INTERNATIONAL STANDARD

ISO 19701

Second edition
2013-04-01

Methods for sampling and analysis of fire effluents

Méthodes d’échantillonnage et d’analyse des effluents du feu

Reference number
ISO 19701:2013(E)

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Published in Switzerland

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 19701 was prepared by Technical Committee ISO/TC 92, *Fire safety*, Subcommittee SC 3, *Fire threat to people and environment*.

This second edition cancels and replaces the first edition (ISO 19701:2005).

Introduction

The analysis of fire gases for use in toxic hazard and life threat assessment and other purposes (e.g. impact on the environment) is a great challenge for the analyst. Fire atmospheres are by nature hostile environments. Temperatures in excess of 1 000 °C are common, the gas phase can contain many corrosive, toxic, irritant or combustible species together with relatively large quantities of condensable water.

These properties are largely incompatible with most instrumental analytical methods where a "clean" sample is required. This poses many problems both for the qualification and quantification of the chemical species and particulates in fire atmospheres. In presenting a sample to the measuring instrument that it will tolerate, it can be necessary to filter particulates and remove other species. Losses in the sampling train must therefore be quantifiable and taken into account in the final analysis.

Techniques also exist for measuring chemical species *in situ;* this will be the subject of a future document.

The methods described in Clause 5 have been used successfully by a number of laboratories. Studies of repeatability and reproducibility of many of the methods covered in this International Standard have been taken from AFNOR NF X70-100-1[1] and AFAP-3.[2]

For methods that involve a commercial instrument, uncertainty in the measured values may be estimated from the manufacturer's data and other information, e.g. allowance for losses in the sampling process. For other methods, uncertainty in the measured values can occur through a variety of reasons, such as sensitivity to the strength of reagents or the visibility of a colourimetric end point. In these cases, it is assumed that best practice by qualified personnel is applied.

This International Standard is structured as follows.

- Clause 1 describes the scope of this standard
- Clause 4 describes methods of sampling.
- Clause 5 describes analytical methods for gases in fire atmospheres:
- Annex A provides information on techniques that were found not suitable with fire effluents.
- Annex B briefly describes the use of aspirated chemical colour-change tubes.
- Annex C is a summary of the main instrumental methods available for fire gas analysis, expanding the information provided under the clauses for each individual chemical species.
- Annex D presents a method for continuous measurement of HF concentration using ion selective electrode.

Methods for sampling and analysis of fire effluents

SAFETY PRECAUTIONS — Due consideration must be given to the fact that both the fire gases for analysis and many of the reagents used for their analysis can be toxic and/or present serious health hazards. It is assumed throughout that the procedures described in this document will be carried out by suitably qualified professional personnel, adequately trained in the hazards and risks associated with such analyses and aware of any safety regulations that may be in force. Consideration must also be given to the safe and ecologically acceptable disposal of all chemicals used for analyses. This can require extensive treatment prior to release of the waste into the environment. Again, it is assumed in this document that the personnel responsible for the safe disposal of such reagents are suitably qualified and trained in these techniques and are aware of the regulations which may be in force.

1 Scope

This International Standard presents a range of sampling and chemical analytical methods suitable for the analysis of individual chemical species in fire atmospheres. The procedures relate to the analysis of samples extracted from an apparatus or effluent flow from a fire test rig or physical fire test model and are not concerned with the specific nature of the fire test.

This International Standard doesn't cover aerosols (detailed in Reference [3]) and FTIR technique (detailed in Reference [4]). The gases of environmental interest, such as PAH, dioxins, furans, endocrinal disturbers, will be developed in a future document by ISO TC92/SC3.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 13943, *Fire safety — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 13943 apply.

4 Methods of sampling

4.1 General considerations

Sampling is perhaps the most critical part of the procedures for analysis of gases in fire effluents. Whereas sampling and analysis are commonly in use for many gaseous species in other fields, sampling from fire atmospheres presents unusual and difficult problems.

The sample presented to the analyser shall be as representative as possible of the test atmosphere, without having been changed by the sampling system. The sampling procedure should influence the test atmosphere as little as possible (e.g. by depletion of the test volume). The sampling procedure should be as uncomplicated as possible, while incorporating all necessary features detailed in this International Standard. The sampling procedure shall be capable of operating with minimal blockage in the sampling lines, melting or other disruption of probes, and without allowing condensation of the species for analysis.

IMPORTANT — It is important to appreciate that the overall accuracy of the analysis of fire effluent species is significantly dependent on the sampling procedures adopted, in particular the quantification of losses in probes, sampling lines, and filtering systems.

4.2 Concentration and volume fraction

The concentration of fire effluent or of a toxic gas is its mass divided by the volume in which it is contained. For a fire effluent the typical units are $g.m^{-3}$.However, for a toxic gas, concentration is usually expressed as a volume fraction at T = 298 K and P = 1 atm, and is expressed in terms of $\mu L.L^{-1}$ (equivalent to $cm^3/m^3 = 10^{-6}$).

NOTE 1 The concentration of a gas at a temperature, T, and a pressure, P can be calculated from its volume fraction (assuming ideal gas behaviour) by multiplying the volume fraction by the density of the gas at that temperature and pressure.

NOTE 2 Volume fractions of toxic gases used to be expressed in terms of “ppm by volume” but “ppm” is a deprecated term and therefore “$\mu L.L^{-1}$” is now used.

4.3 Special considerations

There are many factors that have a direct influence on the specific type of sampling methodology selected to ensure that a suitable sample is presented to the analyser. For example, consideration shall include the range of concentrations anticipated, the limits of detection, reactivity of the species of interest, presence of interferences, and peak and average concentration values. Sampling of the extremely complex atmosphere produced during combustion requires a very thorough evaluation and assessment of all potential factors that might affect optimum conditions for sample collection and analysis.

The large number of different products frequently encountered in fire effluents often requires the use of a variety of sampling procedures and approaches to ensure accurate identification and quantification of combustion products. The selected sampling procedure also depends on the instrumentation and analytical procedures available for the specific species being measured.

Sampling may involve either continuous, online analysis (e.g. non-dispersive infrared) or non-continuous batch sampling (e.g. evacuated flask or bubbler samples). Batch-type sampling can be further subdivided into two categories:

a) “Instantaneous”, or “grab”;

b) Average, or integrated.

Although there is no sharp distinction between categories a) and b), it is generally understood that grab samples relate to samples taken over a short time period (i.e. usually less than 1 min), whereas integrated samples are usually taken over a longer time period (i.e. a substantial portion of the total test period).

In some cases, continuous or semi-continuous online or frequent instantaneous sampling can be well suited for following the rapidly changing combustion environment and will provide a representative concentration profile. Frequently however, the minimum detectable limit of the species of interest requires larger sample volumes than can be taken with these techniques. If this analytical limitation exists, it is necessary to carry out the sampling over a longer period. While using longer sampling periods permits the analysis of lower concentrations, this approach has some limitations. For example, these types of samples permit a determination only of the integrated average concentration obtained over the sampling period and do not discern any abrupt change in the evolution of the species of interest. However, abrupt concentration changes can also be missed with instantaneously obtained samples, if samples are not taken frequently enough.

When batch-sampling procedures are used, it is essential to specify sampling frequency, the starting time of each sample and the total sampling time. This information is essential in order to ensure proper evaluation of the data in conjunction with other fire properties that are being monitored (e.g. heat release, temperatures, mass loss, smoke evolution, flame spread).

Test fires can be classified as “small” (laboratory or “bench” size), “intermediate” or “large” (usually full-scale). The sampled gases can be hot or near room temperature. It is generally necessary to extract the gases from the test atmosphere through suitable tubing using a suction pump. Stainless steel tubing, as short as possible, is often used. In the case of the production of hot gases, the sampling line shall be heated to at least 100 °C. Several analytical methods require a dry, particulate-free sample. Glass wool may be used (in most cases) as a particulate filter, with another trap of a drying agent (e.g. calcium sulfate or calcium chloride) for removing moisture. The traps should be located just before the analyser and after any heated sections of sampling tubes. Simple cold traps are often insufficient to remove the quantity of moisture present in fire effluents; however, they can be useful in conjunction with other filters and traps. The individual sampling and analytical system being used dictates flow requirements and the necessity for moisture removal. Precautions should be taken to minimize the volume of the filtering systems to reduce sampling time.

With the exception of hydrogen fluoride (HF), acid gases shall be sampled using glass, epoxy-lined or PTFE tubes to minimize losses due to reactivity and condensation on the tube surfaces. For hydrogen fluoride, tubes lined with PTFE shall be used (glass and glass-lined tubes are unsuitable). For species that are relatively reactive and prone to losses, sampling lines shall be as short as possible, and shall be heated to a sufficient temperature to avoid condensation. Hydrogen chloride (HCl) and hydrogen bromide (HBr) can be adsorbed onto soot particles as well as gas sampling lines (including PTFE lines).

For organic materials (e.g. acrolein), unlined stainless steel tubing is suitable but the sampling lines shall be heated to avoid condensation. Particulate traps, although usually necessary, can be avoided in some cases and instrument requirements should be checked in this regard.

The location and size of sampling probes is influenced by the size of the test apparatus and the requirements of the analytical system. The positioning of sampling probes in specific apparatus, however, is beyond the scope of this International Standard. In general, the possibility of the stratification of gases in chambers without good mixing shall be considered and sampling too near the wall of a test chamber should be avoided.

Calibration of the entire sampling and analysis system, rather than just the analysis system, is recommended in order to ensure that any losses in the sample route can be allowed for. All calibrations should, therefore, take into account such factors as gas leakage (both into and out of the sampling lines) and the adsorption of gases onto probes, sampling lines, filters and other components. Calibration gases are often obtainable in cylinders; however, it is advisable that the concentration stated by the supplier be verified by an independent analysis. This is especially true of reactive gases such as HCl and HF, which can decay over relatively short time periods even in a closed cylinder. The calibration gas shall be introduced at the sampling probe and allowed to travel the same course as a test gas, through filters and traps if present, to the analyser or sampling medium.

4.4 Sampling using gas-solution absorbers

Absorption of gases in solution by the use of gas-washing bottles, bubblers, impingers, etc. all rely on the same principle. The test atmosphere is drawn or pushed through the absorbing media at a measured rate for a specified period of time. At the end of the sampling period, the solution is analysed for the species of interest (e.g. the chloride ion for absorption of hydrogen chloride gas in water). Assuming 100 % efficiency (see discussion below), it is possible to calculate the concentration of the species in the gas phase, as measured in the solution. A typical equation for calculating concentrations is presented in Formula (1):

$$\rho_{\mathrm{G}} = \frac{\rho_{\mathrm{S}} \times V \times (m_{\mathrm{G}} / m_{\mathrm{S}})}{q \times t} \tag{1}$$

where

ρ_{G} is the gas concentration;

ρ_{S} is the solution concentration;

V is the volume, expressed in litres, of solution;

$m_{\mathrm{G}}/m_{\mathrm{S}}$ is the ratio of atomic or molecular weights for the gaseous species, *G*, and solution species, *S*, if different, e.g. HCl/Cl);

q is the rate of gas flow, expressed in litres per minute, through the impinger;

t is the time, in minutes of gas flow.

The volume fraction of the gas, X_{G}, can be calculated by dividing the concentration by the density *d*, of the gas at the ambient temperature and pressure. This density can be found, assuming ideal gas behaviour, as follows:

$$d = \frac{M_{\mathrm{G}}}{H} \tag{2}$$

$$X_{\mathrm{G}} = \rho_{\mathrm{G}} \frac{H}{M_{\mathrm{G}}} \tag{3}$$

where

M_{G} is the molar mass of the gaseous species, *G*;

H is the gaseous volume occupied by 1 mol of an ideal gas at the relevant ambient pressure (*P*) and temperature (*T*).[*H* = 8,314 J.K-1.mol-1 × 1 mol × *T/P*]

EXAMPLE Suppose that the measured solution concentration of chloride ion ($\mathrm{Cl^-}$) was 0,006 g × $\mathrm{dm^{-3}}$ in 0,025 $\mathrm{dm^3}$ of solution, the ambient thermodynamic temperature was 293,15 K, the ambient pressure was 1 bar (10^5 Pa = 10^5 J × $\mathrm{m^{-3}}$), and the flow rate of gas was 0,25 $\mathrm{dm^3}$/min for 2 min. Then the gas concentration of hydrogen chloride is given by:

ρG = [0,006 g.$\mathrm{dm^{-3}}$ x 0,025 $\mathrm{dm^3}$ x (36,461 / 35,453)] / [0,25 $\mathrm{dm^3}$/min x 2 min]

ρG = [0,00015 g x 1,028] / 0,50 $\mathrm{dm^3}$

ρG = 0,0003084 g.$\mathrm{dm^{-3}}$ = 308,4 mg.$\mathrm{m^{-3}}$

The volume fraction of hydrogen chloride is given by:

X_{G} = 308,4 mg.$\mathrm{m^{-3}}$ x (8,314 J.$\mathrm{K^{-1}}$.$\mathrm{mol^{-1}}$ x 293,15 K / 105 J.$\mathrm{m^{-3}}$) / 36,461 g.$\mathrm{mol^{-1}}$

X_{G} = 308,4 mg.$\mathrm{m^{-3}}$ x 0,02437 $\mathrm{m^3}$.$\mathrm{mol^{-1}}$ / 36,461 g.$\mathrm{mol^{-1}}$

X_{G} = 0,0002061 = 206,1 μL/L

The volume of the absorber solution and the total flow of gas directly affect the ratio of the gas and solution concentrations. For a given gas concentration, the smaller the solution volume and/or the larger the gas volume sampled, the higher the solution concentration. The choice of sampling conditions is dictated by the requirements of the analytical technique, including the volume and sampling rate tolerated, expected concentration of gas in the test atmosphere, necessity for frequent sampling, etc.

The efficiency of absorption of a gas in liquid is affected by the following:

a) Solubility of the gas in the solution;

b) Physical characteristics of the absorber;

c) Ratio of gas flow rate to solution volume.

Generally, absorption efficiency is estimated empirically by allowing the flow of a known concentration of the gas of interest through a series of impingers and measuring the “break-through” from the first impinger (i.e. whatever is collected in the other traps). Another check on the efficiency of a given flow/impinger system is to conduct a series of experiments with a known concentration of gas, using different impingers and various flow rates. In practice, however, the choice of apparatus is limited, and gas flow rates and trapping solution volumes are based on Formula (1), taking into account the known characteristics of the analysis methods.

There are basically four types of gas-solution absorbers: simple gas-washing bottles (including midget impingers), spiral or helical absorbers, packed glass-bead columns and fritted bubblers. The gas-washing bottles, or impingers, function by drawing the gas through a tube (usually with a constricted opening), which is immersed in the trapping liquid/solution. This type is most suitable for highly soluble gases because contact time between solution and gas is short and bubble size is relatively large. For less soluble species, the other absorbers offer longer contact time and/or smaller bubble size (which increases relative surface contact). The spiral or helical absorbers are built in specialized shapes to allow a long contact time. The flow rate in these bubblers is limited because of the possibility of trapping solution over-flow with high flow rates. Packed glass-bead columns allow increased gas/liquid contact by dispersing the bubbles through a bed of glass beads. Flow rates can be higher than for the spiral absorbers.

The fritted bubblers contain a sintered or fritted disc on the gas inlet tube to disperse the gas into fine bubbles (the size of the bubbles is dependent on the porosity of the frit). It is necessary to exercise caution in using such bubblers so that frothing does not occur and so that the coalescence of the fine bubbles does not defeat the purpose of the frit. Also, it is necessary to filter smoky atmospheres (containing particulates or liquid aerosols) before drawing them through a fritted bubbler in order to prevent clogging of the frit (which occurs very easily). Such clogging can also occur from the build-up of wax-like deposits. Certain gas species (e.g. HCl) can be absorbed onto a filter, especially if particulates have also been trapped on the filter.

Note that very soluble gases, such as HCl and HF, can cause water to be sucked back along the sampling tube. With these gases, it is often necessary to include an empty bubbler to act as a liquid trap.

4.5 Sampling using solid sorption tubes

Solid sorption tubes are an alternative method to gas-solution absorbers for sampling certain gases from fire effluents. Following sampling, the species of interest is desorbed in water and its analysis can then be performed in a way similar to that for aqueous solution absorbers.

The advantages of solid sorption tubes over solution absorbers are

a) Ease of handling,

b) Compactness,

c) High absorption efficiency,

d) Ability to be located directly at the point of sampling.

This latter advantage can have dramatic consequences in the measurement of HF, HCl and HBr in fire effluents because these species are easily lost to the inside surfaces of sampling lines. With solid sorption tubes (except in areas of extreme heat), a sampling line is not necessary before the sorption tube itself. All associated hardware (e.g. valves, flow meters and pumps) can be located behind the tubes, even far from the sampling point. This ensures that the sample is as representative as possible of the fire atmosphere.

