NATO INTERNATIONAL STAFF - DEFENCE INVESTMENT DIVISION

1157-10/2

ALLIED
FIRE
ASSESSMENT
PUBLICATION

AFAP-3
(Edition 3)

NATO REACTION-TO-FIRE TESTS FOR MATERIALS

TOXICITY OF FIRE EFFLUENTS

AFAP - 3

(Edition 3)

JULY 2010

AFAP-3

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NORTH ATLANTIC TREATY ORGANIZATION

NATO STANDARDISATION AGENCY (NSA)

NATO LETTER OF PROMULGATION

30 July 2010

1. AFAP-3(Edition 3) – NATO REACTION-TO-FIRE TESTS FOR MATERIALS – TOXICITY OF FIRE EFFLUENTS is a non classified NATO publication. The agreement of interested nations to use this publication is recorded in STANAG 4602.

2. AFAP-3(Edition 3) is effective on receipt. It supersedes AFAP-3(Edition 2) which shall be destroyed in accordance with the local procedure for the destruction of documents.

3. It is permissible to distribute copies of this publication to Contractors and Suppliers and such distribution is encouraged.

Cihangir AKSIT, TUR Civ
Director, NATO Standardization Agency

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Record of Changes

Change Date	Date Entered	Effective Date	By Whom Entered

RECORD OF RESERVATIONS

Nation	Reservations

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Preface

1. This Allied Publication forms part of a series as follows:

AFAP-1 NATO reaction-to-fire tests for materials - POLICY FOR THE PRE-SELECTION OF MATERIALS FOR MILITARY APPLICATIONS.
AFAP-2 NATO reaction-to-fire tests for materials - SMOKE GENERATION
AFAP-3 NATO reaction-to-fire tests for materials - TOXICITY OF FIRE EFFLUENTS
AFAP-4 NATO reaction-to-fire tests for materials - SURFACE SPREAD OF FLAME
AFAP-5 NATO reaction-to-fire tests for materials - HEAT RELEASE RATE

2. The contribution to fire hazard from a particular material, depends on a number of interrelated factors. It is not only influenced by the reaction to fire properties of the material, but also by the way in which the material is used in practice and by the fire scenario to which it is exposed. These Allied Publications define methods for the assessment of reaction to fire properties of materials, valid under the specific conditions of each test. They provide comparisons between candidate materials, but do not predict the behaviour of the materials, or combinations of materials, in actual fire conditions. Together, they are intended to be used as part of the comparative screening process for the pre-selection of materials on the basis of their fire characteristics.

3. Any enquiries regarding this Allied Publication in relation to an invitation to tender or a contract in which it is incorporated are to be addressed to the Technical Authority.

NATO REACTION-TO-FIRE TESTS FOR MATERIALS

TOXICITY OF FIRE EFFLUENTS

Warning

This Allied Publication may call for the use of substances and/or procedures that may be injurious to health or damaging to the environment if adequate precautions are not taken. Test operators shall be responsible for implementation of such precautions, in order to ensure the safe operation of the test. The text of this Allied Publication refers only to technical requirements and in no way absolves the user from statutory or other legal obligations relating to health and safety and environmental legislation. Full account shall be taken of further health and safety advice/warnings that appear in the normative references and equipment manuals. Where attention is drawn to particular hazards, those quoted may not be exhaustive.

1. SCOPE

This Allied Publication defines a tube furnace test method for determination of a TOXICITY INDEX value for gases released from small specimens of materials, under sets of specified thermal conditions and analytical parameters specific to various toxic species.

Fire effluents produced during tests at 800°C are analysed for 8 gases (CO, CO_2, NO_X, SO_2, HF, HCl, HBr, HCN). Two further gases (formaldehyde HCOH and acrolein CH_2CHCHO) are analysed in fire effluents obtained during tests at 350°C. Additionally, analysis for phenol (C_6H_5OH) at 800°C may be required if the TOXICITY INDEX from the remaining gases is close to the acceptance criterion (i.e. greater than 6 and less than 10). Contributions from all 10 (or 11) gases are summed to give a global TOXICITY INDEX.

This Allied Publication is intended to form part of the pre-selection screening process for materials and should not be interpreted as an assessment of toxicity hazard under actual fire conditions. The test method is directed at the analysis of a specified set of gaseous species which are commonly present in combustion products of materials used in military applications and which may cause lethality at the time of the fire. It does not address acute mental incapacitation effects, delayed/long term toxicity, or toxicity involving particulate combustion products. The set of gaseous species analysed is not exhaustive and other toxic species, not yet listed, can be evolved from common materials. The current list represents a set designed to give a general assessment of the toxic hazard.

2. NORMATIVE REFERENCES

2.1 The following documents are referred to in this Allied Publication:

IEC 60584-2 Thermocouples – Part 2: Tolerances

ISO 291 Plastics - Standard atmospheres for conditioning and testing: 1997. Incorporating Corrigendum 1: 1998;

ISO 3696 Water for analytical laboratory use - Specifications and test methods: 1987;

ISO 5725-2 Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic methods for the determination of repeatability and reproducibility of a standard measurement method;

ISO 10304-1 Water Quality - Determination of Dissolved Fluoride, Chloride, Nitrite, Orthophosphate, Bromide, Nitrate and Sulphate Ions, Using Liquid Chromatography of Ions - Part 1: Method for Water with Low Contamination: 1992;

ISO 19701 Methods for sampling and analysis of fire effluents;

ISO 19702 Toxicity testing of fire effluents — Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis;

NF X 70-100-1 Fire tests - Analysis of gaseous effluents - Part 1 : methods for analysing gases stemming from thermal degradation: 2006;

SAFIR Final Report (Smoke Gas Analysis by Fourier Transform Infra-Red Spectroscopy) within European Standards Measurement and Testing Programme under contract number SMT4-CT96-2136 (1999).

2.2 This Allied Publication has been prepared with reference to the particular dated versions of the standards specified above, that were current at the time of publication. From time to time, all standards are subject to revision and the responsible NATO standardization committee will keep this prospect under review. Not withstanding this fact, the versions of the standards specified above shall continue to be used, without amendment, until such time as the responsible NATO standardization committee specifies the use of any amendments or revisions published by the relevant standards organisations.

2.3 National and international standards are available from the relevant national standards body for each nation or from ISO. NATO STANAGs and Allied Publications can be obtained from the NATO STANAG point of contact for each nation.

3. DEFINITIONS

3.1 Technical Authority

The relevant national technical authority, responsible for providing regulations and guidance on fire reaction of materials associated with procurement and in service support.

3.2 TI - TOXICITY INDEX

The summation of the toxicity factors C_θ / Cf of selected gases produced by the combustion of a material under the conditions specified in the test.

3.3 C_θ - Concentration from 100 g in 1m^3

The concentration of the gas, produced under the conditions of the test, scaled up for 100 g of material and re-calculated as though the combustion products were diffused into a volume of 1 m^3.

3.4 Cf - Critical factor

The concentration of the gas considered fatal to man for a 30 minute exposure. The values of Cf to be used are given in ANNEX 1.

3.5 LoD - Limit of Detection

The smallest quantity of an analyte in a sample that can be detected as being different to the value of the blank, with a given probability, but not necessarily quantified.

3.6 LoQ - Limit of quantification

The smallest quantity of an analyte in a sample that can be analysed quantitatively, under the experimental conditions of the method, with a defined variability. For the purposes of this Allied Publication, the variability required is defined by the maximum acceptable value of the coefficient of variation (CoV) for the measurement at that point (see Section 7.5).

3.7 CoV - Coefficient of Variation

The standard deviation of a set of analytical measurements divided by the mean (here it is expressed as a percentage). [CoV = (100 x standard deviation)/mean]

4. APPARATUS

Schematic diagrams of the apparatus are shown in Figures 1 and 2.

4.1 Tolerances

All measurements are nominal unless otherwise stated.

4.2 Combustion tube

Transparent silica quartz; internal diameter (40 ± 2) mm, wall thickness 2 mm, nominal length (1000 ± 10) mm.

“Upstream” end of tube fitted with a twin port cap, one for air, the other for the push-rod. The latter shall be equipped with a device able to grip the push-rod to obtain a gas tight seal. A screw and a silicon ring are suitable for this purpose.

“Downstream” end of tube fitted with a single port cap for gas exit.

Tube end-caps to be capable of gas tight coupling to the tube.

Note: It has been observed that test results can adversely be affected by use of tubes that show opacity and/or porosity.

4.3 Tube Furnace

Dimensions:

Work tube length (600 ± 10) mm. Internal diameter (65 ± 5) mm.

Temperature control:

With air passing through the combustion tube at 2 litres/minute, the furnace shall be capable of establishing and controlling a temperature profile as specified in ANNEX 2. The furnace shall also be capable of operating at temperatures >900°C for the purpose of cleaning the combustion tubes (see Section 11.1).

Measurement of temperature profile:

The procedure to measure the furnace temperature profile using the thermocouple described in paragraph 4.12 and establish the centre of the hot zone is given in ANNEX 2. This procedure shall be carried out at least every year, and on commissioning of a new furnace and/or after any repair, alteration or dismantling of the relevant parts of the apparatus.

4.4 Combustion boat

Choose a combustion boat according to the density of the material under test, as specified below (see Figure 3):

4.4.1 Standard combustion boat

For materials with a density of 60 kg/m^3 or greater

Porcelain combustion boat: weight 8.5 ± 0.5 g				
External dimensions (mm)	Length	Width	depth	wall thickness
	48 ± 2	26 ± 2	10 ± 2	1.7 ± 0.1

4.4.2 Large combustion boat

For materials with a density less than 60 kg/m^3

Fused silica combustion boat: weight 22.5 ± 2.0 g				
External dimensions (mm)	Length	Width	depth	wall thickness
	62 ± 2	29 ± 2	13 ± 2	3.1 ± 0.5

4.5 Gas supply

Certificated “synthetic air” cylinder (79% N_2, 21% O_2).

Note 1: Its use negates any need to perform background correction (CO_2) and minimises the moisture content of the combustion gases to combustion product only.

Note 2: However, if the grade of certified air used contains a non-negligible (more than 1 ppm) concentration of CO_2 and/or CO then this must be considered as a baseline value and therefore be subtracted from the measured value.

4.6 Air supply system

Consisting of a gas flow rate meter and a flow control device capable of supplying air at a constant flow rate (2 litres/minute), to achieve a total volume of 40 ± 2 litres in 20 minutes.

The flow meter shall be calibrated for dry air to an accuracy of ± 1% and have a full scale reading such that a flow rate of 2 litres/minutes falls within the range 20% to 80% of that full scale reading.

Note: A rotameter combined with a regulating valve has been found suitable.

4.7 Gas volume meter (for impinger gas collection only)

A dry type gas counter with a cylindrical volume of 2 litres and a minimum flow rate of 25 litres/hour is suitable.

Note 1: For impinger collection, the gas meter is placed at the end of the gas path, after the impingers. At the end of the test, the total volume of gas sampled is checked. This is to ensure that the correct flow rate has been applied and that no leaks have occurred.

