitter values recorded during the test as following described:

$$C_c = C_p * P_c / P_t$$

Where:

C_c is the corrected concentration of gas species (ppm)

C_p is the concentration of the gas species predicted using calibration training spectra method (ppm)

P_c is the absolute pressure measured (pressure transmitter) during collection of training spectra (calibration) expressed in Pa (Pascal)

P_t is the absolute pressure measured (pressure transmitter) during collection of unknown spectra (test) expressed in Pa (Pascal)

Once C_c (vector data) for each detected gas species was calculated convert it in kg/m^3 unit (C_m – mass concentration) using the following formula:



$$C_m = C_c \times \frac{P_{chamber} \times M_{gas}}{R \times T_s}$$

Where:

C_m	is the concentration of gas species expressed into kg/m ³
C_c	is the corrected concentration calculated above expressed in µl/l (ppm)
$P_{chamber}$	is the pressure in the smoke chamber just before starting of test (Pascal)
M_{gas}	is the molar mass of the gas, in kg/mole
R	is gas constant equal to 8.3143 j.mol ⁻¹ /K
T_s	is the sampling temperature during the test (K)

With the following set for example :

C_m	12.31.10-6l/l (12.31 ppm) of carbon monoxide
P_{cl}	99800 Pa
P_t	96430 Pa
$P_{chamber}$	100170 Pa
M_{gas}	0.028 kg/m ³ for CO
R	8.3143 j.mol/K
T_s	69.2 °C = 342.35 K

We have $C_c = 12.554 \text{ mg/m}^3$

26. Report

The test report shall contain the following information for each specimen:

- a. name and address of the test laboratory;
- b. date of test;
- c. Test condition : irradiance level / with or without pilot flame;
- d. data from the test including:
 1. Mass of sample prior and after the test (g)
 2. Mass lost (g)
 3. Initial and final temperature of the chamber wall (°C)
 4. Maximum value of D_s reached during the test and the time (D_m and Time to D_m)
 5. Residual transmittance (%)
 6. Ignition and end flame time (s)
 7. D_s vector data (5s interval)
 8. Concentration (C_c) vector data of each gases detected according to the list in par. 6.3 and corrected in accordance with paragraph 6.3.1 and expressed in ppm (15s interval)
 9. Mass concentration (C_m) vector data of each gases detected according to the list in par. 6.3 and corrected in accordance with paragraph 6.3.1 expressed in mg/m³ (15s interval)



e. Averaged results of 3 replicates shall be given for the following data:

10. Maximum value of D_s reached during the test and the time (D_m and Time to D_m)
11. D_s vector data (5s interval)
12. Concentration (C_c) vector data of each gases detected according to the list in par. 6.3 and corrected in accordance with paragraph 6.3.1 and expressed in ppm (15s interval)
13. Mass concentration (C_m) vector data of the gases detected according to the list in par. 6.3 and corrected in accordance with paragraph 6.3.1 (15s interval)

f. data from the test including:

14. data regarding the test equipment, including
 1. the inner volume of the gas cell and the sampling line
 2. flow rate of the pump
 3. reference to this standard;
 4. reference to a test report of smoke measurement which is carried out in conjunction of the test