Much experience has been gained through using solid sorption tubes, for example in the field of atmospheric sampling and for staff exposure monitoring in the workplace. Similar tubes have been re-examined for potential use in sampling fire effluents. Two studies [5],[6] were carried out using solid sorbents to measure certain gases in real building fires. These tubes were located in portable sampling boxes carried by the firemen who were actually fighting the fire. Tubes of similar design, containing activated charcoal, have been used to sample HF [7] and HCN.[8] Tubes containing flake sodium hydroxide for the absorption of acid gases have also been described.[9] A procedure for successive (e.g. every 3 min or 5 min) sampling with tubes at one location without removing or replacing tubes has been described for sampling gases in full-scale fires.[8]

Calculation of the original gas concentration (e.g. HCl) from the representative species recovered in the desorbent solution (e.g. Cl^-) is the same as that described for solution absorbers, except that the solution volume is the volume of desorbent liquid. In practice, a small aliquot, rather than the entire quantity, of the desorbent solution is often used for the analysis so it is necessary to take this factor into account.

The same considerations that apply to solution absorbers, with respect to inefficient absorption, breakthrough and the relationship of volume sampled to gas and solution concentration, also apply to the use of solid sorbents. Instead of bubble size, it is the particulate size of the absorbent that is important (large particles offer less surface area per unit volume and more opportunity for channelling, smaller particles can cause the tube to plug when sampling moist gas). The tubes should be small enough (typically 100 mm long, 6 mm OD) such that two tubes can easily be placed in series to allow for the possibility of “breakthrough” from the first tube.

Solid sorption tubes are subject to plugging due to soot collection. This can be recognized during sampling by a decrease in sample flow rate. The same flow rate should be maintained over the duration of sampling using a constant flow device; otherwise, an error is introduced in the calculation of gas concentration. A glass wool plug loosely packed into the inlet of the tube reduces the tendency to blocking from soot.

Thermal desorption of the adsorbed sample is also possible; the sample tube is heated in an inert gas stream thus driving off the sample without the need for a liquid solution stage.

4.6 Sampling for spectrometric or spectrophotometric analysis

The uses of spectrometric analysis [direct mass spectrometry (MS)] and spectrophotometric analysis [both non-dispersive infrared (NDIR) and Fourier transform infrared (FTIR)] have become quite widespread in recent years. FTIR techniques in particular are becoming more prominent.[9], [10], [11] The continuous measurement by means of NDIR analysis (e.g. for CO and CO_2) is now so common that several different companies manufacture commercial instruments designed for this purpose.

For two of the methods (direct MS and FTIR), it is important that the fire effluents be free from particles before they are introduced into the analyser. The filter used, which is often placed at the junction of the sampling line and the test chamber, shall be inert so it does not react with any of the gases of interest. A stainless steel filter unit containing a glass-fibre filter (e.g. Whatman multigrade GMF150[1] micro-filter, 1 µm, 47 mm in diameter) has been found suitable. The sample line and the filter (and for FTIR also the absorption cell) are heated to a temperature above 120 °C (120 °C to 150 °C has been found to be suitable), in order to prevent liquid water from forming, to prevent water-soluble gases (e.g. HCN and the acid gases) from dissolving and other gases from condensing.

When a filter is used, it is necessary to check the extent to which the species of interest have been retained by the filter. If retention occurs, it is necessary to correct the measured concentrations. The amount of retained material is dependent principally on the type and capacity of the filter used, the nature of the species and the volume of gas passing through the filter.

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[1] The Whatman GMF150 filter is an example of a suitable product available commercially. This information is given for the convenience of users of ISO 19701 and does not constitute an endorsement by ISO of this product.

4.7 Sampling using gas bags

Sampling with gas bags can be used for most analytical methods. The test atmosphere is pumped, or allowed to flow under pressure, into a gas bag at a measured constant rate for a measured time period, thus obtaining a known volume of sample in the bag. It is necessary to filter the fire effluents before passing into the bag; simple in-line glass wool filters for particulates, and calcium chloride filters for moisture, have been found effective. However, a calcium chloride absorbent removes water vapour and water-soluble gases. At the end of the sampling period, the bag may be stored before it is connected to the analyser; but it is important to appreciate that storage times in bags should be kept to a minimum, preferably less than 1 h. Gases such as HF and HCl can dissolve in condensed/trapped water and this reduces the concentration presented to the analyser.

Bags shall be gas-tight and inert and those with a lining of polyvinylfluoride (PVF) are recommended.

Table 1 summarizes the analytical methods and types of sample required for each method described in this International Standard.

Table 1 — Type of sampling for the analytical methods described

Gas	Analytical Method	Type of sample for analysis
Carbon monoxide (CO)	NDIR	gas
Carbon dioxide (CO_2)	NDIR	gas
Oxygen (O_2)	Paramagnetism	gas
Hydrogen cyanide(HCN)	Colourimetry (Chloramine T) Colourimetry (picric acid) HPIC	solution solution solution
Hydrogen chloride (HCl) Hydrogen bromide (HBr)	ISE HPIC titrimetry	solution solution solution
Hydrogen fluoride (HF)	ISE HPIC Online ISE	solution solution solution
Nitrogen oxides (NO_x)	Chemiluminescence	gas
Nitrogen dioxide (NO_2)	HPIC	solution
Nitrogen monoxide (NO)	Gfx-IR	gas
Acrolein (2-propenal)	Colourimetry HPLC GC-MS	solution solution gas
Formaldehyde (Methanal)	Colourimetry HPLC	solution solution
Acetaldehyde (Ethanal)	HPLC GC-MS	solution solution
Total aldehydes	Colourimetry	solution
Sulfur dioxide (SO_2)	HPIC	solution
Carbon disulphide (CS_2)	GC-MS, GC/FPD	gas
Hydrogene Sulphide (H_2S)	HPIC GC/FPD	solution solution
Ammonia (NH_3)	Colourimetry HPIC Titration	solution solution solution
Antimony compounds	AAS or ICP	solution
Arsenic compounds	AAS or ICP	solution
Phosphorus	ICP	solution
Phosphates	Colourimetry HPIC	solution solution

Table 1 *(continued)*

Gas	Analytical Method	Type of sample for analysis
Phenol	HPLC GC-MS	solution gas
Benzene	HPLC GC-MS	solution gas
Toluene (Methylbenzene)	HPLC GC-MS	solution gas
Styrene (Phenylethene)	HPLC GC-MS	solution gas
Acrylonitrile	GC-MS	solution
Formic acid	HPIC HPLC	solution solution
Hydrocarbons (total)	FID	gas

5 Analytical methods for fire gases

5.1 Carbon monoxide by non-dispersive infrared spectroscopy (NDIR)

5.1.1 Application and limitations

The method provides a continuous analysis/monitoring capability for carbon monoxide. The analysers are commonly self-contained instruments and include sample pumps, sample filtering, analysis hardware and electronics. Direct readout of carbon monoxide concentration is usually provided (either digital or analogue) together with an output for connecting recording devices. Instruments providing carbon monoxide and carbon dioxide analyses in the same case are available.

5.1.2 Sensitivity and selectivity

Instruments are available for measuring carbon monoxide from below 1 µl/l to 50 000 µl/l (5 %) and more with a common resolution of 0,1 % of the selected range. Interferences with nitrogen compounds, water and carbon dioxide have been described.

5.1.3 Other considerations

Multi-range instruments are available to cover all concentrations likely to be encountered in fire effluents, which will normally be over the range 500 µl/l to 50 000 µl/l. The method is non-destructive and the sample can be “passed on” for analysis of other compounds, taking into account that some components of the sample, e.g. particles, acid gases and water, can be lost in filtering and sampling.

5.1.4 Analysis principles

NDIR instruments operate by passing a beam of infrared (IR) radiation of a fixed wavelength through the sample. The IR wavelength used is that which is in a main spectroscopic absorption region for carbon monoxide (and which is not absorbed significantly by other species). The absorption of the radiation is a measure of the concentration of carbon monoxide in the internal gas sample cell. Refinements may include a “double beam” system that can compensate for interfering species and other effects.

5.1.5 Procedure

See Clause 4 for principles of sampling and C.2 for general principles of the method. However, for the analysis of carbon monoxide by NDIR, the specific information in 5.1.6 to 5.1.10 is relevant.

Normally, the instruments have only to be powered and the sampling line attached. It is usually convenient to set one concentration range within which the analysis is carried out and, therefore, it is desirable that the recording system used (e.g. data logger) has sufficient resolution for the chosen range.

5.1.6 Sampling

It is essential that the sample stream entering the instrument be treated to remove particulates and vapours condensable under ambient conditions. Simple in-line glass wool and calcium chloride filters have been found to be effective. Sample flow rates on the order of a few litres per minute are common and where the sampling point is many metres away from the instrument, a separately pumped, heated sample line with a higher flow rate can be used with the instrument sample port “teed” into this.

5.1.7 Analysis

There is no requirement for additional analytical procedures.

5.1.8 Calibration

Calibration is achieved through the introduction of standard (preferably certificated) gas mixtures and “zero gas” (which may be high-purity nitrogen) as provided commercially in pressurized cylinders. It is desirable to calibrate the instrument by introducing the sample both at the inlet port and at the remote sampling point. On multi-range instruments, it is usually possible to calibrate on the lowest range if more than one range is to be routinely used. However, calibration within the range to be used for measurement is recommended. It should be noted that the ambient concentration could vary significantly from these values depending on location. It is, therefore, important to recognize that a significant ambient reading can be obtained at the beginning of a fire experiment due to local conditions. The calibration and the analysis of the fire effluents shall be carried out using the same flow-rate through the analyser.

5.1.9 Calculations

There are no calculations required; the carbon monoxide concentration is obtained by direct readout or (more usually) through a connection to an electronic recording apparatus.

Note that some instruments have a nonlinear scale but have the electronic output corrected to provide a linear signal. This linear signal ranges between fixed values and usually does not take account of the selected concentration range.

5.1.10 Repeatability and reproducibility

Regarding the similarity of measurement technique, repeatability and reproducibility have been estimated as equivalent to CO_2 by NDIR (see 5.2.10).

For determination of CO yields according to AFAP-3[2] during combustion of PMMA at 800°C, Repeatability has been estimated as 14 % and reproducibility as 26 %.[12] These values include repeatability and reproducibility of the fire model.

5.2 Carbon dioxide by non dispersive infrared spectroscopy (NDIR)

5.2.1 Application and limitations

NDIR provides a continuous analysis/monitoring capability for carbon dioxide. The analysers are commonly self-contained instruments and include all sampling, pumping, sample filtering, and analysis hardware and electronics. A direct readout of the carbon dioxide concentration is usually provided (either digital or analog) together with an output for connecting recording devices. Instruments providing carbon dioxide and carbon monoxide analyses in the same case are available.

5.2.2 Sensitivity and selectivity

Instruments are available for measuring carbon dioxide from below 1 µl/l to 200 000 µl/l (20 %) and more, with a common resolution of 0,1 % of the selected range. Interferences with nitrogen compounds and water have been described.

5.2.3 Other considerations

Multi-range instruments are available to cover all concentrations of carbon dioxide commonly encountered in fire effluents, which normally are in the range 500 µl/l to 200 000 µl/l. The method is non-destructive and the sample can be “passed on” for analysis of other compounds, taking into account that some components of the sample, e.g. particles, acid gases and water, can be lost in filtering and sampling.

5.2.4 Analysis principles

NDIR instruments operate by passing a beam of infrared (IR) light of fixed wavelength through the sample. The IR wavelength used is that which is in a main spectroscopic absorption region for carbon dioxide (and which is not absorbed significantly by other species). The absorption of radiation is a measure of the concentration of carbon dioxide in the internal gas sample cell. Refinements may include a “double beam” system that can compensate for interfering species and other effects.

5.2.5 Procedure

See Clause 4 for principles of sampling and C.2 for general principles for this method. However, for the analysis of carbon dioxide by NDIR, the specific information in 5.2.6 to 5.2.11 is relevant.

The instruments usually have only to be powered and the sampling line attached. It is usually convenient to set one concentration range within which the analysis is carried out and it is therefore desirable that the recording system used (e.g. data logger) have sufficient resolution for the chosen range.

5.2.6 Sampling

It is essential that the sample stream entering the instrument be treated to remove particulate and vapours condensable under ambient conditions. Simple in-line glass wool and calcium chloride filters have been found to be effective. Sample flow rates of the order of a few litres per minute are common and where the sampling point is many metres away from the instrument, a separately pumped, heated sampling line with a higher flow rate can be used with the instrument sample port “teed” into this.

5.2.7 Analysis

There is no requirement for additional analytical procedures.

5.2.8 Calibration

Calibration is achieved through the introduction of a standard (preferably certificated) gas mixtures and “zero gas” (which may be high-purity nitrogen) as provided commercially in pressurized cylinders. It is desirable to calibrate the instrument by introducing the sample both at the inlet port and at the remote sampling point. On multi-range instruments, it is usually desirable to calibrate on the lowest range if more that one range is to be routinely used. A useful check is the concentration of ambient carbon dioxide (350 µl/l to 355 µl/l in 1997) following a zero gas check. However, it should be noted that the ambient concentration can vary significantly from these values depending on location. It is, therefore, important to recognize that a significant ambient reading can be obtained at the beginning of a fire experiment due to local conditions. The calibration and the analysis of the fire effluents shall be carried out using the same flow-rate through the analyser.

5.2.9 Calculations

There are no calculations required: the carbon dioxide concentration is obtained by direct readout or (more usually) through a connection to an electronic recording apparatus.

Note that some instruments have a nonlinear scale but have the electronic output corrected to provide a linear signal. This linear signal ranges between fixed values and does not usually take account of the selected concentration range.

5.2.10 Repeatability and reproducibility

For determination of CO_2 yields according to AFNOR NF X70-100-1, repeatability has been estimated as 8 % and reproducibility as 21 %, for a yield of around 0,15 kg/kg.[1] These values include repeatability and reproducibility of the fire model.

For determination of CO_2 yields according to AFAP-3[2] during calcinations of Zinc carbonate at 800°C, repeatability has been estimated as 16 % and reproducibility as 28 %.[12] These values include repeatability and reproducibility of the fire model.

5.2.11 Trueness

Trueness of the method has been determined according to AFAP-3[2] during calcinations of Zinc carbonate, with the hypothesis of a raw formula of $3(Zn(OH)_2).2(ZnCO_2)$ and considering the release of all carbonate into CO_2. Theoretical yield is 0,160 kg/kg. Value found (average of 3 determination) was 7,3 % lower than theoretical value.

5.3 Oxygen by paramagnetism

5.3.1 Application and limitations

This method provides a continuous analysis monitoring capability for oxygen. The analysers are commonly self-contained and include sample filtration, analysis hardware and electronics. Sample pumping may be built-in or provided externally. Direct readout, often by digital display, of oxygen concentration is usually provided together with an output for connecting recording devices.

5.3.2 Sensitivity and selectivity

Most instruments operate in the range 0 % to 100 % but may be able to switch ranges to cover narrower concentration ranges, typically 0 % to 25 %. A resolution of 0,1 % oxygen is common. Some instruments can also provide a “differential” reading, i.e. the change from a set starting value. No significant interference is likely but other paramagnetic compounds, e.g. nitrogen dioxide and carbon monoxide, can give a weak interference.

5.3.3 Other considerations

The advent of oxygen-depletion calorimetry has placed new demands on the sensitivity, selectivity and stability of the paramagnetic oxygen analyser. Most heat-release-rate measurements using this technique require a measurement accuracy of 0,02 % oxygen, usually over the range 15 % to 21 % oxygen.

5.3.4 Analysis principles

Oxygen exhibits the property of paramagnetism (i.e. concentrating/attracting an applied magnetic field) because of the electron arrangement in its molecule. Practical instruments utilize this property by measuring the movement of a body placed in a magnetic field, with the oxygen-containing sample flowing around the body.

5.3.5 Procedure

See Clause 4 for principles of sampling and C.3 for general principles of the method. However, for the analysis of oxygen by paramagnetism, the specific information in 5.3.6 to 5.3.10 is relevant.

The instruments usually have only to be powered and the sampling line attached.

5.3.6 Sampling

It is essential that the sample stream entering the instrument be treated to remove particulates and vapours condensable under ambient conditions. Simple in-line glass wool and calcium chloride filters have been found to be effective. In order to protect the delicate mechanism in the measuring cell, sample flow-rates are usually very small, e.g. a few millilitres per minute, in comparison to the normal practical sampling rates required from the fire atmosphere, so a suitable internal by-pass is usually fitted.

5.3.7 Analysis

There is no requirement for additional analytical procedures.

5.3.8 Calibration

Calibration is achieved by the introduction of standard (preferably certificated) gas mixtures and “zero gas” (which may be high-purity nitrogen) as provided commercially in pressurized cylinders.

A useful check is to utilize the ambient oxygen concentration in dry air (20,9 %), this accuracy being adequate for many purposes. When used for oxygen depletion calorimetry, this accuracy for calibration is acceptable as the measurements involve a difference of oxygen concentration from ambient. However, it should be noted that other factors, such as location and atmospheric conditions, could affect the ambient concentration of oxygen. For example, at a relative humidity of 50 %, the ambient oxygen concentration is reduced from that of dry air to approximately 20,6 %.