Note 2: This type of gas meter may not be suitable for use in-line before the impingers or gas collection bag, due to possible condensation / soot blocking, etc. For the purposes of this Allied Publication it shall not be used when the combustion gases are collected with a bag.

4.8 Glass wool filter.

Use a glass wool (non-coated) filter, (3 ± 0.5)g, consisting of a loosely packed plug located at the “downstream” end of the tube (as shown in Figures 1 & 2) in order to retain carbonaceous “soot” particulate products. After rinsing (see Section 9.3 (n) of this Allied Publication) discard the used filter and use fresh glass wool for each new run.

The glass wool shall be cleaned batch-wise prior to use by soaking a bulk portion of unused glass wool in at least 3 changes of deionised water, allowing excess water to drain and then drying in air or an oven. Alternatively, a glass wool “control” shall be prepared and analysed with each batch of test solutions by soaking a small portion of the cleaned glass wool in a corresponding volume of trapping medium.

4.9 Gas collection bag - 40 litres capacity

Collection bag shall be made of a material (see Note 2 below) impermeable to gas, and be able to collect a gas volume of at least 40 litres. It shall be equipped with a tap, or similar device, to seal the sampling orifice after gas collection. A sampling orifice of inner diameter smaller than 3 mm are not recommended due to possible soot blocking.

Note 1: It is recognised that new bags have been supplied containing unacceptably high concentrations of contaminants. New bags shall be filled with nitrogen and purged several times before use. Additional checks for contamination can be performed by carrying out analyses on the gas purged using the appropriate techniques.

Note 2: Teflon or Tedlar have been found suitable. With careful handling and evacuation/purge cleaning, the bags should be capable of being used repeatedly before replacement. See Section 11.2 of this Allied Publication.

4.10 Impingers (bubblers)

Upright glass impinger (Durand washing bottle) of nominal capacity 100 ml, having a straight pipe without a frit, and providing a minimum bubbling height of 10 cm when filled with 75 ml of liquid.

4.11 Timer

Calibrated timing device suitable for monitoring a period of 20 minutes ± 5 seconds.

4.12 Thermocouple

Inconel or stainless steel sheathed mineral insulated K-type thermocouple probe; external diameter 3 mm; length 1000 mm; calibrated with tolerances as defined according to IEC 60584-2.

4.13 Water quality

For analyses performed by IC, HPLC, GC/MS by liquid injection, use water of Grade 1 according to ISO 3696 in the impingers, and for all the stages of collection of solution and analysis.

Note: ISO 3696 defines three grades of water:

- Grade 1 obtained by treatment of quality 2 water (e.g. reverse osmosis-ionisation followed by filtration through a membrane with of 0.2 µm, or re-distillation using a quartz equipment);
- Grade 2 obtained by multiple distillation, multiple de-ionisation or reverse osmosis followed by distillation;
- Grade 3 obtained by only one distillation, de-ionisation or reverse osmosis.

Some characteristics required are given in the following table :

Table 1 - Water quality

Parameter	Grade 1	Grade 2	Grade 3
pH at 25 °C in pH unit	Not applicable	Not applicable	5.0 to 7.5
Conductivity mS/m at 25 °C, max.	0.01	0.1	0.5
Absorbance at 254 nm, with a tube of 1 cm in thickness Absorbance unit, max.	0.001	0.01	Not specified

5. TEST SPECIMEN

5.1 Conditioning

Before any sampling for testing purposes, the material supplied to the laboratory shall be conditioned at (23 ± 2) °C and (50 ± 10) % R.H. until a constant mass is obtained. This shall be considered to have been reached when two successive weighing operations, carried out at an interval of 24 hours, do not differ by more than 0.1 % of the mass of the sample or 0.1 g, whichever is the greater (see ISO 291).

Therefore, the test specimen mass is likely to include a moisture content, but this would be a normal constituent of the material as received and thus is legitimately included in the mass loss.

If the furnace is not located in a conditioned laboratory, the test procedure described in Section 9.2 onwards shall be carried out immediately after the removal of the test specimen from the conditioning enclosure.

5.2 Form of test specimen

The form of the test specimen shall be determined by the Technical Authority. Unless otherwise specified by the Technical Authority the test specimen shall be cut as a single piece.

5.2.1 Specimens for paint systems

Paint systems shall be tested without a substrate (i.e. as pieces of free film). The samples shall be prepared according to the manufacturer's instructions, to include all layers present in end-use conditions (including primary, intermediary, finishing and varnishes). Cut the free film so that it lays flat on the base of the combustion boat. If necessary more than one piece may be used to make sufficient mass of specimen (see 5.3).

Note: Applying paint layers on to a low adhesion surface such as PTFE sheet, then removing the film has been shown suitable to produce test specimens for this Allied

Publication. It is important to ensure that the temporary substrate material does not contaminate the test specimen.

5.3 Mass of test specimen

Use a test specimen mass of (1.000 ± 0.050) g

5.4 Selection of the combustion boat

5.4.1 Materials with a density of 60 kg/m^3 or greater

Use the standard combustion boat described in Section 4.4.1. The maximum height of the test specimen shall be 25 mm. Do not crush or otherwise distort the test specimen in order to fit it into the boat.

5.4.2 Materials with a density less than 60 kg/m^3

Use the large combustion boat described in Section 4.4.2. The maximum height of the test specimen shall be 25 mm. Do not crush or otherwise distort the test specimen in order to fit it into the boat.

Cut a square sided test specimen, with a cross section (normal to the furnace axis) 25 mm high x 19 mm wide and cut the length (parallel to the furnace axis) so that the test specimen mass complies with Section 5.3.

5.4.3 Low density materials

For some materials having a very low density, the dimensions of a 1 g test specimen cannot be accommodated by the large combustion boat as described in Section 5.4.2. In this case it is permissible to reduce the mass of the test specimen just enough to obtain dimensions recommended in Section 5.4.2. This shall be stated in the test report.

If a specimen below 0.5 g is required, this shall be stated in the test report and the following note shall be added. “These results are INDICATIVE ONLY and should not be compared to results achieved using full size test specimens.”

Note: The combustion process may be affected by the ratio of the test specimen size to the air flow and by the heat uptake of the test specimen and boat. It is therefore important to note that results achieved using different test specimen sizes or boats may not be comparable.

6. PROCEDURE

6.1 General description of the test method

For each of the two test temperatures (800°C and 350°C) specimens of pre-determined mass are burnt in the tube furnace, in air flowing at 2 litres/minute, for a fixed period of 20 minutes. The gases produced by combustion of the specimen are collected in a gas collection bag, or trapped by bubbling through impingers containing solutions suitable for particular gases (see Section 8). Various quantitative analysis techniques are used to determine the resulting concentrations of the gases collected in the bag, or in the solutions produced. Gases to be analysed are listed in Section 7.

Different combinations between gas collection techniques and analysis methods are possible depending on the nature of each gas. Multiple combustion runs at each temperature are required, in order to obtain analysis results for all of the gases.

Note: Many of the collection and analysis methods available allow measurement of a number of the gases in the same run. Appropriate choices of techniques should be made to minimise the number of runs.

A TOXICITY INDEX value is calculated from the measured gas concentrations (see Section 12).

6.2 Number of determinations

6.2.1 Duplicate determinations

At each test temperature and for each gas species (see Section 7), obtain two determinations of the concentration C_i.

For each gas to be analysed, C_i is the concentration (expressed in ppm) of the gas in the 40 litre sample of combustion products collected during the test (see Section 12.1).

Each determination shall come from a separate combustion test run, carried out with a new test specimen of the same material.

6.2.2 Gases trapped in solution

For the gas species collected by dissolution in impinger solutions, if the gas is not detected in the first run, it is permissible to omit the second determination and to report a zero value for C_i. This shall be denoted in the test report by entering the words “not detected” for the first run and “not tested” for the second run.

6.3 Repeatability of test results

If, for any gas, the two values of C_θ / Cf (see Sections 12.2 and 12.3) differ by more than 0.3, then carry out a further two determinations for that gas, using two new specimens from the same batch.

Report that the test specimens exhibited irreproducible behaviour and include the results from all four determinations in the test report. Calculate the contribution to TI from the maximum of the four concentrations.

7. GASES TO BE ANALYSED AND ANALYTICAL TECHNIQUES

7.1 Gases to be analysed

Fire effluents can contain a large range of potentially toxic gases, depending on the composition of the material burnt and the conditions of temperature and oxygen availability under which the combustion occurs. The set of gaseous species chosen for analysis in this Allied Publication, listed in Table 3, cannot therefore be exhaustive, but is a selection, considered to be the most common and toxic fire gases, designed to give a general assessment of the hazard. All of these gases shall be analysed for all materials tested in accordance with this Allied Publication with the exception that analysis for phenol is conditional (see Table 3 Note 4).

Table 2 contains references to information about the repeatability and reproducibility of ~~an~~ analytical methods that have been proven and reported at the time this Allied Publication was published. For the remaining species, information on the repeatability and reproducibility of the analysis techniques is under development.

Table 2 - Repeatability and reproducibility of analytical techniques for fire effluents

Gas	**Analytical technique**	**Document reference for repeatability and reproducibility**
Carbon dioxide	NDIR FTIR	NF X 70-100 - 1 / ISO 19701 ISO 19702 and SAFIR final report
Carbon monoxide	NDIR FTIR	NF X 70-100 - 1 / ISO 19701 ISO 19702 and SAFIR final report
Sulphur dioxide	IC	NF X 70-100 - 1 / ISO 19701
Hydrogen fluoride	ISE IC	NF X 70-100 - 1 / ISO 19701 AFAP-3 ANNEX 7
Hydrogen bromide	IC	NF X 70-100 - 1 / ISO 19701
Hydrogen chloride	IC FTIR with specific attention to condensation	NF X 70-100 - 1 / ISO 19701 ISO 19702 and SAFIR final report
Hydrogen cyanide	IC - Spectrophotometry *(picric acid)* FTIR	NF X 70-100 - 1 / ISO 19701 ISO 19702 and SAFIR final report
Oxides of nitrogen ($NO + NO_2$)	Chemiluminescence, FTIR, IC, NDIR	NF X 70-100 - 1 / ISO 19701
Formaldehyde	HPLC	NF X 70-100 - 1 / ISO 19701
Acrolein	HPLC	NF X 70-100 – 1 / ISO 19701
Phenol	HPLC	AFAP-3 Annex 7

7.2 Analytical techniques

Unless otherwise agreed with the Technical Authority, use one of the analytical techniques listed in Table 3 for each gas to be analysed. The primary techniques are considered to offer the most effective combination to reduce the necessary combustion runs to a minimum.

Other techniques may be available or may be developed in the future. Techniques not listed in the Table 3 may be used only with the prior agreement of the Technical Authority, and the laboratory will be required to provide evidence, to the satisfaction of the Technical Authority, that the results obtained are in agreement with those that would be obtained using the primary technique.