5.3.9 Calculations

There are no calculations required; oxygen concentration is by direct readout or (more usually) through connection to electronic recording apparatus.

NOTE Some instruments have a nonlinear scale but have the electronic output corrected to provide a linear signal. This linear signal ranges between fixed values and does not usually take account of the selected concentration range.

5.3.10 Repeatability and reproducibility

No data has been collected yet. Nevertheless, the technique is at the basis of oxygen-depletion calorimetry and confidence in oxygen concentration produced is estimated fewer than 10 %.

5.4 Hydrogen cyanide

5.4.1 Hydrogen cyanide by colourimetry (Chloramine T)

5.4.1.1 Application and limitations

These are covered in 5.4.1.2 and 5.4.1.3.

5.4.1.2 Sensitivity and selectivity

This technique is capable of measuring 0,05 μg cyanide ions in the aliquot taken.

Small negative interferences arise from nitriles, oxides of nitrogen and sulphide.

5.4.1.3 Other considerations

A concentration of 0,01 M sodium hydroxide for the trapping medium prevents breakthrough of hydrogen cyanide in fritted bubblers but does not influence the pH during the colourimetric analysis procedure.

During the colour development, there is a 10 min "window" between 25 min and 35 min during which the blue colour is stable, allowing analysis of multiple samples simultaneously. The solutions containing HCN have been found to be unstable over time. The solutions shall be analysed on the same day as the sample is obtained.

It should be noted that visual comparison of colour hue and intensity could be used as a guide to concentration (i.e. without the use of a spectrophotometer) but such assessments can be relatively subjective and are affected by such factors as colour-blindness and other sight defects.

5.4.1.4 Analysis principles

Cyanide (CN^-) in the test solution, is converted to cyanogen chloride (CNCl) by reaction with chloramine T at pH 7. The CNCl then forms a blue dye on addition of 4-pyridinecarboxylic acid-pyrazolone reagent, which is measured in a spectrophotometer at a wavelength of approximately 638 nm (corresponding to the maximum absorbance of the standard solution); see Reference [13].

5.4.1.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of hydrogen cyanide by chloramine T colourimetry, the specific information in 5.4.1.6 to 5.4.1.9 is relevant.

5.4.1.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml of 0,01 M sodium hydroxide at 0,4 l/min for 4 min to 5 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions. Copper sampling tubes are unsuitable. Flow measurements will contribute to the overall uncertainty in the determination.

5.4.1.7 Analysis

5.4.1.7.1 Reagents

Analytical grade reagents should be used where possible. Water used should be quality 3 as defined in ISO 3696:1987.[14]

5.4.1.7.1.1 Absorbing solution, 0,01 M sodium hydroxide

5.4.1.7.1.2 Phosphate buffer, pH 7.2

Add 19,8 g sodium hydrogen phosphate to 300 ml distilled water and adjust to pH 7,2 with potassium dihydrogen phosphate solution (ρ = 200 g/l). Make up volume to 500 ml with distilled water.

5.4.1.7.1.3 Chloramine T solution, ρ = 1 g/l

Dissolve 0,1 g chloramine T in 100 ml distilled water. Prepare freshly each day.

5.4.1.7.1.4 Pyridine-pyrazolone solution

Mix 1-phenyl-3-methyl-5-pyrazolone (0,3 g in 20 ml dimethyl formamide) with 4-pyridiene carboxylic acid (1,5 g in 20 ml 1 M NaOH; adjust pH to 7,0 with 1 M HCl). Adjust final volume to 100 ml with distilled water. The solution is stable for up to five weeks if refrigerated.

5.4.1.7.1.5 **Stock cyanide solution,** ρ approximately 1 000 µg/ml CN^-

Dissolve 1,29 g potassium cyanide in 500 ml 0,01 M sodium hydroxide.

5.4.1.7.1.6 **Standard cyanide solution,** ρ = 2,0 µg/ml CN^-

Add 1 ml stock solution (5.4.1.7.1.5) to 0,01 M sodium hydroxide contained in a 500 ml volumetric flask and make up to volume. Prepare freshly each day.

5.4.1.7.2 Protocol

To a boiling-tube, add an aliquot of test solution containing up to 4,0 µg CN^-. Add 0,01 M sodium hydroxide (if necessary) to give a total volume of 4 ml. Then add in turn with shaking

- 1,8 ml phosphate buffer,
- 0,8 ml chloramine T (leave 5 min to react),
- 1,8 ml pyridine-pyrazolone solution.

Read absorbance at approximately 638 nm (corresponding to the maximum absorbance of the standard solution) in a 1 cm cell against a reagent blank solution, 30 min exactly after the addition of the chloramine T solution (see 5.4.1.7.1.3).

5.4.1.8 Calibration

Prepare calibration standards containing 2,0 µg and 4,0 µg CN^- using 1 ml and 2 ml aliquots of the standard cyanide solution (5.4.1.7.1.6). Prepare at least two more calibration solutions to cover the range of concentrations required. Make up the volume to 4 ml with 0,01 M sodium hydroxide and develop the colour as described above. Standards should be included with each set of analyses.

5.4.1.9 Calculations

Compare the absorbance of the test solutions with that obtained for the calibration standards and calculate concentrations in the test atmosphere using Formula (4):

$$\rho_{\mathrm{HCN}} = \frac{\rho_{\mathrm{CN}} \times V_{\mathrm{as}} \times 1{,}038}{V_{\mathrm{ta}} \times e} \qquad (4)$$

where

ρ_{HCN} is the hydrogen cyanide concentration, expressed in grams per litre of atmosphere;

ρ_{CN} is the cyanide ions concentration in the absorbing solution, expressed in grams of cyanide ions per litre of the solution;

1,038 is the conversion factor from CN to HCN, equal to 27/26;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.4.1.10 Repeatability and reproducibility

No data has been collected yet.

5.4.2 **Hydrogen cyanide by colourimetry** (picric acid)

5.4.2.1 Application and limitations

These are covered in 5.4.2.2 and 5.4.2.3.

5.4.2.2 Sensitivity and selectivity

This technique is capable of measuring 2 µg/ml cyanide ions.

Interferences arise from acetone and other ketones. Washing flasks with acetone is prohibited with this technique.

5.4.2.3 Other considerations

Sample solutions containing HCN have been found to be unstable over time. It is recommended that the solutions be analysed within 24 h of the collection of the sample. It should be noted that visual comparison of colour hue and intensity could be used as a guide to concentration (i.e. without the use of a spectrophotometer) but such assessments can be relatively subjective and are affected by such factors as colour-blindness and other sight defects.

5.4.2.4 Analysis principles

Cyanide (CN^-) in the test solution, trapped in the form of an alkaline cyanide, forms a red derivative of isopurpurate when added to a picric acid reagent, the absorbance of which is measured in a spectrophotometer at a wavelength of approximately 480 nm (corresponding to the maximum absorbance of the standard solution).

5.4.2.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of hydrogen cyanide by picric acid colourimetry, the specific information in 5.4.2.6 to 5.4.2.11 is relevant.

5.4.2.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml of 0,1 M sodium hydroxide at 0,4 l/min for 4 min to 5 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.4.2.7 Analysis

5.4.2.7.1 Reagents

Analytical grade reagents should be used where possible. Water used should be quality 3 as defined in ISO 3696:1987.[14]

5.4.2.7.1.1 **Absorbing solution**, 0,1 M sodium hydroxide

5.4.2.7.1.2 Colourimetric reagent

Dissolve 50 g of sodium carbonate in distilled water. Add 250 ml of a 1,2 % picric acid solution (commercially available with analysis certificate). Adjust final volume to 1 000 ml with distilled water. The solution is stable for several months if kept in a brown flask.

5.4.2.7.1.3 **Stock cyanide solution**, *ρ* approximately 800 µg/ml CN^-

The solution can be prepared from potassium cyanide dissolved in sodium hydroxide (0,01 M). The exact concentration of the solution has to be checked before use, as potassium cyanide is not stable and oxidation can occur.

5.4.2.7.1.4 **Standard cyanide solution**, *ρ* approximately 40 µg/ml CN^-

Add 5 ml stock solution (5.4.2.7.1.3) to distilled water contained in a 100 ml volumetric flask and make up to volume. Prepare freshly each day.

5.4.2.7.2 Protocol

To a flask or Erlenmeyer, add an aliquot of test solution of between 1 ml and 20 ml. Add 30 ml of colourimetric reagent and make up to 50 ml with 0,1 M sodium hydroxide.

Make a sample blank solution by adding to a flask or an Erlenmeyer 1 ml of test solution and 50 ml of 0,1 M sodium hydroxide. This is to allow for the fact that the sample itself can contain colouring, which interferes with the analysis.

Place the flasks or Erlenmeyers for 10 min in a water-bath kept at 90 °C ± 2 °C.

After cooling to ambient temperature, read the absorbance at approximately 480 nm (corresponding to the maximum absorbance of the standard solution) in a 1 cm cell against a reagent blank and the sample blank. If the absorbance measured is higher than the calibrated range, dilute the test solution using 0,1 M sodium hydroxide and repeat the analysis.

5.4.2.8 Calibration

The reagent blank and standard solutions are prepared in accordance with Table 2.

Table 2 — Preparation of reagent blank and standard solutions

Parameter	CN concentration in µg/ml					
	Reagent blank	**Standard solution**				
		2,4	4,8	7,2	9,6	12
	Volume of reagent added ml					
Standard cyanide solution	0	3	6	9	12	15
0,1 M sodium hydroxide	20	17	14	11	8	5
Colourimetric reagent	30	30	30	30	30	30

Develop the colour as described in 5.4.2.7.2. Standards should be included with each set of analyses.

5.4.2.9 Calculations

Compare the absorbance of the test solutions with those obtained for the calibration standards and calculate solution concentrations using Formula 4, in 5.4.1.9.

5.4.2.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in 0,1 M NaOH solution.[1] For concentration around 8 mg/l, repeatability has been estimated as 7 % and reproducibility has been estimated as 21 %. For concentration around 32 mg/l, repeatability has been estimated as 4 % and reproducibility has been estimated as 23 %.

5.4.2.11 Trueness

Values found during interlaboratory trial were compared with technique by high performance ion chromatography (HPIC). Results were comparable for low concentration (at about 8 mg/l) at less than 13 % and for high concentration (at about 32 mg/l) at less than 4 %.

5.4.3 Hydrogen cyanide by high performance ion chromatography (HPIC)

5.4.3.1 Application and limitations

These are covered in 5.4.3.2 and 5.4.3.3.

5.4.3.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 0,05 µg/ml to 50 µg/ml as cyanide ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to cyanide ions in aqueous solution. An alkaline eluent shall always be used for separation and detection to ensure the cyanide ions exist in the anionic form.

This method allows measurement of hydrogen sulphide simultaneously (see 5.14.1).

5.4.3.3 Other considerations

A glass syringe with a PTFE-tipped plunger is recommended for use during injection to avoid unnecessary reactions with the rubber materials often present in the plungers of plastic syringes. Certain types of columns have been found to be sensitive to the fire-effluent solution in that they can quickly become clogged. The solution should be filtered before injection onto the column. It is often necessary to regenerate the columns regularly.

In routine usage, it has been proven that HPIC separating columns are subject to accelerate aging of solid phase. A special care has to be done checking no degradation of analytical conditions.

5.4.3.4 Analysis principles

The separation is carried out on an anion exchange column followed by Amperometric detection with a silver-working electrode. A silver chloride reference and a stainless steel counter electrode are fitted in the cell.

5.4.3.5 Procedure

See Clause 4 for principles of sampling and C.5 for the general principles of the method. However, for the analysis of hydrogen cyanide by HPIC, the specific information in 5.4.3.6 to 5.4.3.11 is relevant.

5.4.3.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through a non-fritted then a fritter impinger, containing 75 ml and 150 ml, respectively, of 0,1 M sodium hydroxide, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions. Copper sampling tubes are unsuitable.

5.4.3.7 Analysis

5.4.3.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.4.3.7.1.1 Absorbing solution, 0,1 M sodium hydroxide.

5.4.3.7.1.2 Eluents, consisting of 0,1 M sodium hydroxide, 0,5 M sodium acetate or 0,5 % ethylene diamine.

5.4.3.7.1.3 Stock cyanide solution, ρ approximately 1 000 µg/ml CN^-.

Dissolve 1,25 g potassium cyanide in 500 ml 0,1 M sodium hydroxide.

5.4.3.7.1.4 Standard cyanide solutions

Dilute stock cyanide solution in 0,1 M sodium hydroxide contained in volumetric flasks and make up to volume in order to obtain several standard solutions. Prepare freshly each day.

5.4.3.7.2 Protocol

Flow rate should be set at 1 ml/min. The applied voltage setting is zero volts.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.4.3.8 Calibration

Standard cyanide solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared.

5.4.3.9 Calculations

Compare the peak area of the test solution corresponding to cyanide ions with those obtained for the calibration curve and calculate atmospheric concentrations using Formula 4, in 5.4.1.9.

5.4.3.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in 0,1 M NaOH solution.[1] For concentration around 7 mg/l, repeatability has been estimated as 4 % and reproducibility has been estimated as 18 %. For concentration around 33 mg/l, repeatability has been estimated as 2 % and reproducibility has been estimated as 9 %.

5.4.3.11 Trueness

Values found during interlaboratory trial were compared with technique by colourimetry (picric acid), see 5.4.2. Results were comparable for low concentration (at about 7 mg/l) at less than 13 % and for high concentration (at about 33 mg/l) at less than 4 %.

5.5 Hydrogen chloride and hydrogen bromide

5.5.1 Hydrogen chloride and hydrogen bromide by ion selective electrode (ISE)

5.5.1.1 Application and limitations

These are covered in 5.5.1.2 and 5.5.1.3.

5.5.1.2 Sensitivity and selectivity

This technique is capable of measuring 5 µg/ml of hydrogen chloride or hydrogen bromide in the test solution. However, mixtures of bromide and chloride will produce strong positive interference. Sulphide ions will also produce a strong positive interference.

If both bromide and chloride ions are present in the same test solution, then a total hydrogen halide concentration can be measured and expressed as halide equivalents, as the sensitivities to Cl^- and Br^- are equal.

5.5.1.3 Other considerations

Hydrogen cyanide, phosphates and total phosphorus can be quantified in the same test solution.

5.5.1.4 Analysis principles

Hydrogen chloride and/or bromide is collected in 0,01 M sodium hydroxide contained in fritted bubblers. Halide ions in the test solutions are measured by a determination of the electrode potentials with halide-selective and reference electrodes; see Reference [16].

5.5.1.5 Procedure

See Clause 4 general sampling requirements and C.7 for general principles of the method. However, for the analysis of hydrogen chloride and hydrogen bromide by ISE, the specific information in 5.5.1.6 to 5.5.1.10 is relevant.

5.5.1.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml of 0,01 M sodium hydroxide at 0,4 l/min for 4 min to 5 min and record the volume of test atmosphere sampled. These sampling parameters may be varied if necessary to suit conditions.

5.5.1.7 Analysis

5.5.1.7.1 Reagents

Analytical grade reagents should be used where possible.

5.5.1.7.1.1 Absorbing solution, 0,01 M sodium hydroxide

5.5.1.7.1.2 Standard chloride solution, approximately 200 µg/ml, equivalent to 5,6 µmol/ml

Dissolve 0,329 6 g sodium chloride in 1 000 ml 0,01 M sodium hydroxide.

5.5.1.7.1.3 Standard bromide solution, approximately 450 µg/ml equivalent to 5,6 µmol/ml

Dissolve 0,669 8 g sodium bromide 1 000 ml 0,01 M sodium hydroxide.

5.5.1.7.2 Protocol

Chloride and/or bromide in the solution are quantified against calibration standards (for example, 200 µg/ml Cl^-, equivalent to 5,6 µmol/ml Cl^-) according to the procedure specified by the manufacturer of the ISE instrument.

5.5.1.8 Calibration

Prepare calibration standards with the 0,01 M sodium hydroxide solution used as trapping medium. Generally, standards up to 5,6 µmol/ml are used. For everyday use, conditioning/calibration of the ISE is carried out with a single specified standard.

5.5.1.9 Calculations

For an ISE used as a halide analyser, the concentration of hydrogen chloride and/or hydrogen bromide in the test atmosphere is calculated from Formula (5):

$$\rho_{\mathrm{HX}} = \frac{\rho_{\mathrm{X}} \times V_{\mathrm{as}} \times \frac{M_{\mathrm{HX}}}{M_{\mathrm{X}}}}{V_{\mathrm{ta}} \times e} \qquad (5)$$

where

ρ_{HX}	is the hydrogen halide concentration, expressed in grams per litre of atmosphere;
ρ_{X}	is the halide ions concentration in the absorbing solution (chloride or bromide), expressed in grams of halide ions per litre of the solution;
$\frac{M_{\mathrm{HX}}}{M_{\mathrm{X}}}$	is the conversion factor from halide ion to hydrogen halide, equal to 1,028 for chloride (36,45 / 35,45) and 1,013 for bromide (80,9 / 79,9);
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.5.1.10 Repeatability and reproducibility

No data has been collected yet.