Table 3 - Gases & analytical techniques

Gas [1]		**Analytical Techniques** [2, 3]	**Primary analytical techniques**
Gases to be analysed at 800 °C			
Carbon dioxide	CO_2	**FTIR**	**NDIR**
Carbon monoxide	CO	**FTIR**	**NDIR**
Oxides of nitrogen	NO_x ($NO + NO_2$)	**Chemiluminescence**, Spectrophotometry, **FTIR** **IC** (NO_2 only)	**NDIR**
Sulphur dioxide	SO_2	**FTIR**	**IC**
Hydrogen fluoride	HF	**IC**	**ISE**
Hydrogen bromide	HBr	FTIR	**IC**
Hydrogen chloride	HCl	**FTIR**	**IC**
Hydrogen cyanide	HCN	**Spectrophotometry, FTIR**	**IC**
Phenol [4]	C_6H_5OH	**GC/FID**, GC/MS [5]	**HPLC**
Gases to be analysed at 350 °C			
Formaldehyde (Methanal)	HCHO	IC, GC/MS, Titration, spectrophotometry	**HPLC**
Acrolein (2-Propenal)	CH_2CHCHO	GC/MS, Titration	**HPLC**
Note 1	IUPAC chemical names are shown in brackets.		
Note 2	Acronyms for analytical techniques are shown in Table 4.		

Gas[1]	Analytical Techniques[2, 3]	Primary analytical techniques
Note 3	Techniques for which the repeatability and reproducibility have been proven (see Table 2) are shown in **bold type.** Other techniques were studied during the development of this Allied Publication. Only techniques that have been proven to be effective for the analysis of these gases within fire effluents in such tests have been retained.	
Note 4	Phenol is analysed only depending on the result obtained for the other gases (see Section 12.4).	
Note 5	For analysis of phenol by GC/MS, liquid injection shall be used (see Section 8.2.2).	

Table 4 - Analysis techniques - Acronyms

FTIR	Fourier Transform Infra Red
GC/NPD	Gas Chromatography / Nitrogen Phosphorus thermionic Detection
GC/FPD	Gas Chromatography / Flame Photometric Detector (see Annex 6)
GC/MS	Gas Chromatography / Mass Spectrometry
GC/FID	Gas Chromatography / Flame Ionisation Detector
IC	Ion Chromatography
ISE	Ion Selective Electrodes
NDIR	Non Dispersive Infra Red
HPLC	High Performance Liquid Chromatography

7.3 Prohibition of colorimetric gas detector tubes

Colorimetric gas detector tubes shall not be used for tests in accordance with this Allied Publication.

7.4 Prohibition of elemental analysis

Simple qualitative analytical techniques for particular chemical elements (e.g. the Lassaigne tests for Cl, Br, F, N, S). are known and sometimes used to try to predict the presence or absence of corresponding combustion gases (HCl, HBr, etc). However, in this case, the lower limit of detection for these techniques is too high for use in this Allied Publication and moreover, false negative results have been reported. Their use is hereby prohibited as a means of pre-determining the need for analysis for any gases in this way.

7.5 Determination of LoQ.

For the purpose of this Allied Publication, LoQ is determined as the lowest concentration for which a variability (coefficient of variation) of ± 10% is evaluated. A number of different methods can be applied to determine LoD and LoQ.

Note: The determination of LoQ can be obtained through various references, e.g. EURACHEM Guide “The fitness for purpose of analytical methods”.

For the purposes of this Allied Publication, when a non-zero concentration is measured which is below the LoQ for the analytical measurement technique, a value of zero shall be entered for the gas concerned in the calculation of Toxicity Index (see Section 12), but the concentration value shall be recorded in the test report as an observation (see Section 13). Table 5 below gives the maximum acceptable LoQ values for each gas.

Table 5 - Maximum acceptable Limit of Quantification (LoQ)

Gas		***Maximum Acceptable LoQ***	
		(ppm/40l)	**(ppm/100g/m^3)**
Carbon dioxide	**CO_2**	**100**	**400**
Carbon monoxide	**CO**	**20**	**80**
Oxides of nitrogen	**NOx**	**2**	**8**
Sulphur dioxide	**SO_2**	**3**	**12**
Hydrogen fluoride	**HF**	**3**	**12**
Hydrogen bromide	**HBr**	**2**	**8**
Hydrogen chloride	**HCl**	**4**	**16**
Hydrogen cyanide	**HCN**	**3**	**12**
Phenol	**C_6H_5OH**	**3**	**12**
Formaldehyde	**HCHO**	**1**	**4**
Acrolein	**CH_2CHCHO**	**0.04**	**0.12**

8. SELECTION OF A GAS COLLECTION METHOD

8.1 USE OF GAS COLLECTION BAGS

8.1.1 Chemiluminescence

For oxides of nitrogen ($NO_X = NO + NO_2$) analysed by Chemiluminescence, collect the combustion gases in the 40 litre gas collection bag (see Section 4.9) as illustrated in Figure 1 and perform the analysis within 10 minutes.

The chemistry of the oxides of nitrogen is complex and highly sensitive to many parameters. Studies performed for the development of this Allied Publication show positive interferences from other species such as NH_3 or HCN. Interferences using chemiluminescence can be limited if care is taken in the selection of the converter of nitrogen oxides into NO before the measurement. High temperature stainless-steel converters may require to be equipped with acid and NH_3 pre-scrubbers. Also, lower temperature molybdenum converters may be suitable. In all cases, the laboratory shall validate the effect of interfering species on the device.

8.1.2 GC/MS analysis

For species analysed by GC/MS (with exception of Phenol, see Section 8.2.2) collect the combustion gases in the 40 litre gas collection bag (see Section 4.9) as illustrated in Figure 1.

Note: Informative guidance on the use of GC/MS for analysis of acrolein in the gas phase, is given in ANNEX 4.

8.1.3 NDIR and FTIR analysis

For species analysed by NDIR or FTIR, collect the combustion gases in the 40 litre gas collection bag (see Section 4.9) as illustrated in Figure 1 and perform the analysis within 10 minutes.

Studies performed during the development of this Allied Publication show that there is a significant tendency for some species to be trapped in pipes, filters and devices. Species such as HCl and moreover HBr are especially sensitive to these phenomena. Tests performed show that FTIR measurement is not suitable for low concentrations of HBr, while higher concentrations induce no analytical problem.

Depending on apparatus and experimental conditions, FTIR analysis needs to be used with caution for these species. These species can be underestimated for concentrations of 100 ppm or less, which can have an effect on final classification.

8.2 USE OF IMPINGERS

8.2.1 General recommendations

Impingers can be used for all the gases compatible with wet chemical analysis techniques (IC, HPLC, GC/MS, etc.).

After the test, solutions obtained with impingers must be filtered to remove soot, prior to analysis. At the end of the test after the impingers have been emptied, the inside of connection pipes must be rinsed with fresh trapping solution. The rinsing solution is added to bubbling solution.

8.2.2 Collection of Phenol for GC/MS or HPLC analysis

Phenol is particularly prone to condensation on the walls of gas collection bags, leading to false low test results. Therefore, the analysis of phenol in the gas phase by this method is prohibited for the purposes of this Allied Publication.

When phenol is to be analysed by GC/MS, use liquid injection of an impinger solution collected using the procedures and trapping solutions described in Sections 8.3 & 8.4

8.2.3 Collection for IC analysis

Numerous gases can be analysed as the anions they produce when they dissolve into a liquid phase using impingers. HF, HCl, NO_2, HBr, SO_2 can be analysed by ionic liquid chromatography under the form F^-, Cl^-, Br^-, NO_2^- and NO_3^-, SO_4^{2-}.

Note: Useful information for guidance on the use of Ion Chromatography for analysis of some of the combustion products required by this Allied Publication, is given in ISO 10304-1.

8.3 IMPINGER CONFIGURATIONS

The configuration is composed of four impingers in series, each containing 75 ml of trapping solution (see Section 4.10). When test is performed to determine HF, the filtering silica wool downstream of the tube furnace shall not be used, due to its strong affinity with hydrogen fluoride.

WARNINGS:

COMBUSTION PRODUCTS THAT ABSORB WATER RAPIDLY

Some materials produce combustion products that absorb water very rapidly and in extreme cases there is a danger that this may cause "suck-back" of the impinger solution into the hot furnace. Laboratories should take suitable safety precautions. Information on the precautions taken shall be given in the test report. (Inclusion of an extra empty impinger reversely oriented immediately after the exit of the furnace has been found suitable. However loss of gases may result from the use of the extra impinger).

Note : During development of the present document, an alternative configuration has been found suitable for all gases, except HF and aldehydes. In this configuration, two impingers are used in series as follows; one impinger containing approximately 75 ml of trapping solution (see Section 4.10), followed by a second impinger of 250 ml nominal capacity, having a straight pipe ending with a sintered glass disk, "frit", (porosity P160: pore size 100 μm to 160 μm – grade 1) and providing a bubbling height of 60 mm to 70 mm, when filled with 150 ml of trapping solution.

However, note that that this alternative configuration can produce problems with sooty specimens because of blocking of the "frit" in the second impinger, inducing higher pressure in the apparatus which may be unsafe and may cause modifications of combustion conditions.

8.4 Trapping solutions

The solutions used for dissolution of combustion gases depend on the subsequent analysis technique (selected from the Table 3) and the gaseous species being determined. Examples of suitable solutions are given below. Other concentrations or solutions may be suitable, depending on the technique(s) and equipment parameters in use and may be used if it can be demonstrated to the satisfaction of the Technical Authority, that such solutions are capable of trapping all of the intended combustion gas for analysis.

Fluoride ions have a tendency to react with silicate glass, so it is important that the impinger solution is of sufficient strength to impede this reaction. 1M NaOH has been found suitable.

Solutions obtained with impingers shall be stored in a sealed container in refrigerator, and the analysis shall be performed within 48 hours.

Table 6 - Trapping solutions

Method	Analyte(s)	Solution
IC analysis:	Cl^-, Br^-, CN^-	0.1 M KOH or NaOH or H_2O_2/water or eluent used for chromatography technique that will be used.
	F^-	1.0 M NaOH or KOH
	SO_4^{2-}	add 10 ml H_2O_2 30% (V/V) per litre of water (prepare the solution immediately prior to use)
	HCHO	0.1M KOH or NaOH or eluent used for chromatography technique that will be used.
		by oxidation of a portion of the solution using ClO_4 (or H_2O_2). If formaldehyde is to be analysed in the presence of formic acid, both oxidised and un-oxidised portions of the solution must be analysed in order to distinguish. Alternatively, a different analytical technique (see Table 3) may be used to distinguish between them.
HPLC analysis	HCHO CH_2CHCHO	HCl 2M saturated with DNPH (decant the solution before use to eliminate the excess of DNPH)
	C_6H_5OH	Methanol / water (60/40)
GC/MS analysis (liquid injection):	C_6H_5OH	Methanol / water (60/40)

9. SET UP AND TEST RUN PROCEDURE

9.1 Furnace set-up

9.1.1 First set up of the furnace for tests according to this Allied Publication

Determine the temperature profile using the procedure given in ANNEX 2 for each temperature.

9.1.2 Daily set up of the furnace

With the furnace stabilized at the required test temperature, set the air supply to a constant flow rate of 2 litres/minute (see Section 4.6).

Verify the test temperature by inserting the thermocouple probe (ANNEX 2) to the position determined as being the centre of the hot zone. Allow the furnace stabilize for 10 min, before measuring the temperature.