5.5.2 Hydrogen chloride and hydrogen bromide by high performance ion chromatography (HPIC)

5.5.2.1 Application and limitations

These are covered in 5.5.2.2 to 5.5.2.3.

5.5.2.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 0,05 µg/ml to 50 µg/ml as chloride or bromide ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to chloride and bromide ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions can also be analysed by this technique with appropriate trapping solutions.

Details on method sensitivity and selectivity can be found in Reference [17].

5.5.2.3 Other considerations

0,1 M sodium hydroxide may be used as the trapping solution. This will trap a wider range of anions and may allow longer storage of samples.

5.5.2.4 Analysis principles

The separation is carried out on an anion exchange column followed by conductimetric detection. It is necessary to use chemical or electrochemical suppression.

NOTE Hydrogen bromide can be also detected using a UV-visible detector. In this case, chemical or electrochemical suppression is not needed.

5.5.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of hydrogen chloride and hydrogen bromide by HPIC, the specific information in 5.5.2.6 to 5.5.2.11 is relevant.

5.5.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of distilled water, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.5.2.7 Analysis

5.5.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.5.2.7.1.1 **Absorbing solution,** distilled water or 0,1 M sodium hydroxide

5.5.2.7.1.2 **Eluents,** consisting of 0,001 7 M sodium hydrogen carbonate and 0,001 8 M sodium carbonate

5.5.2.7.1.3 **Stock chloride** or **bromide solution** ~1 000 µg/ml Cl$^-$ or Br$^-$

Dissolve sodium chloride (0,82 g) and/or bromide (0,64 g) in 500 ml distilled water.

5.5.2.7.1.4 **Standard chloride** or **bromide solution**

Dilute stock chloride or bromide solution in distilled water contained in a volumetric flask and make up to volume in order to obtain several standard solutions. Prepare freshly each day.

5.5.2.7.2 Protocol

The sample flow rate should be set at 2 ml/min.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.5.2.8 Calibration

Standard chloride or bromide solutions are injected into the system and the detector response is monitored by a chart recorder or an integrator. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared for the chloride and/or bromide.

5.5.2.9 Calculations

Compare the peak area of the test solution corresponding to chloride and bromide ions with those obtained for the calibration curve and calculate concentrations in the test atmosphere using Formula (5) in 5.5.1.9.

5.5.2.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in water solution.[1]

For hydrogen chloride, for concentration around 4 mg/l, repeatability has been estimated as 15 % and reproducibility has been estimated as 35 %. For concentration around 37 mg/l, repeatability has been estimated as 6 % and reproducibility has been estimated as 17 %. For concentration around 78 mg/l, repeatability has been estimated as 5 % and reproducibility has been estimated as 16 %.

For hydrogen bromide, for concentration around 2 mg/l, repeatability has been estimated as 6 % and reproducibility has been estimated as 15 %. For concentration around 34 mg/l, repeatability has been estimated as 4 % and reproducibility has been estimated as 15 %.

5.5.2.11 Trueness

Trueness of the method has been determined according to AFNOR NF X70-100-2[15] fire model. This determination has been performed using reference PVC at known quantity, with the hypothesis of conversion of chloride present in the polymer exclusively into hydrogen chloride. Theoretical yield of HCl is 0,584 kg/kg. Value found (average of 3 determination) was less than 1,1 % different from theoretical value.

5.5.3 Hydrogen chloride and hydrogen bromide by titrimetry

5.5.3.1 Application and limitations

These are covered in 5.5.3.2 to 5.5.3.4.

5.5.3.2 Sensitivity and selectivity

This technique is capable of measuring within the range over 4 µg/ml as chloride or bromide ions in solution. For measurement of high concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to chloride and bromide ions in aqueous solution. Important concentrations of hydrogen cyanide or sulphide ions can interfere. Details on method sensitivity and selectivity can be found in Reference [17].

5.5.3.3 Other considerations

Depending on proportions between Cl^- or Br^-, specific corrections may apply if both ions are present. The salts produced by precipitation reaction have different solubilities, according to Formula (6):

$$\frac{(K_s)_{\mathrm{AgBr}}}{(K_s)_{\mathrm{AgCl}}} = 5\times10^{-3} \tag{6}$$

There is a good separation, with error below 5 % when the bromide and chloride mass concentrations are such that:

$$0{,}1 \le \frac{\left[Cl^-\right]}{\left[Br^-\right]} < 5 \tag{7}$$

However, in other cases, measurement is less accurate due to precipitation of the two halides.

5.5.3.4 Analysis principles

Chloride and bromide ions in an acid solution form a precipitate with silver ions (from a $AgNO_3$ solution) according to the following reactions:

$$\begin{aligned} &Ag^{+} + Cl^{-} \rightarrow \underrightarrow{AgCl} \\ &Ag^{+} + Br^{-} \rightarrow \underrightarrow{AgBr} \end{aligned} \qquad (8)$$

The titration method is carried out by measuring variations in potential U using a combined silver electrode. The end of the reaction is indicated by a jump in potential caused by a sharp increase in the concentration of free silver ions. The equivalent measurement point for all chloride and bromide ions in solution is precisely determined on the potential curve U as function of the volume of $AgNO_3$ added to the solution.

If both of these ions are present in analysed solution, then the first jump in potential is associated with bromide ions and the second with chloride ions.

5.5.3.5 Procedure

See Clause 4 for principles of sampling and C.9 for general principles of the method. However, for the analysis of hydrogen chloride and hydrogen bromide by titrimetry, the specific information in 5.5.3.6 to 5.5.3.9 is relevant.

5.5.3.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of distilled water, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.5.3.7 Analysis

5.5.3.7.1 Reagents

5.5.3.7.1.1 Nitric acid, in around 69 % solution

5.5.3.7.1.2 Silver nitrate, solution with a known concentration c_{AgNO3} ranging between 0,02 mol/l and 0,10 mol/l

5.5.3.7.2 Protocol

Take a volume V_1, in millilitres, of the solution to be analysed and add a sufficient volume of nitric acid to obtain a final pH less than 2. Stir the mixture and titrate with appropriate silver nitrate solution. Plot the potential curve U as function of the volume of $AgNO_3$ added to the solution and determine the equivalent measurement volume V_{eq} for each jump in potential.

It is suitable to confirm association of jump potentials with chloride and bromide ions by addition of a known aliquote of each of these ions.

5.5.3.8 Calculations

If only one jump in potential is observed and confirmed to be associated with chloride ions by addition, the total mass, in milligrams, of HCl released during the test is equal to:

$$HCl(mg) = c_{\mathrm{AgNO_3}} \times V_{\mathrm{eq}} \times \frac{V}{V_1} \times M_{\mathrm{HCl}} \qquad (9)$$

where

$c_{\mathrm{AgNO_3}}$ is the concentration, expressed in moles per litre, of the silver nitrate solution;

V_{eq} is the volume of silver nitrate used at the inflexion point of the jump in potential corresponding to the chloride ions, expressed in millilitres;

V is the volume of the solution to be analysed, expressed in millilitres;

V_1 is the volume of the test sample, expressed in millilitres;

M_{HCl} is the molar mass of HCl (36,45 g/mol).

If only one jump in potential is observed and confirmed to be associated with bromide ions by addition, the total mass, in milligrams, of HBr released during the test is equal to:

$$HBr(mg) = c_{\mathrm{AgNO_3}} \times V_{\mathrm{eq}} \times \frac{V}{V_1} \times M_{\mathrm{HBr}} \qquad (10)$$

where

$c_{\mathrm{AgNO_3}}$ is the concentration, expressed in moles per litre, of the silver nitrate solution;

V_{eq} is the volume of silver nitrate used at the inflexion point of the jump in potential corresponding to the bromide ions, expressed in millilitres;

V is the volume of the solution to be analysed, expressed in millilitres;

V_1 is the volume of the test sample, expressed in millilitres;

M_{HBr} is the molar mass of HBr (80,9 g/mol).

If two jumps in potential are observed and confirmed to be associated respectively with bromide and chloride ions by additions, the interpretation is more complex and two cases are possible.

Case 1:

$$0{,}1 \le \frac{\left[Cl^-\right]}{\left[Br^-\right]} < 5$$

The total mass, in milligrams, of HBr and HCl released during the test is equal to:

$$HBr(mg) = c_{\mathrm{AgNO_3}} \times V_{\mathrm{eq1}} \times \frac{V}{V_1} \times M_{\mathrm{HBr}} \qquad (11)$$

$$HCl(mg)=c_{\mathrm{AgNO_3}}\times\left(V_{\mathrm{eq2}}-V_{\mathrm{eq1}}\right)\times\frac{V}{V_1}\times M_{\mathrm{HCl}} \qquad (12)$$

where

$c_{\mathrm{AgNO_3}}$	is the concentration, expressed in moles per litre, of the silver nitrate solution;
V_{eq1}	is the volume of silver nitrate used at the inflexion point of the first jump in potential corresponding to the bromide ions, expressed in millilitres;
V_{eq2}	is the volume of silver nitrate used at the inflexion point of the second jump in potential corresponding to the bromide and chloride ions, expressed in millilitres;
V	is the volume of the solution to be analyzed, expressed in millilitres;
V_1	is the volume of the test sample, expressed in millilitres;
M_{HCl}	is the molar mass of HBr (80,9 g/mol).

Case 2:

$$\frac{\left[Cl^-\right]}{\left[Br^-\right]}\leq 0{,}1 \quad \text{or} \quad \frac{\left[Cl^-\right]}{\left[Br^-\right]}>5$$

In this case, the direct titrimetric method cannot correctly measure the amounts of chloride and bromide ions. The measurement can be achieved using titrimetry by adding a known quantity of the minor halide and then subtracting this added halide from the result of the measurement.

5.5.3.9 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in water solution.[1]

For hydrogen chloride, for concentration around 4 mg/l, repeatability has been estimated as 8 % and reproducibility has been estimated as 10 %. For concentration around 16 mg/l, repeatability has been estimated as 2 % and reproducibility has been estimated as 10 %. For concentration around 165 mg/l, repeatability has been estimated as 3 % and reproducibility has been estimated as 4 %.

For hydrogen bromide, for concentration around 7 mg/l, repeatability has been estimated as 9 % and reproducibility has been estimated as 34 %. For concentration around 16 mg/l, repeatability has been estimated as 4 % and reproducibility has been estimated as 15 %.

5.6 Hydrogen fluoride

5.6.1 Hydrogen fluoride by an ion-selective electrode (ISE)

5.6.1.1 Application and limitations

The method described has been successfully and reliably used for the analysis of hydrogen fluoride in fire atmospheres as described in AFNOR NF X70-100-1[1] and in References [2],[18] and [19].

5.6.1.2 Sensitivity and selectivity

This technique is capable of measuring 0,1 µg/ml of hydrogen fluoride in the test solution.

The nature of the fluoride-selective electrode (lanthanide fluoride) and the buffer solution makes this method very specific for hydrogen fluoride.

Hydroxide ion and some metal ions can interfere, but addition of an ionic strength/pH-adjuster buffer compensates for these.

5.6.1.3 Other considerations

Sampling equipment shall be non-reactive to HF. Losses are minimal compared to other techniques.

A trapping medium of approximately 1 M sodium hydroxide contained in non-fritted impingers has been successfully used.

Lanthanide Fluoride (LaF) crystal surface of ISE is subject to aging, inducing degradation of sensitivity. Laboratory has to take care of this aspect and ISE need regular care by polishing crystal surface. Similar care concerns reference electrode.

5.6.1.4 Analysis principles

The test solution is buffered at pH 6 to pH 8 with HCl (6 mol/l) and fluoride ions measured by determination of the electrode potentials with fluoride selective and reference electrodes. Fluoride selective electrode is made of Lanthanide Fluoride (LaF) crystal. Reference electrode commonly used is classical Ag/AgCl electrode specific to complex solutions.

5.6.1.5 Procedure

See Clause 4 for general sampling requirements and C.7 for general principles of the method. However, for the analysis of hydrogen fluoride by an ISE, the information in 5.6.1.6 to 5.6.1.11 is relevant.

5.6.1.6 Sampling

Because of the reactivity of HF, sampling lines, probes etc. should be constructed from non-reactive materials (e.g. PTFE).

5.6.1.7 Analysis

5.6.1.7.1 Reagents

Analytical grade reagents should be used where possible.

5.6.1.7.1.1 Acetic acid for analysis

5.6.1.7.1.2 Total ionic strength activity buffer (TISAB), pH 5,5 as supplied by an electrode manufacturer or as prepared

Dissolve 37 g potassium chloride, 68 g sodium acetate and 36 g cyclohexylenediaminetetraacetic acid (CDTA) in water. Adjust to pH (5 ± 0,2) with hydrochloric acid. Dilute to 1 l.

5.6.1.7.1.3 Stock fluoride solution, ~100 µg/ml F^-

Dissolve 0,221 1 g sodium fluoride (dried at 105 °C for 2 h) in deionised water and dilute to 1 l.

5.6.1.7.1.4 Standard fluoride solutions

Dilute stock fluoride solution by adding known amounts (up to 12,5 ml) to 25 ml of the TISAB solution and make up to 50 ml with water, to obtain several standard solutions. Table 3 gives an example of the calibration curve data.

5.6.1.7.2 Protocol

Fluorine in the solution is quantified against calibration standards according to the procedure specified by the manufacturer of the ISE instrument.

5.6.1.8 Calibration

The calibration standards are prepared with two solutions having F⁻ concentrations of 1,9 × 10^{-1} µg/ml and 1,9 × 10^{2} µg/ml. Table 3 shows the calibration solutions which have been found to be suitable for a range of fluorine concentrations.

Table 3 — Preparation of fluorine calibration solutions

Reagent	**Concentration of calibration solution** µg/ml				
	1,9 × 10^{-2}	1,9 × 10^{-1}	1,9	1,9 × 10^{1}	1,9 × 10^{2}
	Volume of reagent added ml				
Solution with 1,9 × 10^{2} µg/ml fluoride	—	—	0,2	2	20
Solution with 1,9 × 10^{-1} µg/ml fluoride	2	20	—	—	—
Water	18	0	19,8	18	0
Buffer solution	20	20	20	20	20

The calibration is not linear, but logarithmic for large variations of concentrations, due to Nernst law.

5.6.1.9 Calculations

The concentration of hydrogen fluoride in the test atmosphere is calculated from Formula (13):

$$\rho_{\mathrm{HF}} = \frac{\rho_{\mathrm{F}} \times V_{\mathrm{as}} \times 1{,}053}{V_{\mathrm{ta}} \times e} \qquad (13)$$

where

ρ_{HF} is the hydrogen fluoride concentration, expressed in grams per litre of atmosphere;

ρ_{F} is the fluoride ions concentration in the absorbing solution, expressed in grams of fluoride ions per litre of the solution;

1,053 is the conversion factor from F to HF, equal to 20/19;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.6.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in 1 M NaOH solution.[1] For concentration around 1 mg/l, repeatability has been estimated as 7 % and reproducibility has been estimated as 25 %. For concentration around 357 mg/l, repeatability has been estimated as 2,5 % and reproducibility has been estimated as 6 %.

5.6.1.11 Trueness

Values found during interlaboratory trial were compared with technique by colourimetry (SPADNS) presented in AFNOR NF X70-100-1.[1] Results were comparable for high concentrations (at about 350 mg/l) at less than 2 %. Colourimetric method (SPADNS) is not suitable for low concentrations and is not considered in the present standard. This method allows repeatability around 6 % for high concentrations.[1]

5.6.2 Hydrogen fluoride by high performance ion chromatography (HPIC)

5.6.2.1 Application and limitations

See 5.6.2.2 and 5.6.2.3.

5.6.2.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 0,05 µg/ml to 50 µg/ml as fluoride ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to fluoride ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions can also be analysed by this technique with appropriate trapping solutions.

Details on method sensitivity and selectivity can be found in Reference [17].

5.6.2.3 Other considerations

Glass materials are not suitable because of the reactivity of HF. Non-reactive materials and equipment (e.g. PTFE or other plastics such as PVC and PE) shall be used. One M sodium hydroxide may be used as the trapping solution. This will trap a wider range of anions and can allow longer storage of samples. A 0,1 M sodium hydroxide solution may be used for low HF content solutions.

5.6.2.4 Analysis principles

The separation is carried out on an anion exchange column followed by conductimetric detection. Chemical suppression shall be used.

5.6.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of hydrogen fluoride by HPIC, the specific information in 5.6.2.6 to 5.6.2.10 is relevant.