If the value differs by ± 5°C from the temperature recorded for the previous use, then re-determine the temperature profile using the procedure given in ANNEX 2.

9.2 Pre-weighing of test specimen and combustion boat

Dry the combustion boat in an oven and then store in a desiccator (containing drying agent) to cool to room temperature. Immediately before the test, determine the masses, in grams to 3 decimal places, of the empty combustion boat (= m_1) and of the combustion boat plus conditioned test specimen (= m_2).

Determine the test specimen mass m from the equation :

$$m = m_2 - m_1$$

Note 1: The test specimen is conditioned in accordance with Section 5.1 and if the balance and/or furnace are not in a conditioned laboratory, this procedure shall be carried out with minimum delay after removal of the test specimen from the conditioning enclosure.

Note 2: m is to be used in the calculation in Section 12.2.

9.3 Test run procedure

(a) Stabilize the furnace to the appropriate conditions (temperature, settings for the rotameter to deliver a 2.0 l/min flow rate). Then remove the upstream end cap without stopping the flow rate.

Introduce a fresh glass wool filter in the “downstream” end part of the tube, and plug the “downstream” end cap. (Note this glass wool filter is not used when analysis of HF is carried out, see Section 8.3);

(b) Couple the evacuated gas collection bag / impinger system to the “downstream” end cap (see Figure 1 or 2).

(c) Place the boat containing the test specimen into the “upstream” end part of the combustion tube.

(d) Replace the “upstream” tube end cap and push rod.

(e) Insert the combustion boat at a steady rate and release it at the centre of the hot zone[1], using the manual push rod. The insertion time shall be between 5 and 10 seconds.

(f) Start the timer and withdraw the push rod as far to the upstream end of the tube as possible (but without removing the end cap). Immediately grip the push rod

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[1] The position corresponding to the centre of the hot zone is determined during the procedure to measure the furnace temperature profile. (ANNEX 2 & Section 4.3)

with the tightening device to seal the system and establish gas flow across the furnace (the bag will start to inflate, or bubbles appear in impingers).

(g) With impingers :

Note immediately, the initial reading measured by the gas volume meter (see Section 4.7 & Figure 2). Throughout the test, monitor and when necessary, re-adjust the air supply using the rotameter. The flow rate shall be kept within the required tolerance (see Section 4.6)

With a gas collection bag :

There is no gas meter in the sampling circuit (see Section 4.7 Note 2). Throughout the test, monitor and when necessary, re-adjust the air supply using the rotameter as previously with impingers.

When using a bag (no gas-meter), re-adjusting air supply is particularly important, to collect exactly the volume used to determine the concentrations for the TOXICITY INDEX calculations (Section 12).

(h) If applicable, record the time to ignition of the test specimen, and the time to extinction of flaming combustion.

Note: Because of obscuration by soot/smoke and the location of the specimen within the tube, it is not always possible to observe ignition and/or extinction. A mirror placed near the entrance to the opening of the furnace may assist (safety precautions shall be observed).

(i) Throughout the test, make observations when possible, of any characteristics of the burning behaviour of the test specimen (e.g. charring, flaming, melting, severe shrinkage, erratic burning, explosive decomposition/spitting, loss of material from the combustion boat, after-glow, etc.)

(j) Throughout the test, make observations of any other significant events (e.g. breaking or cracking of the combustion boat, blockage of impinger frits, the need to adjustment the air supply to maintain the required flow rate, etc)

(k) At the end of the 20 minute combustion period, turn off the air supply. Seal the 40 litres gas collection bag or disconnect the impingers as appropriate.

(l) When impingers are used, note the final volume reading measured by the gas meter. Check that the total volume sampled is within the required tolerance (see Section 4.6). If it is outside the tolerance, this may indicate that a leak has occurred and the test results shall be discarded. The leak shall be traced and repaired, before further tests are carried out.

(m) For bag collection, ensure analysis of fire effluents within 10 min. Solutions produced with impingers shall be filtered prior to analysis (except DNPH solutions).

(n) When impingers are used :

- Solutions obtained shall be filtered to remove soot. Collect the solutions into a flask of maximum volume 500 ml after filtration. Wash empty impingers with some fresh trapping solution and add the solution to the flask.

- Remove the silica wool filter from the downstream part of the tube furnace. Wash the glass wool with some trapping solution and add the washings to the flask.

Conduct steps (d) to (e) with minimum time delay.

9.4 Determination of specimen mass loss

At the end of the 20 minute test period, remove the combustion boat, containing the specimen residue and place it in a desiccator containing drying agent to cool to room temperature. Depending on the size of the boat, this may take up to 1 hour. When cooled, remove from the desiccator and immediately determine the combined mass of the combustion boat and residue (=m_3).

Care should be taken not to lose any of the residue material from the boat, during the transfer from furnace tube to desiccator or from desiccator to weighing device. During combustion, some specimens may lose material from the combustion boat e.g. by explosive decomposition / spitting etc. This would lead to additional mass loss that is not caused by chemical reaction as part of the combustion process. Where this occurs it shall be recorded in the test report.

Determine the specimen mass loss from the equation;

$$\text{Specimen mass loss} = m_2 - m_3$$

Note: The residue will be dry when removed from the furnace. It is placed immediately into a desiccator so that it will remain dry while it cools. This is because, depending on the material, after heating the residue may contain hygroscopic salts, or salts which react chemically with atmospheric moisture, such as calcium oxide for example.

10. GUIDANCE FOR ANALYSES

10.1 HF determination by Ion Chromatography (IC)

When IC is used to determine amount of HF trapped as fluoride ions in the solution, there may be matrix effects, due to large amounts of carbonate ions present in the solution. It comes from dissolution of CO_2 in 1M NaOH. These effects depend on equipment variables, retention times and the presence of various chemical species in the solution. To limit this effect, ICH+ cartridges may be used for injection.

When first using any given type of ICH+ cartridges, it is necessary to check their capacity by testing them with 1.0 ml sodium hydroxide solution. This is particularly important if the real sample to neutralise is not available in large amount. ICH+ cartridges available on the market generally have an internal volume ranging between 1 and 2 ml. It may be necessary to plug several cartridges together to treat a 1M NaOH solution. With most types, two cartridges are sufficient with 1M NaOH injected in IC. The following procedure is suitable:

- Plug two cartridges together,

- With a 1.0 ml syringe, pass 2ml NaOH through the cartridges, and collect the liquid into a flask.
- Measure the pH of the solution obtained with a indicator paper having a resolution of 1 pH unit or better, in the range 5 to 11. The first millilitres collected are acidic. Add some more sample from the cartridges into the flask, drop by drop, and control the pH again. Add sample slowly until the pH obtained is around 7.
- Note the total amount of solution injected to obtain this result. It corresponds to the neutralizing capacity for two cartridges. Generally, the addition of few more drops of sample at this point leads to a very quick rise of the pH.

The pH of samples to be injected are require to be between 6 and 8. Higher values lead to an hydroxide peak on IC chromatogram. Extreme pH leads to a rapid degradation of the separation columns.

10.2 Acrolein and formaldehyde determination using DNPH solution

When DNPH is used as impinging solution, aldehydes and ketones are trapped as hydrazones. These compounds are not totally soluble in the solution. Extraction of the hydrazones to be analyzed shall be performed immediately after the thermal degradation. An extraction solvent (chloroform) is used to rinse impingers and glass wool filter. All the content of impingers and rinse solution are put in a separating funnel. After two extractions, the organic phase is retained and adjusted to a volume of no more than 500 ml. The chloroform collected can be analysed by HPLC for determination of hydrazones concentrations. Acrolein and formaldehyde concentration can be deduced from those results.

Note: To improve the limit of detection of the method, pre-concentration of extracted products by rotary evaporator and re-solvating dried hydrazones, or by pre-concentration columns can be performed after validation of the method.

10.3 Dilution of sample solution

It may be necessary to carry out a controlled dilution of the sample solution to bring the concentration within the calibrated range of the analysis instrument (IC or HPLC). Details on the dilution ratio(s), etc shall be reported (see Section 13). The effect of dilution shall be taken into consideration for the uncertainty of the results.

10.4 Consideration on calibration range

For analytical purposes the range of calibration must be adapted to the level of concentration expected. However for combustion gas analysis it is difficult to adapt the calibration range as for some gases a wide range of concentration can be analysed. Annex 4 gives some guidance on calibration ranges proven to be acceptable.

11. CLEANING

11.1 Combustion Tubes

Cleaning of the tube is to be conducted for each new material, unless the specimen produces an excessively "sooty" burn, when it should be conducted between each burn.

- Remove the downstream and upstream tube end cap for ambient air to pass through the tube furnace..

- Raise the furnace temperature up to >900 °C. When the higher temperature has stabilised the “down stream” part of the tube shall be drawn into the “hot zone” of the furnace such that any combustion residue within the tube is “burnt off”. The "burning off" process shall be continued until the soot is visually clean or for 30 minutes whichever is the sooner. If the tube shows signs of deterioration it shall be replaced (see Section 4.2).

11.2 Gas collection bags

Cleaning shall be conducted prior to every burn.

Procedure; by a process of evacuation and purging with dry air or nitrogen. This is to be repeated at least three times. If excessively high HCl concentration has been determined it is recommended that the bag is not re-used.

Check the bag for contamination from previous tests at regular intervals by filling with air and carrying out analysing using the appropriate techniques.

12. EXPRESSION OF RESULTS

12.1 Calculation of C_i

Where the gas analysed has been collected by trapping in an impinger solution, use the following equation to calculate the concentration, C_i (ppm), that would result if the same quantity of that species were diffused, as a gas, into a volume of 40 litres;

$$C_i = \frac{5.6035 \times 10^2 \times C_S \times V_S}{I}$$

Where,

C_S = concentration of the gas in the solution (ppm or mg/l)
(When the measured concentration is below the LoQ, $C_S = 0$, see Section 7.5)

V_S = volume of the solution (litres)
(See Section 8.3)

I = molecular weight of the ion or gas molecule in solution, taken from the Table in ANNEX 5

Note: The factor 5.6035 x 10^2 (=10^{-3} x 22.414 x 10^6)/40) is used to convert the units to ppm in the gas phase, taking account of the volume of 1 mole of an ideal gas at standard temperature (20°C) and pressure (1 atm.)

12.2 Calculation of C_θ

For each determination of C_i, use the following equation to calculate C_θ (ppm), the concentration of the gas, produced under the conditions of the test, scaled up for 100 g of material and re-calculated as though the combustion products were diffused into a volume of 1 m^3:

$$C_\theta = \frac{C_i \times 100 \times V}{m}$$

Where,

C_i = concentration of the gas in the 40 litre volume of combustion gas (ppm) (When the measured concentration is below the LoQ, C_i = 0, see Section 7.5)

V = volume of the sample of combustion products (m^3)

m = test specimen mass (g)

12.3 Calculation of TOXICITY INDEX, *TI*

Use the following equation to calculate the TOXICITY INDEX with the results produced at both temperatures;

$$TI = \sum \frac{C\theta 1}{Cf_1} + \frac{C\theta 2}{Cf_2} + \frac{C\theta 3}{Cf_3} + \ldots + \frac{C\theta n}{Cfn}$$

Where,

$C\theta_{1,2,3,\ldots,n}$ = the average of the two values of C_θ (ppm) for each gas that has been analysed (see Section 7).

n is the total number of gases analysed. n = 10 or 11 if phenol is required (see Section 12.4) at 800°C and 2 at 350°C.