5.6.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through three non-fritted impingers, each containing 75 ml of 1 M sodium hydroxide, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.6.2.7 Analysis

5.6.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.6.2.7.1.1 Absorbing solution, 1 M sodium hydroxide

5.6.2.7.1.2 **Eluents,** 0,000 3 mol/l sodium hydrogen carbonate and 0,002 7 mol/l sodium carbonate

5.6.2.7.1.3 **Stock fluoride solution,** ~1 000 µg/ml F^-

Dissolve 1,10 g sodium fluoride in 500 ml distilled water.

5.6.2.7.1.4 Standard fluoride solutions

Dilute stock solution in distilled water contained in volumetric flasks and make up to volume in order to obtain several calibration solutions. Prepare freshly each day.

5.6.2.7.2 Protocol

The sample flow rate should be set at 1,5 ml/min.

Before injecting the sample into the chromatograph, it is important that it be neutralized to avoid interferences with the F^- peak. Neutralization should be carried out with sulphuric acid or with pH adjustment cartridges.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.6.2.8 Calibration

Standard solutions of fluoride are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.6.2.9 Calculations

Compare the peak area of the test solution corresponding to fluoride ions with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (13) in 5.6.1.9.

5.6.2.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in 1 M NaOH solution.[2] For concentration around 1,03 mg/l, reproducibility has been estimated as 25 % (no repeatability was calculated). For concentration around 2,11 mg/l, reproducibility has been estimated as 17 % (no repeatability was calculated). For concentration around 14,8 mg/l, repeatability has been estimated as 6,1 % and reproducibility has been estimated as 8,1 %.

5.7 Oxides of nitrogen

Oxides of nitrogen are reactive species. There are a lot of equilibriums between them, depending on temperature and oxygen concentration. For example, nitric oxide (NO) reacts with oxygen to form nitrogen dioxide (NO_2). Depending on concentration, it should be assumed that the conversion of NO into NO_2 could be slow enough and neglected. Nevertheless, the user of analytical techniques described hereunder for nitric oxides has to take care of these considerations to interpret the result of its measurement and a possible deviation between gas expected and gas analysed.

5.7.1 Oxides of nitrogen by chemiluminescence

5.7.1.1 Application and limitations

Continuous or delayed analysis of oxides of nitrogen (NO_x) is possible, and the analysers are self-contained units containing all sampling, analysis and electronics hardware with direct readout of nitric oxide (NO) or combined NO and nitrogen dioxide (NO_2) from which the NO_2 concentration is estimated by difference. However, other nitrogen compounds can be detected as NO_x. The use of specifically designed modern instruments is recommended, even if some interference can occur.

5.7.1.2 Sensitivity and selectivity

Typical sensitivities routinely achievable are less than 1 µL/L NO_x. Nitrogen-containing compounds other than NO_2 can be detected as NO_x. In the NO_x “mode”, background interferences can be higher than 10 % of the reading.

In terms of selectivity, some interference can occur during the chemiluminescence analysis of NO_x in fire effluents.

— There are five main oxides: N_2O, NO, N_2O_3, NO_2 and N_2O_5 and chemical equilibriums between them. The measurement with a chemiluminescence apparatus represents, then, not solely the sum of NO + NO_2.

— H_2O, CO, CO_2, O_2 and HNO_3 have been shown to interfere significantly in the chemiluminescence analysis of nitrogen oxides in fire effluents. These interferences can be positive or negative, depending on the gases concerned. In the case of a delayed analysis with a sample collected in a gas bag, these interferences have been shown to decrease as the fire effluents (gas of interest and interfering gases) are diluted. Quantification of these interferences can be achieved only by separate analysis of the individual components using the same instrument.

5.7.1.3 Other considerations

Instruments with a molybdenum-based NO_2 to NO converter are recommended, as older instruments which use a carbon-based converter actually increase interferences and require periodic replacement of the carbon material.

Practical use of the instruments has shown that some drift of calibration can occur over relatively short time intervals (i.e. over the period of a fire test) and allowance should be for this. The use of oxygen as opposed to air in the ozone generator will lead to greater linearity and increased signal strength. Adoption of this procedure, however, requires oxygen-tolerant materials in the pumping systems.

Concentrations of both NO_2 and NO can be derived and it should be noted that these species are often required to be separately analysed, as the entity “NO_x” has limited value in toxic-hazard assessment.

5.7.1.4 Analysis principles

Chemiluminescence refers to the light emitted when nitric oxide (NO) reacts with ozone. Nitrogen dioxide (NO_2) is produced, a small proportion of which is in an electronically excited state which, on decaying, emits light with a wavelength of between approximately 0,6 µm and 3,0 µm.

The light intensity is measured by a photomultiplier and is proportional to the concentration of NO in the sample. NO_2 does not exhibit chemiluminescence and if analysis of NO_2 is required, the whole sample is passed through a “converter” where the NO_2 is reduced to NO. The resulting signal is then from both the original NO content and the NO_2 content, the latter being obtained by difference.

5.7.1.5 Procedure

The instruments normally need only to be powered for a short period to allow the converter to achieve the required temperature and to stabilize the electronics. A separate twin pumping system may be utilized for sample inlet and for the chemiluminescence detector when operated at low pressure.

See Clause 4 for principles of sampling and C.8 for general principles of the method. However, for the analysis of nitrogen oxides by chemiluminescence, the specific information in 5.7.1.6 to 5.7.1.11 is relevant.

5.7.1.6 Sampling

It is essential that the sample stream entering the instrument be treated to remove particulate and vapours condensable under ambient conditions. Simple in-line glass wool and calcium chloride filters have been found to be effective.

5.7.1.7 Analysis

There is no requirement for additional analytical procedures.

5.7.1.8 Calibration

Calibration is achieved through sampling standard gas mixtures of nitric oxide in air or nitrogen as supplied commercially. Standard gases of nitric oxide in nitrogen are preferred, as they are more stable in nitrogen than in air. For checking the converter efficiency and the response to NO_2, gas mixtures containing NO_2 can be obtained but they are only stable for relatively short periods. Zero gas can be "zero grade" air or nitrogen, commercially available.

5.7.1.9 Calculations

There are no calculations required for the NO concentration, which is provided as a direct readout or (more usually) through connection to electronic recording apparatus. For NO_2 the difference between the "NO_x" signal after conversion and the NO signal is an estimation of the NO_2 concentration.

Note that some instruments have a nonlinear scale but have the electronic output corrected to provide a linear signal. This linear signal ranges between fixed values and does not usually take into account the selected concentration range.

5.7.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated on yields in fire effluents from various materials[1] in AFNOR NF X70-100-2 fire model.[15]

For nitrogen monoxide (NO), for yield around 0.47 mg/g, repeatability has been estimated as 15 % and reproducibility has been estimated as more than 100 %. For yield around 1,54 mg/g, repeatability has been estimated as 53 % and reproducibility has been estimated as 94 %. For yield around 6,65 mg/g, repeatability has been estimated as 20 % and reproducibility has been estimated as 35 %.

For nitrogen oxides (NO_x), for yield around 0.82 mg/g, repeatability has been estimated as 21 % and reproducibility has been estimated as 75 %. For yield around 2,26 mg/g, repeatability has been estimated as 56 % and reproducibility has been estimated as 70 %. For yield around 11,25 mg/g, repeatability has been estimated as 21 % and reproducibility has been estimated as 53 %.

These repeatabilities and reproducibilities were determined on different sample tests and concern both the fire model and the analysis.

5.7.1.11 Trueness

Values found during interlaboratory trial were compared to technique by FTIR according to ISO 19702[4] using AFNOR NF X70-100-2 fire model.[15]

For nitrogen monoxide (NO), results were 60 % different for yields over 1 mg/g. For nitric oxides (considered for FTIR as the sum of NO, NO_2 and N_2O), results were 16 % different for yields over 10 mg/g.

5.7.2 Nitrogen dioxide by high performance ion chromatography (HPIC)

5.7.2.1 Application and limitations

See 5.7.2.2 and 5.7.2.3.

5.7.2.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 0,5 µg/ml to 50 µg/ml as nitrite and nitrate ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to nitrite and nitrate ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions may also be analysed at the same time.

Details on method sensitivity and selectivity can be found in Reference [17].

5.7.2.3 Other considerations

Only NO_2 can be analysed using HPIC. At working temperatures, NO_2 is in the form of a dimer N_2O_4, which dissociates in aqueous solution to NO_2^- and NO_3^- ions as shown in the following Formulae (14):

$$\begin{aligned} &2NO_2 \rightleftarrows N_2O_4 \\ &N_2O_4 + H_2O \rightleftarrows H^+NO_2^- + H^+NO_3^- \end{aligned} \qquad (14)$$

5.7.2.4 Analysis principles

The separation is carried out on an anion-exchange column followed by conductimetric detection. Chemical suppression shall be used.

5.7.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of nitrogen oxides by HPIC, the specific information in 5.7.2.6 to 5.7.2.10 is relevant:

5.7.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of 0,1 M sodium hydroxide, at 2 l/min for 20 min and record the total volume sampled.

5.7.2.7 Analysis

5.7.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.7.2.7.1.1 Absorbing solution, 0,1 M sodium hydroxide

5.7.2.7.1.2 Eluents, 0,001 7 M sodium hydrogen carbonate and 0,001 8 M sodium carbonate

5.7.2.7.1.3 Stock nitrite solution, approximately 1 000 µg/ml NO_2

Dissolve 0,75 g sodium nitrite in 500 ml distilled water.

5.7.2.7.1.4 Stock nitrate solution, approximately 1 000 µg/ml NO_3^-

Dissolve 0,69 g sodium nitrate in 500 ml distilled water.

5.7.2.7.1.5 Standard nitrite and nitrate solutions

Dilute the stock solution (5.7.2.7.1.3 or 5.7.2.7.1.4) in distilled water contained in volumetric flasks and make up to volume in order to obtain several calibration solutions. Prepare freshly each day.

5.7.2.7.2 Protocol

Flow rate should be set at 2 ml/min. Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.7.2.8 Calibration

Standard solutions of nitrite and nitrate are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.7.2.9 Calculations

Compare the peak area of the test solution corresponding to nitrite and nitrate ions with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (15):

$$\rho_{NO_2} = \frac{\left(\rho_{NO_3^-} \times \frac{M_{NO_2}}{M_{NO_3}} + \rho_{NO_2^-} \right) \times V_{as}}{V_{ta} \times e} \qquad (15)$$

where

ρ_{NO_2}	is the Nitrogen dioxide-equivalent concentration, expressed in grams per litre of atmosphere;
$\rho_{NO_2^-}$	is the nitrite ions concentration in the absorbing solution, expressed in grams of nitrite ions per litre of the solution;
$\rho_{NO_3^-}$	is the nitrate ions concentration in the absorbing solution, expressed in grams of nitrate ions per litre of the solution;
$\frac{M_{NO_2}}{M_{NO_3}}$	is the conversion factor from nitrates to nitrites, equal to 0,742;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.7.2.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a mixture issued from trapping fire effluents from various materials in 0,1 M NaOH solution.[1] For yield around 0,03 mg/g, repeatability has been estimated as 67 % and reproducibility has been estimated as more than 100 %. For yield around 0,87 mg/g, repeatability has been estimated as 36 % and reproducibility has been estimated as more than 100 %.

5.7.3 Nitrogen monoxide (Nitric oxide) by Gas-Filter correlation Infra-Red (Gfx-IR)

5.7.3.1 Application and limitations

The method provides a continuous analysis/monitoring capability for nitrogen monoxide, based on IR absorbance. The analysers are commonly self-contained instruments and include sample pumps, sample filtering, analysis hardware and electronics. Direct readout of nitrogen monoxide concentration is usually provided (either digital or analogue) together with an output for connecting recording devices.

5.7.3.2 Sensitivity and selectivity

Instruments are available for measuring nitrogen monoxide from below 1 µl/l to 5 000 µl/l (0,5 %) and more with a common resolution of 0,1 % of the selected range. Interferences with water have been described.

5.7.3.3 Other considerations

Multi-range instruments are available to cover all concentrations likely to be encountered in fire effluents, which will normally be on the range 1 µl/l to 1 000 µl/l. The method is non-destructive and the sample can be “passed on” for analysis of other compounds, taking into account that some components of the sample, e.g. particles, acid gases and water, can be lost in filtering and sampling.

5.7.3.4 Analysis principles

Gas-Filter correlation Infra-Red instruments operate by passing a wide-band beam of infrared (IR) radiation through rotating gas filters support, then through the sample. One of both rotating filters contains gas to be measured and the other contains nitrogen. The IR beam passes alternatively one or the other filters, then passes through a measurement cell. The IR differential signal measured between both positions of filter support is then detected and linked to nitric oxide concentration after suitable calibration.

5.7.3.5 Procedure

Normally, the instruments have only to be powered and the sampling line attached. It is usually convenient to set one concentration range within which the analysis is carried out and, therefore, it is desirable that the recording system used (e.g. data logger) has sufficient resolution for the chosen range.

5.7.3.6 Sampling

It is essential that the sample stream entering the instrument be treated to remove particulates, water and vapours condensable under ambient conditions. Simple in-line glass wool and calcium chloride filters have been found to be effective. Sample flow rates on the order of a few litres per minute are common and where the sampling point is many metres away from the instrument, a separately pumped, heated sample line with a higher flow rate can be used with the instrument sample port “teed” into this.

5.7.3.7 Analysis

There is no requirement for additional analytical procedures.

5.7.3.8 Calibration

Calibration is achieved through the introduction of standard (preferably certificated) gas mixtures and “zero gas” (which may be high-purity nitrogen) as provided commercially in pressurized cylinders. It is desirable to calibrate the instrument by introducing the sample both at the inlet port and at the remote sampling point. On multi-range instruments, it is usually possible to calibrate on the lowest range if more than one range is to be routinely used. However, calibration within the range to be used for measurement is recommended. It should be noted that the ambient concentration could vary significantly from these values depending on location. It is, therefore, important to recognize that a significant ambient reading can be obtained at the beginning of a fire experiment due to local conditions. The calibration and the analysis of the fire effluents shall be carried out using the same flow-rate through the analyser.

5.7.3.9 Calculations

There are no calculations required; the nitrogen monoxide concentration is obtained by direct readout or (more usually) through a connection to an electronic recording apparatus.

Note that some instruments have a nonlinear scale but have the electronic output corrected to provide a linear signal. This linear signal ranges between fixed values and usually does not take account of the selected concentration range.

5.7.3.10 Repeatability and reproducibility

Repeatability was estimated on yields in fire effluents from various materials[1] in AFNOR NF X70-100-2 fire model.[15] No determination of reproducibility is available yet.

For yield around 0,48 mg/g, repeatability has been estimated as 48 %. For yield around 1,05 mg/g, repeatability has been estimated as 42 %. For yield around 5,46 mg/g, repeatability has been estimated as 35 %.

These repeatabilities were determined on different sample tests and concern both the fire model and the analysis.

5.7.3.11 Trueness

Values found during interlaboratory trial were compared with technique by FTIR according to ISO 19702[4] using AFNOR NF X70-100-2 fire model.[15] Results were 30 % different for yields over 4 mg/g.

5.8 Acrolein

5.8.1 Acrolein by colourimetry

5.8.1.1 Application and limitations

See 5.8.1.2 to 5.8.1.4.

5.8.1.2 Sensitivity and selectivity

This technique is capable of measuring 0,5 µg acrolein in the aliquot taken.

Small positive interferences arise from 1,3-pentadiene, crotonaldehyde, furan and furfuraldehyde. There is no interference from formaldehyde or acetaldehyde.

5.8.1.3 Other considerations

The bisulphite test solution can be used to analyse for both acrolein and formaldehyde.

5.8.1.4 Analysis principles

Acrolein is collected in 1 % sodium metabisulphite contained in fritted bubblers, then analysed colourimetrically within a few hours of sampling by the modified mercuric chloride/hexylresorcinol procedure.

The reaction of acrolein, with 4-hexylresorcinol in ethyl alcohol-trichloroacetic acid solvent medium in the presence of mercuric chloride, results in a blue product with a strong absorption maximum at approximately 605 nm; see References [20],[21].

5.8.1.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of acrolein by colourimetry, the specific information in 5.8.1.6 to 5.8.1.10 is relevant.

5.8.1.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml of a 1 % sodium metabisulphite absorbing solution at 0,4 l/min for 4 min to 5 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit the conditions.

5.8.1.7 Analysis

5.8.1.7.1 Reagents

Analytical grade reagents must be used.

5.8.1.7.1.1 Absorbing solution

Dissolve 10 g sodium metabisulphite in1 l distilled water. Prepare freshly each day.

5.8.1.7.1.2 Ethanolic mercuric chloride solution, 0,6 %

Dissolve 1,5 g mercuric chloride in 250 ml 95 % ethanol.

5.8.1.7.1.3 Solution of mercuric chloride in 4-hexylresorcinol

Dissolve 1,5 g 4-hexylresorcinol in 30 ml of reagent (5.8.1.7.1.2). This solution is stable for three weeks if kept refrigerated.

5.8.1.7.1.4 Saturated trichloroacetic acid (TTCA) solution

Add 5,1 ml distilled water and 5,6 ml ethanol to 100 g TCAA and warm until dissolved.