$Cf_{1,2,3,\ldots,n}$ = the concentration of the gas considered fatal to man for a 30 minute exposure (ppm)

(the values to be used are given in ANNEX 1 of this Allied Publication)

12.4 Analysis of phenol

Initially, phenol is not analysed. If the value of TI for the other species is greater than 6 and less than 10, phenol is then analysed and its contribution is added to TI.

13. TEST REPORT

The test report shall include a reference to this Allied Publication together with the following information:

Note: Some of the following information may be required by the Technical Authority for the database described in AFAP-1.

a) the name and address of the laboratory undertaking the test;

b) the name and address of the supplier and where different, of the manufacturer (original source) of the material tested;

c) the date(s) of the test;

d) a full description of the material tested including, where applicable and/or known;

- name
- application
- type of material (chemical composition)
- type of product (form or shape e.g. sheet or tube etc.)
- essential dimensions (including mass or density, sheet size/thickness etc.)
- colour (facing colour)
- details of any coatings (including substrates, surface preparation techniques, no. of layers, colour, coverage rates, etc.)
- specifications
- NATO Stock No.s or other Unique Identification No.s
- details of any previous tests known
- other relevant technical data

e) a full description of the test specimen construction and preparation;

f) details of the collection and analytical techniques used for each gas, including;

- trapping solution composition
- detection limit
- other relevant technical information (e.g. for IC column type, etc)

g) any gases not analysed at each temperature by entering “not tested” as appropriate in tables of test data (e.g. as shown in Annex 3 of this Allied Publication) Section 6.2.2 refers;

h) for each test specimen, where applicable, observations of time to ignition and time to extinction and all observations made during the test, as described in Section 9.3 (i) and (j).

i) for each valid determination at each temperature, where appropriate, values of C_S, V_S, I, C_i, V, m, C_θ and specimen mass loss;

j) for each gas detected at each temperature, the average value of C_θ and of C_θ / Cf;

k) trace concentration values for any gases detected below their LoQ (identified as Not Detected : ND)

l) the value of TOXICITY INDEX;

m) the statement: "These results relate only to the behaviour of the specimens of the material under the particular conditions of test."

Note: The Materials Fire Characteristics Data Sheets from the database described in STANAG 4602 may, optionally, be used for recording some of the test results. (Copies are shown in ANNEX 3 of this Allied Publication).

Figure 1 - Schematic of tube furnace apparatus (Gas collection bag)
(not to scale)

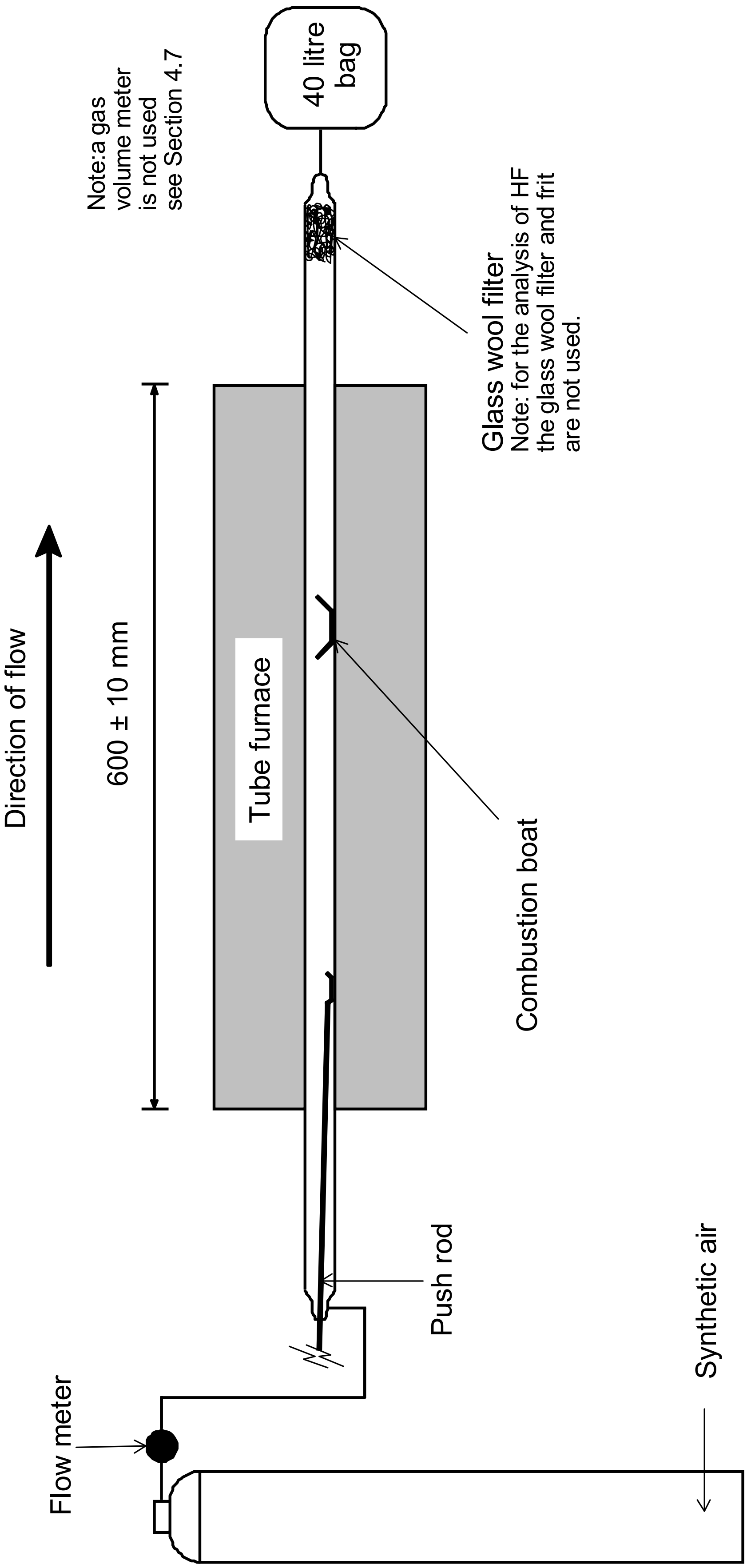


Figure 2 - Schematic of tube furnace apparatus (Impingers)

(not to scale)

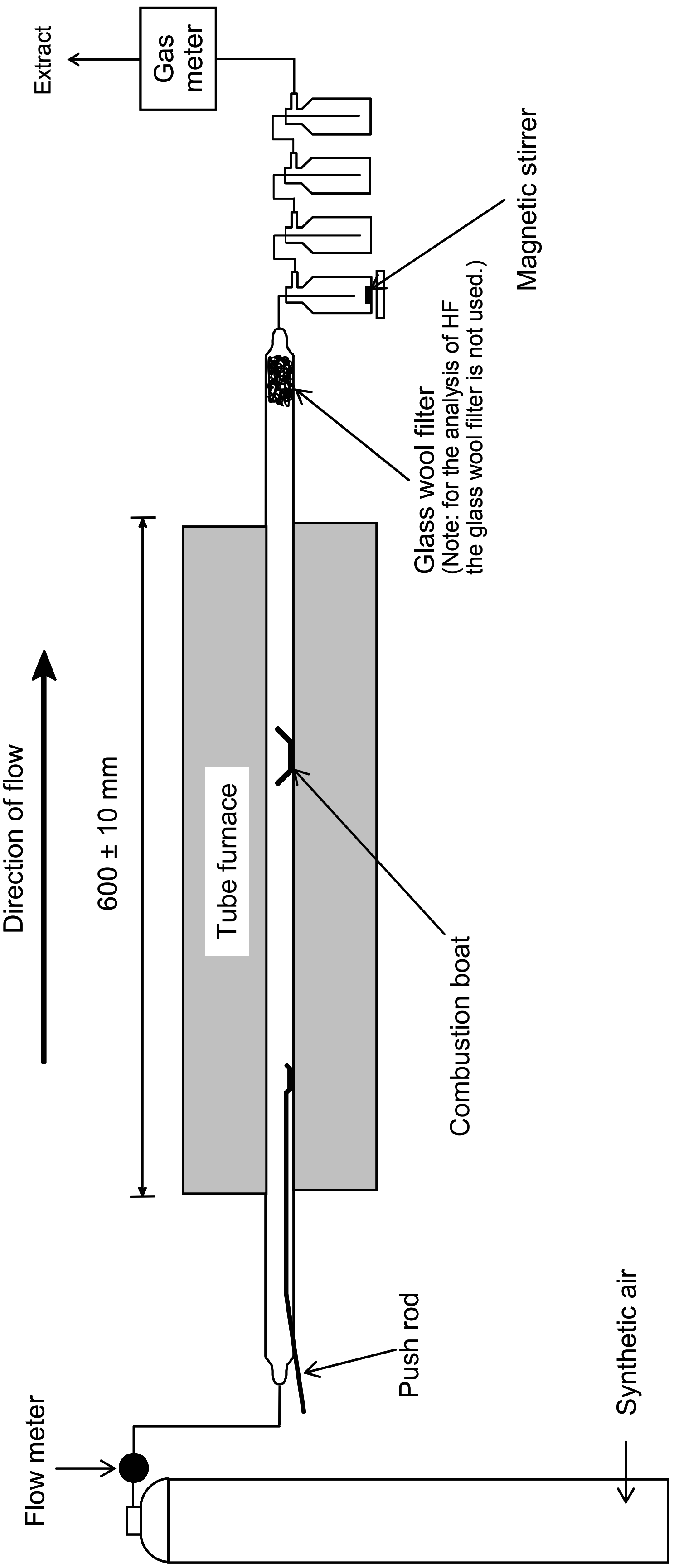
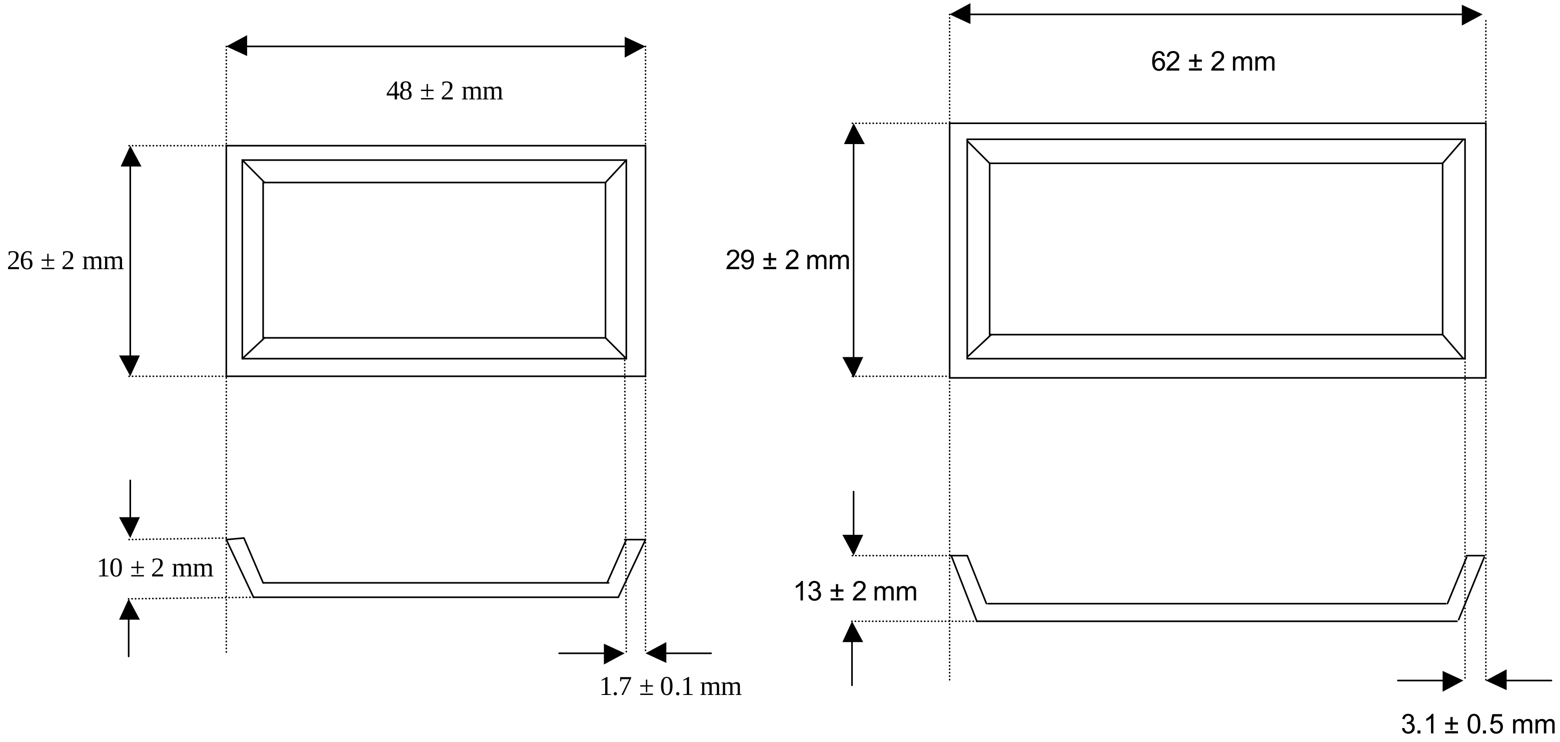


Figure 3 - Combustion boats
(not to scale)



Standard boat
(for materials density ≥ 60 kg/m^3)

Large boat
(for materials density < 60 kg/m^3)

ANNEX 1 - CRITICAL FACTORS Cf

Gas	Formula	Cf (ppm)
Carbon Dioxide	CO_2	100000
Carbon Monoxide	CO	4000
Oxides of Nitrogen	NO_x ($NO + NO_2$)	100
Sulphur Dioxide	SO_2	400
Hydrogen Fluoride	HF	50
Hydrogen Bromide	HBr	150
Hydrogen Chloride	HCl	500
Hydrogen Cyanide	HCN	90
Phenol	C_6H_5OH	250
Formaldehyde	HCHO	500
Acrolein	CH_2CHCHO	5

Note: The Cf values are taken from the following reports, which can be obtained from:

- Defence Science & Technology Laboratories - Knowledge Services[*], Kentigern House, 65 Brown Street, Glasgow, G2 8EX, UK:
- Report for DERA Holton Heath on toxicity of inhaled gases. IL1003/1/TM/BIO/U/999/95. October 1995. (DRIC Ref. CDL 57733)
- Toxicity of inhaled gases. DERA/CBD/CR96/046/1.0. January 1997. (DRIC Ref. CDL 56521)

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[*] formerly, Defence Research Information Centre, DRIC

ANNEX 2 - FURNACE TEMPERATURE PROFILE

Apparatus

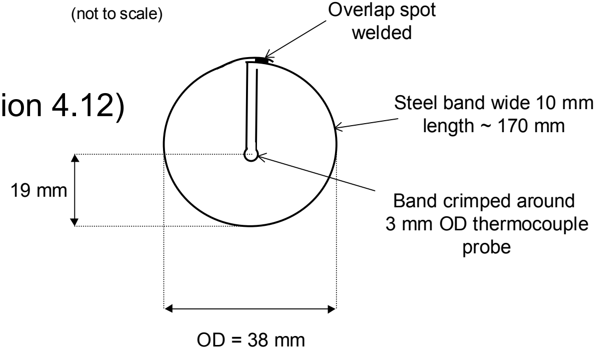
Timing device (see Section 4.11).

Thermocouple probe (calibrated) (see Section 4.12)

Thermocouple supports (as shown below).

Thermocouple supports

(not to scale)



Procedure for the measurement of furnace temperature profiles

a) Set up the apparatus as described in Section 4, with the air supply flow rate set to achieve a total volume of 40 ± 2 litres in 20 minutes (2 litres/minute) with the furnace operating at the test temperature.

b) Insert the thermocouple probe, from the downstream (gas exit) end and use the supports to locate its tip at centre of the cross-section of the combustion tube, at the position of the exit to the furnace work tube and immediately start the timer, as shown in the diagram below.

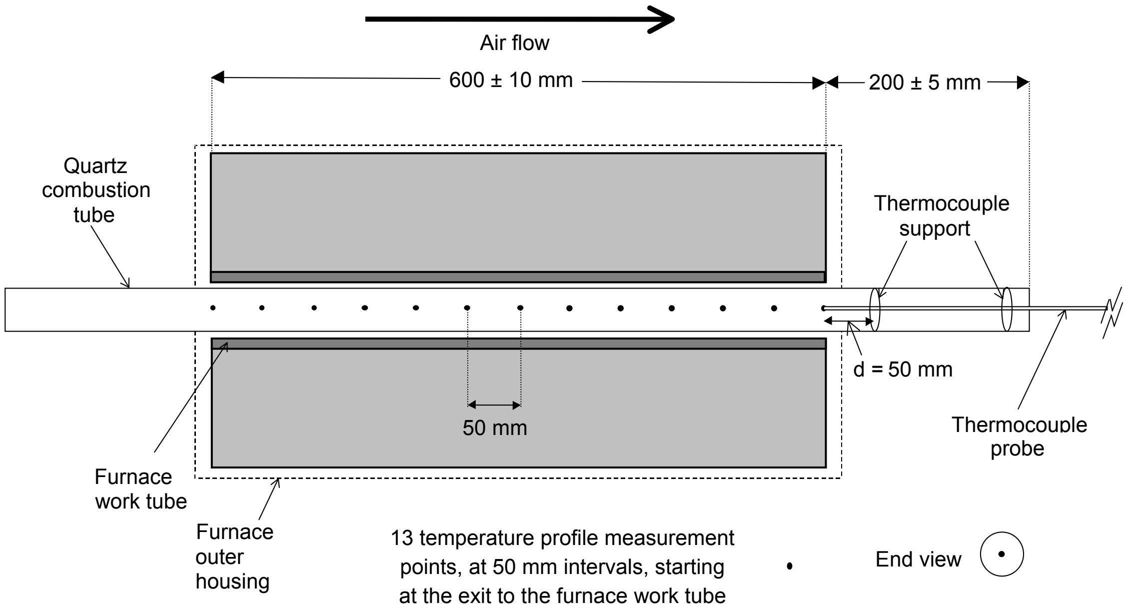
c) Record the temperature after 10 minutes (600 ± 5 seconds).

d) Immediately move the thermocouple further into the furnace by 50 mm and repeat the procedure recording the temperature after a further 10 minute period.

e) Repeat this process for each 50 mm interval, up to the end of the furnace work tube.

f) Record the position and temperature of the centre of the hot zone to be that where the highest of the measured temperatures occurred along the length of the furnace.

g) If necessary, adjust the set point(s) on the furnace controller(s) so that the temperature at the centre of the hot zone is as close a possible to nominal test temperature (i.e. 350 °C or 800 °C), while still maintaining the temperature at the other specified points within the required tolerances (see Table 7 in Annex 2).



Thermocouple positions

(not to scale)

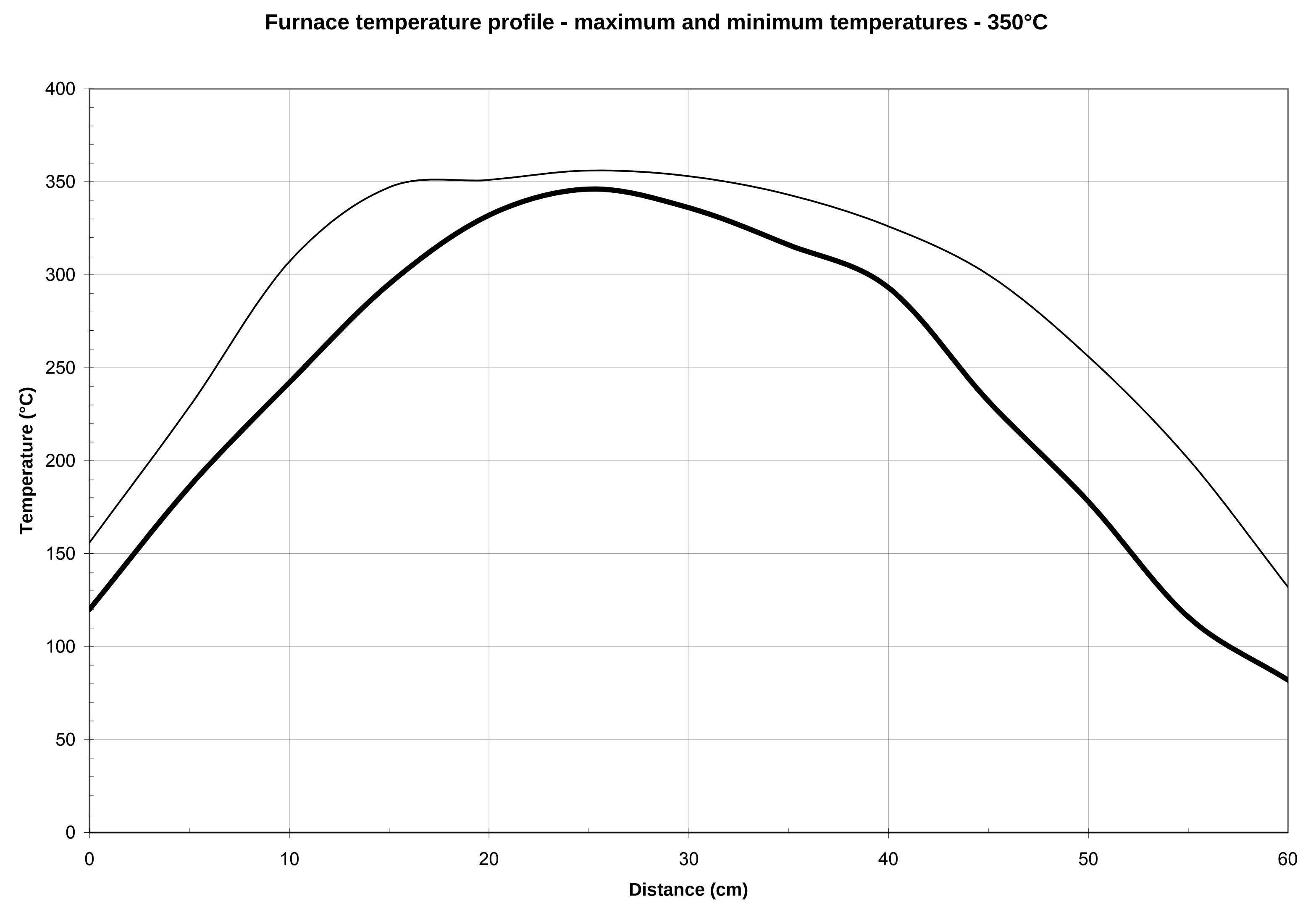
Requirements for furnace temperature profiles :

A round robin between 5 laboratories has been performed. Temperature profiles at 350°C and 800°C have been measured. The following figures give the envelope of temperature profile inside which the furnaces can be considered as fulfilling the requirements of this Allied Publication.