5.8.1.7.1.5 Standard acrolein solution, 16,8 µg/ml

Dissolve 5,0 µl acrolein approximately 2 ml in ethanol contained in a vial and immediately add to 250 ml 1,0 % sodium metabisulphite solution contained in a conical flask. Prepare freshly every day.

5.8.1.7.2 Protocol

To a semi-micro test tube, add an aliquot of test solution containing up to 20 µg acrolein. Add 1 % sodium metabisulphite (if necessary) to give a total volume of 2,4 ml. Then add in turn

> 0,6 ml of mercuric chloride/n-hexylresorcinol reagent,
>
> 3,0 ml of the TCAA reagent.

Stopper, clip and shake test tube and immerse in a water bath at 60 °C for 45 min. Remove from water bath, cool and centrifuge. After a total reaction time of 90 min, read the absorbance in a 1 cm cell at approximately 605 nm (corresponding to the maximum absorbance of the standard solution) against a reagent blank solution.

5.8.1.8 Calibration

Prepare calibration standards containing 10,1 µg and 20,2 µg acrolein using 0,6 ml and 1,2 ml aliquots of the standard acrolein solution (see 5.8.1.7.1.5). Make up the volume to 2,4 ml with 1 % sodium metabisulphite and develop the colour as described above. Standards should be included with each set of analyses.

5.8.1.9 Calculation

Compare the absorbance of the test solutions with that obtained for the calibration standards and calculate atmospheric concentrations using Formula (16):

$$\rho_{\mathrm{a}} = \frac{\rho_{\mathrm{as}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \tag{16}$$

where

ρ_{a} is the acrolein concentration, expressed in grams per litre of atmosphere;

ρ_{as} is the acrolein concentration in the absorbing solution, expressed in grams of acrolein per litre of the solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.8.1.10 Repeatability and reproducibility

No data are available yet.

5.8.2 Acrolein by high performance liquid chromatography (HPLC)

5.8.2.1 Application and limitations

See 5.8.2.2 to 5.8.2.3.

5.8.2.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of acrolein (in the form of hydrazones) in solution.

No known interference except with possible co-elutants.

5.8.2.3 Other considerations

Chloroform used to extract the 2,4-dinitrophenylhydrazone from the adsorbing solution is miscible with the eluent at best in a 1:10 ratio. The solution of extraction has to be diluted at least 10 times in the eluent before injection.

This method permits the analysis of several other aldehydes and ketones at the same time. A sufficient running time (about 30 min) is necessary to ensure all the peaks have been eluted.

It should also be noted that the trapping solution is very reactive towards ketones and aldehydes. The laboratory environment and apparatus should therefore be free from these compounds.

5.8.2.4 Analysis principles

Acrolein is converted to its 2,4-dinitrophenylhydrazone which is not soluble in an aqueous medium. 2,4-dinitrophenylhydrazone is then extracted with chloroform before being analysed.

The separation is carried out on a reverse-phase column (for example, C18) followed by ultraviolet detection or by atmospheric pressure chemical ionization-mass spectrometry (APCI-MS); see References [22],[23],[24],[25],[26].

5.8.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of acrolein by HPLC, the specific information in 5.8.2.6 to 5.8.2.10 is relevant.

5.8.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through 2 non-fritted impingers, containing 250 ml of 2 M chlorhydric acid saturated with 2,4-dinitrophenylhydrazine at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary to suit conditions.

Extract the 2,4-dinitrophenylhydrazone with 2 aliquots of 250 ml of chloroform.

5.8.2.7 Analysis

5.8.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.8.2.7.1.1 Absorbing solution, 2 M chlorhydric acid saturated with 2,4-dinitrophenylhydrazine

5.8.2.7.1.2 Eluent, methanol/water, 65/35

5.8.2.7.1.3 Chloroform

5.8.2.7.1.4 Stock DNP-acrolein solution, approximately 100 µg/ml

Dissolve 0,01 g dry and purified hydrazone derivative of acrolein in 100 ml of chloroform.

5.8.2.7.1.5 Standard solutions

Dilute stock solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 10 mg/l. Prepare freshly every day.

5.8.2.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 360 nm (240 nm can also be suitable if the solution does not contain other absorbing compounds that interfere).

Dilute the extracted unknown solution at least 10 times with eluent.

Analysis of the unknown solution can then be carried out. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.8.2.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared.

5.8.2.9 Calculations

Compare the peak area of the test solution corresponding to hydrazone derivative of acrolein with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (17):

$$\rho_{\text{a}} = \frac{\rho_{\text{DNP-acr.}} \times V_{\text{as}} \times 0{,}237}{V_{\text{ta}} \times e} \tag{17}$$

where

ρ_{a}	is the acrolein concentration, expressed in grams per litre of atmosphere;
$\rho_{\text{DNP-acr.}}$	is the hydrazone concentration in the absorbing solution, expressed in grams of hydrazone per litre of the solution;
0,237	is the conversion factor from DNP-acrolein to acrolein equal to 56/236;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.8.2.10 Repeatability and reproducibility

Repeatability was estimated on yields in fire effluents[1] in AFNOR NF X70-100-2 fire model.[15] For yield around 0,07 mg/g, repeatability has been estimated as 130 % and reproducibility has been estimated as 228 %. For yield around 3,54 mg/g, repeatability has been estimated as 2,5 % and reproducibility has been estimated as 63 %.

5.8.3 Acrolein by solid-state trapping and HPLC

5.8.3.1 Application and limitations

See 5.8.3.2 to 5.8.3.3.

5.8.3.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of acrolein (in the form of hydrazone) in solution.

No known interference except with possible co-elutants.

5.8.3.3 Other considerations

Acetonitrile or chloroform used to extract the 2,4-dinitrophenylhydrazone from the adsorbing solution has to be diluted at least 10 times in the eluent before injection.

This method permits the analysis of several other aldehydes and ketones at the same time. A sufficient running time (about 30 min) is necessary to ensure all the peaks have been eluted.

5.8.3.4 Analysis principles

Acrolein is sampled on cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH). Due to their reactivity, aldehydes have to be stabilized prior to analysis. During sampling, they are thus derivatized by reaction with DNPH in order to form hydrazones.

The cartridges are subsequently extracted with acetonitrile. The collected hydrazones are separated by reversed-phase column (for example, C18) in a High Performance Liquid Chromatography (HPLC).

The column is followed by ultraviolet detection or by atmospheric pressure chemical ionization-mass spectrometry (APCI-MS); see References [22],[23],[24],[25],[26]. This method is also suitable for all other aldehydes and ketones.

5.8.3.5 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through 2 cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) placed in series at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary to suit conditions.

Extract the 2,4-dinitrophenylhydrazone with 2 aliquots of 20 ml of acetonitrile or chloroform.

5.8.3.6 Analysis

The analysis is performed as stated in 5.8.2.7.

5.8.3.7 Calibration

The calibration is performed as stated in 5.8.2.8.

5.8.3.8 Calculations

Calculation is performed as stated in 5.8.2.9.

5.8.3.9 Repeatability and reproducibility

No data has been collected yet.

5.8.4 Acrolein by GC-MS in gas-phase

5.8.4.1 Application and limitations

Acrolein is collected in gas phase, then analysed by GC-MS.

5.8.4.2 Sensitivity and selectivity

The limit of detection is 0,04 µl/l of acrolein in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in carbon disulphide, benzene, toluene, xylene, styrene, acrylonitrile, formaldehyde and acetaldehyde.

5.8.4.3 Analysis principles

Acrolein is collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS “quadrupole” mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.8.4.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.8.4.5 Analysis

5.8.4.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.8.4.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with an stainless steel loop of 0.5 ml.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.8.4.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.8.4.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are 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-l 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. Fragmentation of acrolein is described in the following table:

Table 4 — Fragmentation of acrolein in analytical conditions proposed

Compound	Principal peak (parent) at m/z (normalized 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

5.8.4.6 Calibration

Standard gas mixtures are prepared by injecting acrolein into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid acrolein and samples are then taken from the bag for analysis in the GC-MS.

Acrolein is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below.

Table 5 — Preparation of gas standards of acrolein

Reagent	**Volume of acrolein introduced** µl									
	1,0	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L									
Mass of acrolein introduced in gas bag (mg)	0.84	1.68	4.21	8.41	16.8	21.0	42.1	84.1	168	210
Concentration of acrolein (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	21.0	42.1	105	210	421	526	1051	2102	4205	5256

If other gases are analysed at the same time, it is often needed to prepare them in separate gas standards because of the immiscibility of some compounds.

5.8.4.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.8.4.8 Repeatability and reproducibility

No data has been collected yet.

5.9 Formaldehyde

5.9.1 Formaldehyde by colourimetry

5.9.1.1 Application and limitations

See 5.9.1.2 and 5.9.1.3.

5.9.1.2 Sensitivity and selectivity

This technique is capable of measuring 0,2 µg formaldehyde in the aliquot taken.

There is very little interference from other aldehydes. Saturated aldehydes give less than 0,01 % positive interference. Unsaturated aldehydes, e.g. acrolein, result in a few percent positive interference. Ethanol and higher molecular weight alcohols and olefins in mixtures with formaldehyde are negative interferences.[29]

5.9.1.3 Other considerations

The bisulphite test solution can be used to analyse for both formaldehyde and acrolein.

5.9.1.4 Analysis principles

Formaldehyde is collected in 1 % sodium metabisulphite contained in fritted bubblers, then analysed colourimetrically within 24 h of sampling using a chromotropic acid (CTA) reagent.

Chromotropic acid (1,8-dihydroxy-naphthalene-3,6-disulfonic acid) reacts with formaldehyde, in the presence of strong sulphuric acid, to give a reddish violet hydroxydiphenylmethane derivative which is acid-soluble. In a second reaction stage, this derivative is converted into a deeply coloured quinoid product; see References [1],[29],[30].

5.9.1.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of formaldehyde by colourimetry, the specific information in 5.9.1.6 to 5.9.1.10 is relevant.

5.9.1.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml of a 1 % sodium metabisulphite absorbing solution at 0,4 l/min for 4 min to 5 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.9.1.7 Analysis

5.9.1.7.1 Reagents

Analytical grade reagents should be used where possible.

5.9.1.7.1.1 Absorbing solution

Dissolve 10 g sodium metabisulphite in 1 l distilled water. Prepare freshly each day.

5.9.1.7.1.2 Chromotropic acid solution, 5 %

Dissolve 5 g chromotropic acid in 100 ml distilled water. Prepare freshly each day.

5.9.1.7.1.3 Concentrated sulphuric acid, “AnalaR” grade

5.9.1.7.1.4 Stock formaldehyde solution, approximately 5 000 µg/ml.

Dissolve 13,5 ml formalin solution (37 % to 40 %) in distilled water and dilute to 1 l. Determine the actual concentration using a standard 0,05 M iodine solution back-titrated against a 0,1 M sodium thiosulphite solution with a starch indicator. This solution is stable if refrigerated.

5.9.1.7.1.5 Standard formaldehyde solution, 10 µg/ml.

Add 2,0 ml stock solution (5.9.1.7.1.4) to 1 % sodium metabisulphite and make up to 1 l. Prepare freshly each day.

5.9.1.7.2 Protocol

To a boiling-tube, add an aliquot of test solution containing up to 20 µg formaldehyde. Add 1 % sodium metabisulphite (if necessary) to give a total volume of 2,5 ml. Then add in turn with shaking

0,5 ml 5 % chromotropic acid,

5 ml concentrated sulphuric acid.

Immerse in boiling water for 10 min, cool, and read the absorbance at approximately 570 nm (corresponding to the maximum absorbance of the standard solution) in a 1 cm cell against the reagent blank.

5.9.1.8 Calibration

Prepare calibration standards containing 5 µg, 10 µg, 15 µg and 20 µg formaldehyde using 0,5 ml, 1,0 ml, 1,5 ml and 2,0 ml aliquots, respectively of the standard formaldehyde solution 5.9.1.7.1.5 Make the volume up to 2,5 ml with 1 % sodium metabisulphite and develop the colour as described above.

The calibration gives a reproducible curve for a given batch of CTA; therefore, it should not be necessary to include standards with each set of analyses.

5.9.1.9 Calculation

Compare the absorbance of the test solutions with those obtained for the calibration standards and calculate atmospheric concentrations using Formula (18):

$$\rho_{\mathrm{f}} = \frac{\rho_{\mathrm{fs}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \qquad (18)$$

where

ρ_{f} is the formaldehyde concentration, expressed in grams per litre of atmosphere;

ρ_{fs} is the formaldehyde concentration in the absorbing solution, expressed in grams of formaldehyde per litre of the solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.9.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a solution issued from trapping fire effluents from various materials in absorbing solution.[1] For yield around 0,49 mg/g, repeatability has been estimated as 51 % and reproducibility has been estimated as more than 100 %. For yield around 0,67 mg/g, repeatability has been estimated as 10 % and reproducibility has been estimated as more than 100 %. For yield around 8,29 mg/g, repeatability has been estimated as 6 % and reproducibility has been estimated close to 100 %. For yield around 24,46 mg/g, repeatability has been estimated as 5 % and reproducibility has been estimated as 90 %.

5.9.2 Formaldehyde by high performance liquid chromatography (HPLC)

5.9.2.1 Application and limitations

See 5.9.2.2 and 5.9.2.3.

5.9.2.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of formaldehyde (in the form of hydrazone) in solution.

No known interference except with possible co-elutants.

5.9.2.3 Other considerations

Chloroform used to extract the 2,4-dinitrophenylhydrazone from the adsorbing solution is miscible with the eluent at best in a 1:10 ratio. The solution of extraction has to be diluted at least 10 times in the eluent before injection.

This method permits the analysis of several other aldehydes and ketones at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

It should also be noted that the trapping solution is very reactive towards ketones and aldehydes. The laboratory environment and apparatus should therefore be free from these compounds.

5.9.2.4 Analysis principles

Formaldehyde is converted into its 2,4-dinitrophenylhydrazone which is not soluble in an aqueous medium; the 2,4-dinitrophenylhydrazone is then extracted with chloroform before being analysed.

The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.9.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of formaldehyde by HPLC, the specific information in 5.9.2.6 to 5.9.2.10 is relevant.

5.9.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of 2 M chlorhydric acid saturated with 2,4-dinitrophenylhydrazine, at 2 l/min for 20 min and record the total volume sampled.

Extract the 2,4-dinitrophenylhydrazone two times with 250 ml of chloroform.

5.9.2.7 Analysis

5.9.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.9.2.7.1.1 Absorbing solution, 2 M chlorhydric acid saturated with 2,4-dinitrophenylhydrazine.

5.9.2.7.1.2 Eluent, methanol/water, 65/35.

5.9.2.7.1.3 Chloroform

5.9.2.7.1.4 Stock DNP-formaldehyde solution, approximately 100 µg/ml.

Dissolve 0,01 g of the dry and purified hydrazone derivative of formaldehyde in 100 ml of chloroform.

5.9.2.7.1.5 Standard solutions

Dilute stock solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 10 mg/l. Prepare freshly every day.

5.9.2.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 360 nm (240 nm can also be suitable if the solution does not contain absorbing interfering compounds).

Dilute the extracted unknown solution at least 10 times with eluent.

Analysis of the unknown solution can then be carried out. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.9.2.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.9.2.9 Calculations

Compare the peak area of the test solution corresponding to the hydrazone derivative of formaldehyde with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (19):

$$\rho_\mathrm{f} = \frac{\rho_\mathrm{DNP\text{-}f.} \times V_\mathrm{as} \times 0{,}143}{V_\mathrm{ta} \times e} \qquad (19)$$

where

ρ_f is the formaldehyde concentration, expressed in grams per litre of atmosphere;

$\rho_\mathrm{DNP\text{-}f.}$ is the hydrazone concentration in the absorbing solution, expressed in grams of hydrazone per litre of the solution;

0,143 is the conversion factor from DNP-formaldehyde to formaldehyde equal to 30/210;

V_as is the total volume, expressed in litres, of absorbing solution;

V_ta is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.9.2.10 Repeatability and reproducibility

Repeatability was estimated on yields in fire effluents[1] in AFNOR NF X70-100-2 fire model.[15] For yield around 2,17 mg/g, repeatability has been estimated as 10 % and reproducibility has been estimated as 46 %. For yield around 4,70 mg/g, repeatability has been estimated as 2 % and reproducibility has been estimated as 42 %.

5.9.3 Formaldehyde by solid-state trapping and HPLC

5.9.3.1 Application and limitations

See 5.9.3.2 to 5.9.3.3.

5.9.3.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of formaldehyde (in the form of hydrazone) in solution.

No known interference except with possible co-elutants.

5.9.3.3 Other considerations

Acetonitrile or chloroform used to extract the 2,4-dinitrophenylhydrazone from the adsorbing solution has to be diluted at least 10 times in the eluent before injection.

This method permits the analysis of several other aldehydes and ketones at the same time. A sufficient running time (about 30 min) is necessary to ensure all the peaks have been eluted.