The temperature profiles at 350°C and 800°C shall be verified for the first use of the furnace, after each maintenance operation on the furnace and/or at least one time per year. The temperature at the centre of the hot zone of the furnace shall checked before any series of tests.

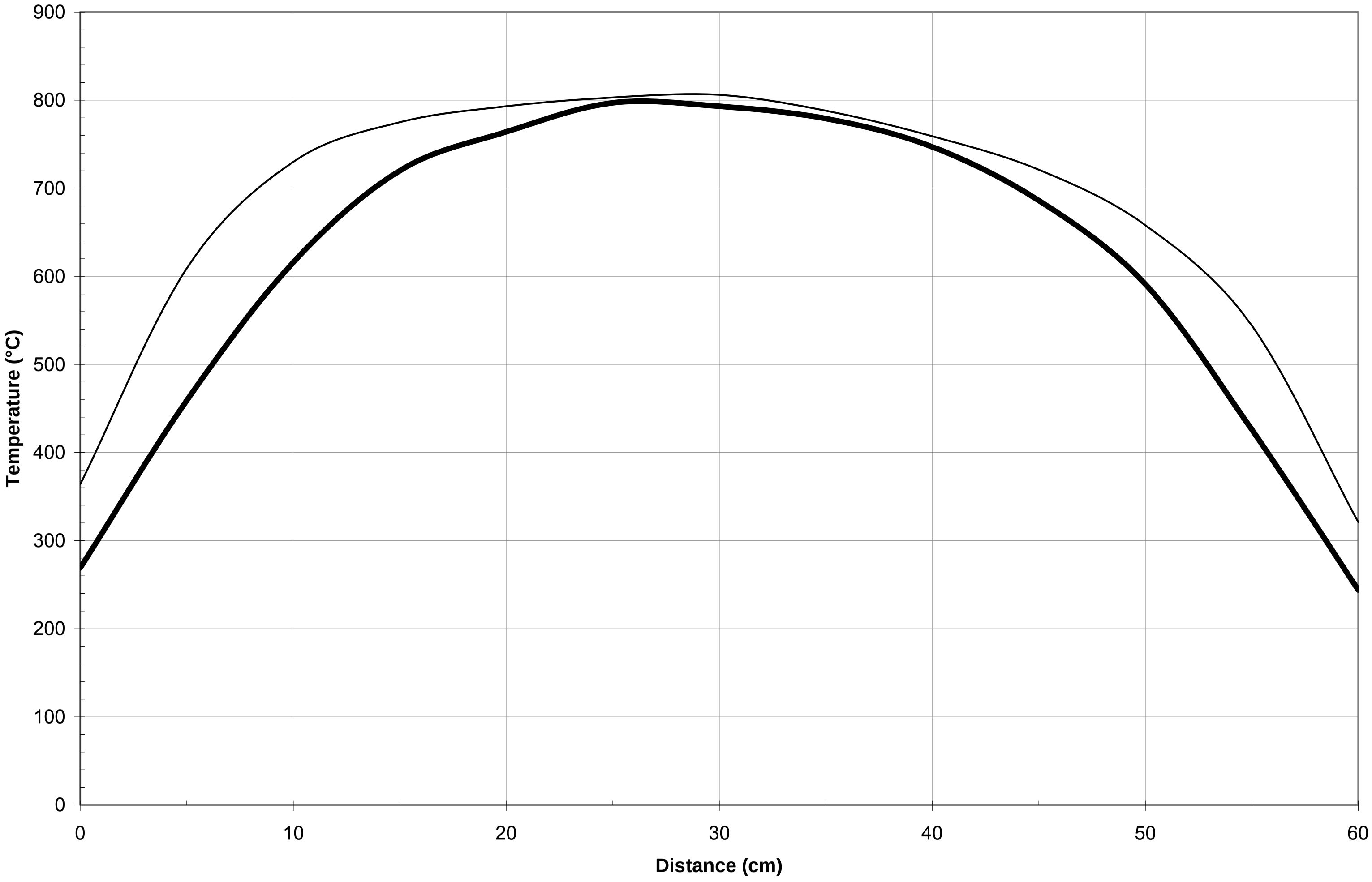
Table 7 - Furnace temperature profile - maximum and minimum temperatures

	350°C		800°C	
distance from downstream (gas exit) end of the furnace (cm)	Maximum Profile temperature (°C)	Minimum Profile temperature (°C)	Maximum Profile temperature (°C)	Minimum Profile temperature (°C)
0	156	120	364	269
5	229	186	609	459
10	307	242	730	616
15	347	295	775	720
20	351	332	793	765
25	355	346	803	797
30	353	336	806	793
35	331	316	788	779
40	326	293	759	747
45	300	232	721	686
50	256	178	658	591
55	201	116	544	426
60	132	82	321	244



Furnace temperature profile - maximum and minimum temperatures - 350°C

Furnace temperature profile - maximum and minimum temperatures - 800°C



ANNEX 3 - DATASHEETS (optional)

TOXICITY of FIRE EFFLUENTS **SECURITY MARKING** **STANAG 4602**

AFAP-3 **Edition No.** **Item Ref.**

Report No.	**Report Date**
Report Title	
Test Laboratory Address	**Supplier Address**
Material	

Test Specimen

(i) Thickness mm or µm:

(ii) Specimen construction and preparation:

(iii) Coatings:

(iv) Combustion boat size (Standard or Large):

TOXICITY INDEX AFAP-3 **Classification:**

TOXIC GAS	FORMULA	Cf (ppm)	Test Temperature °C	C_θ (ppm)	Contribution to Index $\frac{C\theta}{Cf}$
Carbon Dioxide	CO_2	100000	800		
Carbon Monoxide	CO	4000	800		
Nitrogen Oxides	NO_X ($NO + NO_2$)	100	800		
Sulphur Dioxide	SO_2	400	800		
Hydrogen Fluoride	HF	50	800		
Hydrogen Bromide	HBr	150	800		
Hydrogen Chloride	HCl	500	800		
Hydrogen Cyanide	HCN	90	800		
Phenol	C_6H_5OH	250	800 (see note)		
Formaldehyde	$HCHO$	500	350		
Acrolein	CH_2CHCHO	5	350		
				Toxicity Index =	

Note: A contribution from Phenol is only included if the Toxicity Index determined for the other gases is greater than 6 and less than 10.

This document contains commercial information - See conditions of release. These results relate only to the behaviour of the specimens of the material under the particular conditions of test (See appropriate Standard)

SECURITY MARKING

TOXICITY OF FIRE EFFULENTS **SECURITY CLASSIFICATION** **STANAG 4602**

AFAP-3 **Item Ref.**

Repeat Tests:

(details of any repeat tests required in accordance with AFAP-3)

Observations:

(Observations of the specimens and times from the start of the test at which the observations were made, together with details of any invalid tests and the reasons for these)

This document contains commercial Information – See conditions of release. These results relate only to the behaviour of the specimens of the material under the particular conditions of test (See appropriate Standard)

SECURITY CLASSIFICATION

AFAP-3 Toxicity Index

Serial No. : ____________________
Material: ____________________
Supplier: ____________________
Date: ____________________
Operator: ____________________

Comments: ____________________

Gas	Formula	Test Temperature °C	Analytical Technique	Concentration relative to 100g sample in 1 m^3 C_θ (ppm)			Critical values Cf ppm	TI contribution C_θ/Cf
				Analysis No. 1	Analysis No. 2	Mean		
Carbon Dioxide	CO_2	800					100000	
Carbon Monoxide	CO	800					4000	
Oxides of Nitrogen	NO_x	800					100	
Sulphur Dioxide	SO_2	800					400	
Hydrogen Fluoride	HF	800					50	
Hydrogen Bromide	HBr	800					150	
Hydrogen Chloride	HCl	800					500	
Hydrogen Cyanide	HCN	800					90	
Phenol (see note)	C_6H_5OH	800					250	
Formaldehyde	HCHO	350					500	
Acrolein	CH_2CHCHO	350					5	

Toxicity Index	

Note: A contribution from Phenol is only included if the Toxicity Index determined for the other gases is greater than 6 and less than 10.

AFAP-3 Toxicity Index at 350°C - Raw Data

Serial No. : ____________________

Material: ____________________

Supplier: ____________________

Date: ____________________

Operator: ____________________

Comments: ____________________

		Run 1	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Run 7**	**Run 8**
Test specimen mass (g)	m (= m_2 - m_1)								
Empty combustion boat (g)	m_1								
Combustion boat plus test specimen (g)	m_2								
Combustion boat plus residue (g)	m_3								
Specimen mass loss (g)	(= m_2 - m_3)								
Time to ignition, if applicable (seconds)									
Time to extinction, if applicable (seconds)									

		Test Temperature °C	**Analytical Technique**	C_i (concentration of the gas in the 40 litre volume of combustion gas, ppm) **or** C_S (concentration of the gas in the solution, ppm)							
Carbon Dioxide	CO_2	800									
Carbon Monoxide	CO	800									
Oxides of Nitrogen	NO_x	800									
Sulphur Dioxide	SO_2	800									
Hydrogen Fluoride	HF	800									
Hydrogen Bromide	HBr	800									
Hydrogen Chloride	HCl	800									
Hydrogen Cyanide	HCN	800									
Acrylonitrile	CH_2CHCN	800									
Phenol (see note)	C_6H_5OH	800									
Formaldehyde	HCHO	350									
Acrolein	CH_2CHCHO	350									

Note: A contribution from Phenol is only included if the Toxicity Index determined for the other gases is greater than 6 and less than 10.

ANNEX 4 - GC/MS GAS PHASE ANALYSIS FOR ACROLEIN

The following provides informative guidance on the use of GC/MS for analysis of acrolein in the gas phase.

The principles of the methodology:

- GC separation of the different compounds;
- Detection with MS : (“quadrupole” used in E.I. mode), detection of retention time for each - compound on characteristic fragment of the considered compound;
- Quantification with analysis of total ionic current (TIC) obtained on fragments.