5.9.3.4 Analysis principles

Formaldehyde is sampled on cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH). Due to their reactivity, aldehydes have to be stabilized prior to analysis. During sampling, they are thus derivatized by reaction with DNPH in order to form hydrazones.

The cartridges are subsequently extracted with acetonitrile. The collected hydrazones are separated by reversed-phase column (for example, C18) in a High Performance Liquid Chromatography (HPLC). The column is followed by ultraviolet detection or by atmospheric pressure chemical ionization-mass spectrometry (APCI-MS); see References [2],[22],[23],[24],[25]. This method is also suitable for all other aldehydes and ketones.

5.9.3.5 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through 2 cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) placed in series at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary to suit conditions.

Extract the 2,4-dinitrophenylhydrazone with 2 aliquots of 20 ml of acetonitrile or chloroform.

5.9.3.6 Analysis

The analysis is performed as stated in 5.9.2.7.

5.9.3.7 Calibration

The calibration is performed as stated in 5.9.2.8.

5.9.3.8 Calculations

Calculation is performed as stated in 5.9.2.9.

5.9.3.9 Repeatability and reproducibility

No data has been collected yet.

5.9.4 Formaldehyde by GC-MS

Method presented in 5.8.2 for acrolein is applicable for formaldehyde.

No data on repeatability and reproducibility have been collected yet.

5.10 Acetaldehyde

5.10.1 Acetaldehyde by HPLC

Methods presented in 5.8.2 for acrolein and in 5.9.2 for formaldehyde is applicable for acetaldehyde.

Repeatability was estimated on yields in fire effluents in AFAP3 fire model[2] on HPLC and GC-MS techniques. Results are available in Reference [12].

5.10.2 Acetaldehyde by solid-state trapping and HPLC

Methods presented in 5.8.3 for acrolein and in 5.9.3 for formaldehyde is applicable for acetaldehyde.

No data on repeatability and reproducibility have been collected yet.

5.10.3 Acetaldehyde by GC-MS

Method presented in 5.8.2 for acrolein is applicable for acetaldehyde.

No data on repeatability and reproducibility have been collected yet.

5.11 Total aldehydes by colourimetry

5.11.1 Application and limitations

See 5.11.2 and 5.11.3.

5.11.2 Sensitivity and selectivity

This technique is capable of measuring 0,2 µg total aliphatic aldehydes in the aliquot taken.

Aromatic amines, iminoheterocyclics, carbazoles, azo dyes, stilbenes, Schiff bases, the aliphatic aldehydes, 2,4-dinitrophenylhydrazones, and compounds containing the p-hydroxystyryl group react with 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) to produce coloured products. Most of these compounds are not gaseous or water-soluble and, consequently, should not interfere with the analyses.[31]

5.11.3 Other considerations

An aliquot of test solution can also be analysed for formaldehyde using a chromotropic acid reagent.

Stability has not been verified, but it is thought that any acrolein present in the fire atmosphere test solution decays within 24 h. However, it has been reported that formaldehyde in 0,05 % MBTH is fairly stable for up to 13 days.[31]

5.11.4 Analysis principles

Aliphatic aldehydes are collected in 0,05 % aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) solution contained in fritted bubblers. Oxidation of the resulting azine by a ferric chloride-sulfuric acid solution leads to the formation a blue cationic dye, which is measured in a spectrophotometer. The aldehydes are expressed as equivalents of formaldehyde; see References [31],[32],[33].

5.11.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of total aldehydes by colourimetry, the specific information in 5.11.6 to 5.11.9 is relevant.

5.11.6 Sampling

Pump the fire atmosphere through a fritted bubbler, containing a 20 ml 0,05 % MBTH absorbing solution, at 0,1 l/min for 4 min to 5 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit the conditions.

5.11.7 Analysis

5.11.7.1 Reagents

Analytical grade reagents should be used where possible.

5.11.7.1.1 Absorbing solutions

Dissolve 0,5 g 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) in 1 l distilled water.

5.11.7.1.2 Oxidizing solution

Add 1,5 g sulphuric acid and1 g ferric chloride to 100 ml distilled water.

5.11.7.1.3 Stock formaldehyde solution, approximately 5 000 µg/ml

Dissolve 13,5 ml formalin solution (37 % to 40 %) in distilled water and dilute to 1 l. Determine the actual concentration using a standard 0,05 M iodine solution back-titrated against a 0,1 M sodium thiosulphite solution with a starch indicator. This solution is stable if refrigerated.

5.11.7.1.4 Intermediate standard solution, approximately 100 µg/ml.

Dilute 1,0 ml stock solution (5.11.7.1.3) to 50 ml with distilled water.

5.11.7.1.5 Standard formaldehyde solution, approximately 10 µg/ml.

Dilute 5 ml intermediate standard solution (5.11.7.1.4) to 50 ml with 0,05 % MBTH. Leave 1 h for formaldehyde to react with MBTH before carrying out calibration.

5.11.7.2 Protocol

Leave test solution standing for at least 1 h after sampling to react with the MBTH before carrying out the analysis.

To a boiling-tube, add an aliquot of test solution containing up to the equivalent of 10 µg formaldehyde. Add 0,05 % MBTH (if necessary) to give a total volume of 5 ml. Add 1 ml ferric chloride-sulfuric acid oxidizing solution and mix thoroughly. Leave standing for at least 10 min, then read the absorbance at approximately 628 nm (corresponding to the maximum absorbance of the standard solution) in a 5 mm cell against a reagent blank solution.

5.11.8 Calibration

Prepare calibration standards containing 2 µg, 4 µg, 6 µg, 8 µg and 10 µg formaldehyde using 0,2 ml, 0,4 ml, 0,6 ml, 0,8 ml and 1,0 ml aliquots of the standard formaldehyde solution (5.11.7.1.5). Make up the volume to 5 ml with 0,05 % MBTH and develop the colour described above.

5.11.9 Calculation

Compare the absorbance of the test solutions with that obtained for the calibration standards and calculate atmospheric concentrations using Formula (20):

$$\rho_{\text{aa}} = \frac{\rho_{\text{aas}} \times V_{\text{as}}}{V_{\text{ta}} \times e} \qquad (20)$$

where

ρ_{aa} is the concentration, expressed in grams equivalent of formaldehyde per litre of atmosphere;

ρ_{aas} is the concentration of the absorbing solution, expressed in grams per litre of aldehydes as equivalent of formaldehyde;

V_{as} is the total volume, expressed litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of trapping system experimentally determined using a train of two traps.

5.11.9.1 Repeatability and reproducibility

No data has been collected yet.

5.12 Sulfur dioxide by high performance ion chromatography (HPIC)

5.12.1 Application and limitations

See 5.12.2 and 5.12.3.

5.12.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 0,5 µg/ml to 50 µg/ml as sulfate ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to sulfate ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions can also be analysed at the same time.

Details on method sensitivity and selectivity can be found in Reference [1].

5.12.3 Other considerations

An oxidizing absorbing solution is required in order to keep SO_2 in the form of sulfate ions and prevent the formation of sulphite ions. Hydrogen peroxide solution has been found suitable.

5.12.4 Analysis principles

The separation is carried out on an anion exchange column followed by conductimetric detection. It is necessary to use chemical suppression.

5.12.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of sulfur dioxide by HPIC, the specific information in 5.12.6 to 5.12.9 is relevant.

5.12.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of absorbing solution, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit the conditions.

5.12.7 Analysis

5.12.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.12.7.1.1 Absorbing solution, water with 0,2 % H_2O_2 (30 %)

5.12.7.1.2 Eluents, 0,001 7 M sodium hydrogen carbonate and 0,001 8 M sodium carbonate

5.12.7.1.3 Stock sulfate solution, approximately 1 000 µg/ml

Dissolve 0,62 g sodium sulfate in 500 ml of water.

5.12.7.1.4 Standard sulfate solutions

Dilute stock solution in distilled water contained in volumetric flasks and make up to volume in order to obtain several calibration solutions. Prepare freshly each day.

5.12.7.2 Protocol

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.12.8 Calibration

Standard solutions of sulphates are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared.

5.12.9 Calculations

Compare the peak area of the test solution corresponding to sulfate ions with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (21):

$$\rho_{SO_2} = \frac{\rho_{SO_4^{2-}} \times V_{as} \times 0{,}667}{V_{ta} \times e} \tag{21}$$

where

ρ_{SO_2}	is the sulfur dioxide concentration, expressed in grams per litre of atmosphere;
$\rho_{SO_4^{2-}}$	is the sulfate ions concentration in the absorbing solution, expressed in grams of sulfate ions per litre of the solution;
0,667	is the conversion factor from sulfate to SO_2 equal to 64/96;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.12.9.1 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a solution issued from trapping fire effluents from various materials in hydrogen peroxide solution.[1] For concentration around 3 mg/l, repeatability has been estimated as 133 % and reproducibility has been estimated as more than 300 %. For concentration around 19 mg/l, repeatability has been estimated as 21 % and reproducibility has been estimated as 100 %.

5.13 Carbon disulfide by GC-MS in gas phase

5.13.1 Application and limitations

Carbon disulfide is collected in gas phase, then analysed by GC-MS. GC/FPD has been also used.[2] Infrared techniques can also be used to measure carbon disulfide concentrations.[34]

5.13.2 Sensitivity and selectivity

The limit of detection is 1 µl/l of carbon disulfide in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in acrolein, benzene, toluene, xylene, styrene, acrylonitrile, formaldehyde and acetaldehyde.

5.13.3 Analysis principles

Carbon disulfide is collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS “quadrupole” mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.13.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.13.5 Analysis

5.13.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.13.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with a stainless steel loop of 0.5 ml.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then 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).

5.13.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.13.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of a known quantity of carbon disulfide in a 40-l 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. Fragmentation of carbon disulfide is described in the following table:

Table 6 — Fragmentation of acrolein in analytical conditions proposed

Compound	Principal peak (parent) at m/z (normalized 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 disulfide	76	No other important fragments	2.9	76

5.13.6 Calibration

Standard gas mixtures are prepared by injecting carbon disulfide into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid carbon disulfide and samples are then taken from the bag for analysis in the GC-MS.

Carbon disulfide is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below:

Table 7 — Preparation of gas standards of carbon disulfide

Reagent	**Volume of carbon disulfide introduced** µl								
	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L								
Mass of carbon disulfide introduced in gas bag (mg)	2.53	6.32	12.6	25.3	31.6	63.2	126	253	316
Concentration of carbon disulfide (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	63.2	158	316	632	789	1579	3158	6315	7894

If other gases are analysed at the same time, it is often needed to prepare them in separate standards because of the immiscibility of some compounds.

5.13.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.13.8 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model.[2] For yield around 0,8 mg/g, repeatability has been estimated as 21 % and reproducibility has been estimated as 142 %. For yield around 1,5 mg/g, repeatability has been estimated as 18 % and reproducibility has been estimated as 261 %.[12]

These results include repeatability and reproducibility of the fire model.

5.14 Hydrogen sulphide

5.14.1 Hydrogen sulphide by HPIC

5.14.1.1 Application and limitations

These are covered in 5.14.1.2 and 5.14.1.3.

5.14.1.2 Sensitivity and selectivity

This technique is capable of measuring within the range of 1 µg/ml to 50 µg/ml of hydrogen sulphide as HS^- and S^{2-} ions in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to HS^- and S^{2-} ions in aqueous solution. An alkaline eluent shall always be used for separation and detection to ensure the HS^- and S^{2-} ions exist in the anionic form.

This method allows measurement of hydrogen cyanide simultaneously (see 5.4.3).

5.14.1.3 Other considerations

A glass syringe with a PTFE-tipped plunger is recommended for use during injection to avoid unnecessary reactions with the rubber materials often present in the plungers of plastic syringes. Certain types of columns have been found to be sensitive to the fire-effluent solution in that they can quickly become clogged. The solution should be filtered before injection onto the column. It is often necessary to regenerate the columns regularly.

5.14.1.4 Analysis principles

The separation is carried out on an anion exchange column followed by Amperometric detection with a silver-working electrode. A silver chloride reference and a stainless steel counter electrode are fitted in the cell.

5.14.1.5 Procedure

See Clause 4 for principles of sampling and C.5 for the general principles of the method. However, for the analysis of hydrogen sulphide by HPIC, the specific information in 5.14.1.6 to 5.14.1.10 is relevant.

5.14.1.6 Sampling

The following procedure has been found suitable; see AFAP-3.[2] Pump the fire atmosphere through a non-fritted then a fritter impinger, containing 75 ml and 150 ml, respectively, of 0,1 M sodium hydroxide, at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.14.1.7 Analysis

5.14.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.14.1.7.1.1 Absorbing solution, 0,1 M sodium hydroxide.

5.14.1.7.1.2 Eluents, consisting of 0,1 M sodium hydroxide, 0,5 M sodium acetate or 0,5 % ethylene diamine.

5.14.1.7.1.3 Stock sulphide ions solutions

Dissolve 7.2 g of glass-clear, if necessary washed crystals of sodium sulphide hydrate approx. 35 % GR with distilled water in a 1000-ml volumetric flask and make up to the mark with distilled. The stock solution prepared according to this procedure has a concentration of approx. 1000 mg/l in ions sulphide.

Determination of the concentration of stock solution for sulphide:

Place 100 ml of distilled water and 5 ml of sulphuric acid 25 % GR in a 500 ml ground-glass conical flask. To this solution add 25.0 ml of the sulphide stock solution of approx. 1000 mg/l and 25.0 ml of iodine solution 0.05 mol/l. Titrate with sodium thiosulphate solution 0.1 mol/l until the yellow iodine colour has disappeared, add 1 ml of zinc iodide-starch solution, and continue to titrate until a milky, pure white colour emerges. The concentration of sulphide of stock solution, expressed in mg/l, is then:

$$C_{sol} = (C_2 - C_1) \times 64{,}1026 \tag{22}$$

where

C_1 consumption of sodium thiosulphate 0.1 mol/l

C_2 quantity of iodine solution 0.05 mol/l (25.0 ml)

Further investigational concentrations may be prepared from the stock solution exactly determined according to the procedure described above by diluting accordingly. When stored in a cool place, the stock solution remains stable for at most one day. The diluted investigational solutions must be used immediately.

5.14.1.7.1.4 Standard sulphide ions solutions

Standard solutions of sulphide ions are prepared in 0,1 M sodium hydroxide contained in volumetric flasks, in order to obtain several standard solutions. Prepare freshly each day.

5.14.1.7.2 Protocol

Flow rate should be set at 1 ml/min. The applied voltage setting is zero volts.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.14.1.8 Calibration

Standard sulphide solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared.

5.14.1.9 Calculations

Compare the peak area of the test solution corresponding to sulphide ions with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (23) :

$$\rho_{H_2S} = \frac{\rho_{Sts} \times 1{,}0625 \times V_{as}}{V_{ta} \times e} \tag{23}$$

where

ρ_{H_2S}	is the hydrogen sulphide concentration, expressed in grams per litre of atmosphere;
ρ_{Sts}	is the concentration, expressed in grams per litre, of sulphide ions in the test solution;
1,0625	is the conversion factor from S^{2-} to H_2S, equal to 34/32;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere;
e	is the collection efficiency of trapping system experimentally determined using a train of two traps.

5.14.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model,[2] with both FTIR and IC techniques.[12] For yield around 0,4 mg/g, repeatability has been estimated as 27 % and reproducibility has been estimated as 107 %. For yield around 17,7 mg/g, repeatability has been estimated as 6 % and reproducibility has been estimated as more than 300 %.

5.15 Ammonia

5.15.1 Ammonia by colourimetry

5.15.1.1 Application and limitations

See 5.15.1.2 and 5.15.1.3.

5.15.1.2 Sensitivity and selectivity

This method is capable of measuring 1,7 µg ammonia in the aliquot taken.

There are no known interferences.

5.15.1.3 Other considerations

The method does not distinguish between free and combined ammonia.

Stability of the test solution has not been verified, but it is thought to be stable for a few days if kept in the dark at 4 °C. It should be noted that the Nessler's reagent used is highly toxic and requires special treatment for disposal. An alternative method is by HPIC (see 5.15.2).

5.15.1.4 Analysis principles

Ammonia is bubbled through 0,02 M sulphuric acid to form ammonium sulfate. Nessler's reagent, a commercially available reagent comprised of mercuric chloride and potassium iodide in a potassium hydroxide solution, produces a yellow-brown complex on reaction with ammonia and ammonium salts which is measured in a spectrophotometer; see Reference [35].

5.15.1.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of ammonia by colourimetry, the specific information in 5.15.1.6 to 5.15.1.10 is relevant.

5.15.1.6 Sampling

Pump the fire atmosphere through a fritted bubbler containing 20 ml 0,02 M sulphuric acid at 0,4 l/min for 4 min to 5 min and record the total volume sampled.

5.15.1.7 Analysis

5.15.1.7.1 Reagents

Analytical grade reagents should be used where possible.