Preliminary tests – tests conditions

The objective of the preliminary tests is to determine the best analytical conditions for the analysis of acrolein.

Compounds	Chemical formulae	Molecular mass CAS number	Chemical family
acrolein	CH_2CHCHO	56 CAS : 107-02-8	vinyl aldehydes

Typical analytical conditions

GC separation :

- Injection of the volume of gas with an automatic valve equipped with an stainless steel loop of 0.5 ml,
- Splitless injection
- Injection in pulsed mode :
- flow of gas vector 3 ml/min at the injection for 12 seconds
- followed by a flow rate of gas vector of 1 ml/minute.
- gas vector : helium (1 ml/minute)
- capillary column >30 m x 0.25 mm I.D. x df 0.25 µm
- stationary phase : 5% methylphenylsilicone or equivalent
- 30 m long
- internal diameter : 0.25 mm
- thickness of non polar phase (reverse phase) 0.25 µm.

Furnace ramp:

- initial temperature : 2°C or lower for 6 min (oven cooled with liquid N_2) (the objective is to avoid the lost of low boiling point compounds).
- followed by a temperature ramp : 15°C/min until 180°C, in order to elute high boiling point compounds,
- 180°C until the end of analysis

This temperature programme allows:

- a first separation of volatile compounds and the peak of air,
- to elute the gases with high boiling points and to eliminate other heavy compounds from the column (not analysed for the purposes of this Allied Publication).

MS detection.

- Type: quadrupole mass selective detector
- Electronic impact (fragmentation)
- Time interval: one spectra every 1.5 seconds on the fragments obtained after screening from 25 m/z to 200 m/z.

This enables the fragments of air injected in the inlet valve to be eliminated without loss of the compounds to be analysed.

Analysis using TIC (total ionic current)

- The NIST[⊕] library is used for qualitative recognition of compounds.
- A standard containing the required gas is prepared by injection of a known quantity of acrolein in a 40 litre bag containing air. (The mixture must be prepared the same day as the analysis).
- The peak areas representative of the compounds to be analysed are compared to those given by the standards and the concentration of compounds is calculated using TIC chromatogram on specific fragments of each compound.

Compound	Principal peak (parent) at m/z (normalised to 100%)	Importance of other fragments in % compared to parent peaks (>50% compared to parent)	Typical retention times (minutes)	Fragments used for quantification (in m/z)
acrolein	27	4 fragments 56 (74%) = molar 26 (54%) 28 (65%) 55 (52%)	2.4	56

[⊕] National Institute of Standards and Technology

GC/MS calibration

Standard solutions containing acrolein are prepared and injected into a gas collection bag containing 40 litres of air. Analytical grade chemicals are used. The bag is then warmed to ensure evaporation of the solutions and samples are then taken from the bag for analysis in the GC/MS.

Example calibration solutions;

« STANDARD 1 »	acrolein : ~5.3 g

The concentration in 1µl of solution is calculated as follows.

The total volume of the calibration solution is given by;

$$V_{\text{solution}} = \frac{M_{\text{solution}}}{\rho_{\text{solution}}}$$

Where,

V_{solution} = total volume of the calibration solution (µl)

M_{solution} = total mass of the calibration solution (mg)

ρ_{solution} = density of the calibration solution (measured by pycknometry) (mg/µl)

The concentration of acrolein in 1 µl is then given by;

$$C_Z = \frac{M_Z}{V_{\text{solution}}}$$

Where,

C_Z : concentration of acrolein in the solution (mg/µl)

M_Z : mass of acrolein in the solution (mg)

Standard gas mixture

In the 40 litre gas collection bag the following standard concentrations are prepared:

- 2.0 µl solution « STANDARD 1 »
- 5.0 µl solution « STANDARD 1 »
- 10.0 µl solution « STANDARD 1 »
- 20 µl solution « STANDARD 1 »
- 25 µl solution « STANDARD 1 »
- 50 µl solution « STANDARD 1 »
- 100 µl solution « STANDARD 1 »
- 200 µl solution « STANDARD 1 »
- 250 µl solution « STANDARD 1 »

ANNEX 5 - MOLECULAR WEIGHTS OF IONS IN SOLUTION

Gas	Detection techniques	Analyte measured	Molecular weight(s) of analyte(s)
Carbon dioxide	NDIR, FTIR	CO_2	44.0‡
Carbon monoxide	NDIR, FTIR	CO	28.0‡
Oxides of nitrogen	NDIR, FTIR, Chemiluminescence	NO, NO_2	30.0‡, 46.0‡
	IC (NO_2)	NO_3^-	62.0◊
	Spectrophotometry	NO_3^-	62.0◊
Sulphur dioxide	FTIR	SO_2	64.1‡
	IC	SO_4^{2-}	96.1◊
Hydrogen fluoride	IC, ISE	F^-	19.0◊
Hydrogen bromide	IC	Br^-	79.9◊
Hydrogen chloride	IC	Cl^-	35.5◊
	FTIR	HCl	36.5◊
Hydrogen cyanide	IC, spectrophotometry	CN^-	26.0◊
	FTIR	HCN	27.0‡
Phenol	GC/MS, GC/FID, HPLC	C_6H_5OH	94.1†
Acrolein	HPLC, GC/MS	CH_2CHCHO	56.1†
	Titration	CH_2CHCO^-	55.1◊
Formaldehyde	IC, titration, spectrophotometry	$COOH^-$	45.0◊
	HPLC, GC/MS	HCOH	30.0†

For legend see Table 4
The molecular weights to be used are taken from;
† - CRC (The Chemical Rubber Company Press) Handbook of Chemistry and Physics 51st Edition
‡ - NIOSH (National Institute Occupational Health and Safety) Pocket guide to chemical hazards – June 1997
◊ - Calculated using data from CRC Handbook of Chemistry and Physics 51st Edition

ANNEX 6 - OTHER GASES NOT CONSIDERED

During the development of this AFAP-3, other gases and techniques were studied. The gases studied and not retained were Benzene, styrene, toluene, carbon disulphide, ammonia, acetaldehyde, acrylonitrile, hydrogen sulphide and formic acid For these gases, repeatability and reproducibility were studied and different techniques were selected, but their contribution to TOXICITY INDEX was even so low that they were removed. In fact, they are more characterized by a chronic toxicity than an acute toxicity in case of fire and their quantities are always low enough to consider that their acute toxic effect in smoke is negligible. Cf factors for these species are available in publications referenced in ANNEX 1.

Techniques studied for these species are listed in table below:

Gas[2]		**Analytical Techniques**	**Primary analytical techniques**
Benzene	C_6H_6	HPLC, GC/FID	GC/MS
Toluene (Methyl benzene)	$C_6H_5CH_3$	HPLC	GC/MS
Styrene (Phenylethene)	$C_6H_5CHCH_2$	HPLC	GC/MS
Carbon disulphide	CS_2	GC/FPD	GC/MS
Ammonia	NH_3	Titration, FTIR	IC
Acetaldehyde (Ethanal)	CH_3CHO	GC/MS, Titration	HPLC
Acrylonitrile	CH_2CHCN	GC/NPD	GC/MS
Hydrogen sulphide	H_2S	Titration, GC/FPD	IC
Formic acid	HCOOH	HPLC	IC

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[2] IUPAC chemical names are shown in brackets.

The minimum limit of detection for these species is listed in table below:

Gas		***Maximum Acceptable LoQ***	
		(ppm/40l)	**(ppm/100g/m^3)**
Benzene	C_6H_6	**2**	**8**
Styrene	$C_6H_5CH_3$	**10**	**40**
Toluene	$C_6H_5CHCH_2$	**5**	**20**
Carbon disulphide	CS_2	**3**	**12**
Ammonia	NH_3	**10**	**40**
Acetaldehyde	CH_3CHO	**1**	**4**
Acrylonitrile	CH_2CHCN	**4**	**16**
Hydrogen sulphide	H_2S	**5**	**20**
Formic acid	HCOOH	**7**	**28**

In addition to Annex 4, benzene, toluene, xylene, carbon disulphide and acrylonitrile can be analysed by GC/MS. The table below presents the most common fragments to consider in addition to tables of Annex 4 for analyse of these components:

Compound	**Principal peak (parent) at m/z (normalised to 100%)**	**Importance of other fragments in % compared to parent peaks (>50% compared to parent)**	**Typical retention times (minutes)**	**Fragments used for quantification (in m/z)**
Carbon disulphide	76	No other important fragments	2.9	76
Benzene	78	No other important fragments	7.7	78
Toluene	91	1 fragment 92 (70%) = molar peak	10	91
Styrene	104	No other important fragments	12.4	104
Acrylonitrile	53	2 fragments 26 (85%) 52 (79%)	3.2	53

Calibration can be made adding to “STANDARD 1” presented in ANNEX 4 a quantity of acrylonitrile, and preparing a “STANDARD 2” solution in addition. Two solutions are generally required because of the immiscibility of some of the compounds. A suitable calibration is presented here, in addition to ANNEX 4 parameters. In the 40 litre gas collection bag the following standard concentrations are prepared:

- 2.0 µl solution « STANDARD 1 » + 2.0 µl solution « STANDARD 2 »
- 5.0 µl solution « STANDARD 1 » + 5.0 µl solution « STANDARD 2 »
- 10.0 µl solution « STANDARD 1 » + 10.0 µl solution « STANDARD 2 »
- 20 µl solution « STANDARD 1 » + 20 µl solution « STANDARD 2 »
- 25 µl solution « STANDARD 1 » + 25 µl solution « STANDARD 2 »
- 50 µl solution « STANDARD 1 » + 50 µl solution « STANDARD 2 »
- 100 µl solution « STANDARD 1 » + 100 µl solution « STANDARD 2 »
- 200 µl solution « STANDARD 1 » + 200 µl solution « STANDARD 2 »
- 250 µl solution « STANDARD 1 » + 250 µl solution « STANDARD 2 »

The standard solutions contain the following concentrations :

“STANDARD 1“	Acrolein: ~5.3 g Acrylonitrile: ~3.5 g
“STANDARD 2“	Benzene: ~7.0 g Toluene: ~6.9 g Styrene: ~6.8 g Carbon disulphide: ~11.2 g

ANNEX 7 – ROUND-ROBIN RESULTS

Hydrogen Fluoride (HF) analysis by IC

An inter-laboratory trial on analysis of HF by IC was performed between 5 laboratories using the method described in this Allied Publication. The results were analyzed according to ISO 5725-2 for low concentrations on two series of single measurements and for high concentrations on a series of three measurements. No aberrant values were found according to statistical tests. The results are presented in table below:

Average concentration (mg/l)	Repeatability s_r	Reproducibility s_R
1.03	ND	24.7 %
2.11	ND	16.4 %
14.8	6.1 %	8.1 %

Phenol (C_5H_6OH) analysis by HPLC

An inter-laboratory trial was performed between 6 laboratories on analysis of phenol by HPLC following the method described in this Allied Publication. The results were analyzed according to ISO 5725-2 on a series of two replicates. No aberrant values were found according to statistical tests. The results are presented in table and chart below:

Average concentration (mg/l)	Repeatability s_r	Reproducibility s_R
69.0	8,3 %	10.0 %