5.15.1.7.1.1 Absorbing solution

Dilute 1,1 ml concentrated sulphuric acid (18 M) to 1 l with water to form 0,02 M sulphuric acid.

5.15.1.7.1.2 Nessler's reagent, a mixture of mercuric chloride/potassium iodide in potassium hydroxide solution (commercially available).

5.15.1.7.1.3 Standard ammonia solution, approximately 20 μg/ml.

Dissolve 0,077 6 g ammonium sulfate in 1 l distilled water. Prepare freshly each day.

5.15.1.7.2 Protocol

To a boiling-tube, add an aliquot of test solution containing up to 80 μg ammonia. Add distilled water (if necessary) to give a total volume of 10 ml. Then add 0,4 ml Nessler's reagent and allow colour to develop for at least 10 min. Read the absorbance, α_{NH3}, at approximately 440 nm (corresponding to the maximum absorbance of the standard solution) in a 1 cm cell against a reagent blank solution with absorbance α_0.

Formation of a precipitate on addition of the Nessler's reagent indicates excessive levels of ammonia and a smaller aliquot should be taken for analysis.

Interference from yellow combustion products in the test solution can be taken into account. Prepare control solutions by treating another aliquot of the test solution (same volume as used for the analysis) and diluting to 10,4 ml with distilled water. Measure this solution against distilled water to give a control absorbance reading for each test solution.

5.15.1.8 Calibration

Prepare calibration standards containing 10 μg, 12 μg, 40 μg and 80 μg ammonia using 0,5 ml, 1,0 ml, 2,0 ml and 4,0 ml aliquots of the standard ammonia solution 5.15.1.7.1.3. Make up the volume to 10 ml with distilled water and develop the colour as outlined above.

The calibration is fairly reproducible; therefore it is not necessary to include standards with each set of analyses.

5.15.1.9 Calculation

Compare the absorbance of the test solutions, α_{NH3} and α_0, with that obtained for the calibration standards and calculate atmospheric concentrations using Formula (24):

$$\rho_{NH_3} = \frac{\rho_{NH_3S} \times V_{as}}{V_{ta} \times e} \qquad (24)$$

where

ρ_{NH_3} is the ammonia concentration, expressed in grams per litre of atmosphere;

ρ_{NH_3S} is the ammonia concentration in the absorbing solution, expressed in grams of ammonia per litre of the solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere sampled;

e is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.15.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model,[2] with a combination between HPIC, colourimetry and FTIR techniques.[12] For yield around 7,0 mg/g, repeatability has been estimated as 22 % and reproducibility has been estimated as

268 %. For yield around 14,6 mg/g, repeatability has been estimated as 44 % and reproducibility has been estimated as 104 %.

5.15.2 Ammonia by high performance ion chromatography

5.15.2.1 Application and limitations

See 5.15.2.2 and 5.15.2.3.

5.15.2.2 Sensitivity and selectivity

This technique is capable of measuring the ammonia concentration within the range 0,5 µg/ml to 30 µg/ml in the test solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary. This technique is specific to ammonium ions in aqueous solution. Co-elutants can interfere with the accuracy of the results. Other cations, including lithium, sodium, magnesium or calcium, can also be analysed by this technique.

5.15.2.3 Other considerations

Ammonia gas is extremely soluble in water. The reaction taking place between ammonia and water is a reversible one, as shown in Formula (25):

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \tag{25}$$

If the solution is neutralized with an acid, the corresponding salt of the ammonium ion is formed, for example ammonium chloride $NH_4^+Cl^-$ with hydrochloric acid.

5.15.2.4 Analysis principles

The separation is carried out on a cation exchange column, followed by conductimetric detection. Chemical suppression can be used but is not essential.

5.15.2.5 Procedure

See Clause 4 for general sampling requirements, and C.5.1and C.5.2 for general principles of the method. However, for the analysis of ammonia by HPIC, the specific information in 5.15.2.6 to 5.15.2.10 is relevant.

5.15.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere at 2 l/min for 20 min through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of 25 mM hydrochloric acid solution. Record the total volume sampled.

5.15.2.7 Analysis

5.15.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.15.2.7.1.1 Absorbing solution, 25 mM hydrochloric acid.

5.15.2.7.1.2 Eluent, 3 mM methanesulphonic acid.

5.15.2.7.1.3 Stock ammonium solution, approximately 1 000 µg/ml NH_4^+

Dissolve 1,486 g ammonium chloride in 500 ml distilled water.

5.15.2.7.1.4 Standard ammonium solutions

Dilute stock solution contained in volumetric flasks with distilled water and make up to volume in order to obtain several calibration solutions. Prepare fresh solutions daily.

5.15.2.7.2 Protocol

Flow rate should be set at 1,0 ml/min. Direct analysis of the unknown solution can be carried out. The sample injection volume can be between 5 µl and 25 µl.

5.15.2.8 Calibration

Standard solutions of ammonium are injected into the HPIC and a chart recorder or data handling system monitors the detector response time. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then prepared.

5.15.2.9 Calculations

The ammonium peak area of the test solution is compared to the calibration curve. The atmospheric concentrations are calculated using Formula (26):

$$\rho_{\mathrm{NH_3}} = \frac{\rho_{\mathrm{NH_4^+}} \times V_{\mathrm{as}} \times 0{,}944}{V_{\mathrm{ta}} \times e} \tag{26}$$

where

$\rho_{\mathrm{NH_3}}$	is the ammonia concentration, expressed in grams per litre of atmosphere;
$\rho_{\mathrm{NH_4^+}}$	is the ammonium ions concentration in the absorbing solution, expressed in grams of ammonium ions per litre of the solution;
0,944	is the conversion factor from NH_4 to NH_3, equal to 17/18;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.15.2.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model,[2] with a combination between HPIC, colourimetry and FTIR techniques.[12] For yield around 7,0 mg/g, repeatability has been estimated as 22 % and reproducibility has been estimated as 268 %. For yield around 14,6 mg/g, repeatability has been estimated as 44 % and reproducibility has been estimated as 104 %.

5.16 Antimony compounds by atomic absorption spectrophotometry (AAS) or inductively coupled plasma emission spectrometry (ICP)

5.16.1 Application and limitations

See 5.16.2 and 5.16.3.

5.16.2 Sensitivity and selectivity

The limits of detection in the test solution are 1,0 µg/ml for AAS analysis and 0,01 µg/ml for ICP analysis.

There are no known interferences by either AAS or ICP methods.

5.16.3 Other considerations

Other metallic elements may be quantified in the same test solution.

5.16.4 Analysis principles

Antimony in the test solution is transformed into an atomic vapour and then spectrophotometrically analysed; see References [36],[37].

5.16.5 Procedure

See Clause 4 for principles of sampling and C.10 and C.11 for general principles of the methods. However, for the analysis of antimony compounds by AAS or ICP, of compounds the specific information in 5.16.6 to 5.16.10 is relevant.

5.16.6 Sampling

Pump the fire atmosphere at 0,5 l/min for 4 min to 5 min through a fritted bubbler containing 20 ml 2 M hydrochloric acid and record the total volume sampled. In order that both particulate and vapour forms of antimony can be quantified, the bubbler can be preceded by a glass-fibre filter which is then desorbed in 10 ml M HCl prior to analysis. These sampling parameters may be varied if necessary to suit conditions.

5.16.7 Analysis

5.16.7.1 Reagents

Analytical grade reagents should be used where possible.

5.16.7.1.1 Absorbing solution, 2 M hydrochloric acid

Dilute 167 ml 37 % HCl with 1 l distilled water.

5.16.7.1.2 Stock antimony solution, ~1 000 µg/ml, commercially prepared

5.16.7.2 Protocol

Antimony in the solution is quantified against calibration standards according to the procedure specified by the manufacturer of the AAS or ICP instrument.

5.16.8 Calibration

Prepare calibration standards in the hydrochloric acid used as trapping/desorption media. For AAS instruments, these are usually 10 µg/ml, 50 µg/ml and 100 µg/ml. For ICP instruments, standards up to 50 µg/ml are generally used. Standards should be included with each set of analyses.

5.16.9 Calculations

The concentration of antimony in the test atmosphere is calculated from Formula (27):

$$\rho_{\mathrm{Sb}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}}} \tag{27}$$

where

ρ_{Sb} is the concentration of the antimony, expressed in grams per litre of the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of antimony in the absorbing solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere.

5.16.10 Repeatability and reproducibility

No data has been collected yet.

5.17 Arsenic compounds by atomic absorption spectrophotometry (AAS) or inductively coupled plasma emission spectrometry (ICP)

5.17.1 Application and limitations

See 5.17.2 and 5.17.3.

5.17.2 Sensitivity and selectivity

The limits of detection in the test solution are 1,0 µg/ml for AAS analysis and 0,01 µg/ml for ICP.

There are no known interferences by either AAS or ICP methods.

5.17.3 Other considerations

Other metallic elements can be quantified in the same test solution. Alternative trapping media could be investigated (e.g. dilute alkali, for example 0,1 M NaOH).

5.17.4 Analysis principles

Arsenic in the test solution is transformed into an atomic vapour and then spectrophotometrically analysed by systems that measure the population density of the atoms in the vapour; see References [36],[37].

5.17.5 Procedure

See Clause 4 for principles of sampling and C.10 and C.11 for general principles of the methods. However, for the analysis of arsenic compounds by AAS or ICP, the specific information in 5.17.6 to 5.17.10 is relevant.

5.17.6 Sampling

Pump the fire atmosphere at 0,4 l/min for 4 min to 5 min through a fritted bubbler containing 20 ml 1 M hydrochloric acid and record the volume of test atmosphere sampled. In order that both particulate and vapour forms of arsenic can be quantified, the bubbler can be preceded by a glass fibre filter which is then desorbed by extracting with 5 % HCl at 100 °C for 30 min prior to analysis. These sampling parameters may be varied if necessary to suit the conditions.

5.17.7 Analysis

5.17.7.1 Reagents

Analytical grade reagents should be used where possible.

5.17.7.1.1 Absorbing solution, 1 M hydrochloric acid.

Dilute 83 ml of 37 % HCl with 1 l distilled water.

5.17.7.1.2 Stock arsenic solution, ~1 000 µg/ml, commercially prepared.

5.17.7.2 Protocol

Arsenic in the solution is quantified against calibration standards according to the procedure specified by the manufacturer of the AAS or ICP instrument.

5.17.8 Calibration

Prepare calibration standards in the hydrochloric acid used as the trapping/desorption media. For AAS instruments, these are usually 10 µg/ml, 50 µg/ml and 100 µg/ml. For ICP instruments, standards up to 50 µg/ml are generally used. Standards should be included with each set of analyses.

5.17.9 Calculations

The concentration of arsenic in the test atmosphere is calculated from Formula (28):

$$\rho_{\mathrm{As}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}}} \tag{28}$$

where

ρ_{As} is the concentration of the arsenic, expressed in grams per litre of the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of arsenic in the absorbing solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere.

5.17.10 Repeatability and reproducibility

No data has been collected yet.

5.18 Phosphorus by inductively coupled plasma emission spectrometry (ICP)

5.18.1 Application and limitations

See 5.18.2 and 5.18.3.

5.18.2 Sensitivity and selectivity

The limit of detection in the test solution is 0,01 µg/ml elemental phosphorus.

There are no known interferences.

5.18.3 Other considerations

Phosphate-forming compounds, other elements and chemical species (e.g. hydrogen cyanide and hydrogen halide) may be quantified in the same test solution.

Alternative trapping media could be investigated.

5.18.4 Analysis principles

Phosphorus in the test solution is transformed into an atomic vapour and then spectrometrically analysed by systems that measure the population density of the atoms in the vapour; see Reference [36].

5.18.5 Procedure

See Clause 4 for principles of sampling and C.11 for general principles of the method. However, for the analysis of phosphorus by ICP, the specific information in 5.18.6 to 5.18.10 is relevant.

5.18.6 Sampling

Pump the fire atmosphere at 0,4 l/min for 4 min to 5 min through a fritted bubbler containing 20 ml 0,01 M sodium hydroxide and record the total volume sampled. In order that both particulate and vapour forms of phosphorus-containing compounds can be quantified, a glass fibre filter can precede the bubbler, which is then desorbed in 20 ml 0,01 M NaOH or other suitable aqueous medium prior to analysis. These sampling parameters may be varied if necessary to suit conditions.

5.18.7 Analysis

5.18.7.1 Reagents

Analytical grade reagents should be used where possible.

5.18.7.1.1 Absorbing solution, 0,01 M sodium hydroxide.

5.18.7.1.2 Stock phosphorus solution, ~1 000 µg/ml, commercially prepared.

5.18.7.2 Protocol

Phosphorus in the solution is quantified against calibration standards according to the procedure specified by the manufacturer of the ICP instrument.

5.18.8 Calibration

Prepare calibration standards in the 0,01 M sodium hydroxide solution (or other) used as trapping/desorption media. Standards up to 50 µg/ml are possible and should be included with each set of analyses.

5.18.9 Calculations

The concentration of phosphorus in the test atmosphere is calculated from Formula (29):

$$\rho_{\mathrm{P}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}}} \qquad (29)$$

where

ρ_P is the concentration of phosphorous, expressed in grams per litre of the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of phosphorous in the absorbing solution;

V_{as} is the total volume, expressed in litres, of absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere.

5.18.10 Repeatability and reproducibility

No data has been collected yet.

5.19 Phosphates

5.19.1 Phosphates by colourimetry

5.19.1.1 Application and limitations

See 5.19.1.2 and 5.19.1.3.

5.19.1.2 Sensitivity and selectivity

The limit of detection in the test solution is 5 µg/ml, expressed as phosphorus pentoxide P_2O_5.

There are no known interferences.

5.19.1.3 Other considerations

Total phosphorus, other elements and chemical species (e.g. hydrogen cyanide and hydrogen halide) may be quantified in the same test solution.

The stability of phosphate in the test solution is not known.

Alternative trapping media could be investigated.

5.19.1.4 Analysis principles

An orange-yellow coloured complex vanadimolybdiphosphoric acid is formed when a solution containing orthophosphate is treated with an acid reagent containing molybdic acid and vanadic acids; see Reference [38].

5.19.1.5 Procedure

See Clause 4 for principles of sampling and C.4 for general principles of the method. However, for the analysis of phosphates by colourimetry, the specific information in 5.19.1.6 to 5.19.1.10 is relevant.

5.19.1.6 Sampling

Pump the fire atmosphere at 0,4 l/min for 4 min to 5 min through a fritted bubbler containing 20 ml 0,01 M sodium hydroxide and record the total volume sampled. In order that both particulate and vapour form phosphates can be quantified, a glass fibre filter can precede the bubbler, which is then desorbed in 20 ml 0,01 M NaOH or other suitable aqueous medium prior to analysis. These sampling parameters may be varied if necessary to suit conditions. It should be noted that all phosphates are liquids or solids at ambient temperature.

5.19.1.7 Analysis

5.19.1.7.1 Reagents

5.19.1.7.1.1 Absorbing solution, 0,01 M sodium hydroxide.

5.19.1.7.1.2 Ammonium molybdate solution.

Dissolve 10 g ammonium molybdate in 200 ml of distilled water at 50 °C.

5.19.1.7.1.3 Ammonium vanadate solution.

Dissolve 0,5 g ammonium vanadate in 150 ml of boiling distilled water, cool, then add 70 ml of concentrated nitric acid.

5.19.1.7.1.4 Vanadate-molybdate reagent

Gradually add the molybdate solution (5.19.1.7.1.2) to the vanadate solution (5.19.1.7.1.3) and dilute to 500 ml with distilled water.

5.19.1.7.1.5 Acid-only reagent, for control test solutions.

Dilute 70 ml of concentrated nitric acid to 500 ml with distilled water.

5.19.1.7.1.6 Stock phosphate solution, equivalent to 2 000 μg/ml P_2O_5

Dissolve 3,834 g dry potassium dihydrogen phosphate in 1 l distilled water.

5.19.1.7.1.7 Standard phosphate solution, equivalent to 100 μg/ml P_2O_5.

Dilute 5 ml stock solution to 100 ml in 0,01 M sodium hydroxide solution. Prepare freshly each day.

5.19.1.7.2 Protocol

To 4,0 ml aliquots of test solution containing up to 200 μg P_2O_5, add 1,5 ml vanadate-molybdate reagent and allow colour to develop for at least 10 min. Read the absorbance, α_P, at approximately 420 nm (corresponding to the maximum absorbance of the standard solution) in a 1 cm cell against a reagent blank solution, α_0.

Interference from yellow combustion products in the test solution can be taken into account. Prepare a control solution by treating another 4,0 ml aliquot of the test solution with 1,5 ml of the “acid-only” reagent. Measure this solution against an “acid-only” reagent blank to give a control absorbance reading for each test solution.

5.19.1.8 Calibration

Prepare calibration standards, containing up to 200 μg P_2O_5 using 1,0 ml and 2,0 ml aliquots of the standard phosphate solution (5.19.1.7.1.7) in 0,01 M NaOH, and treat with the colour-forming reagent as outlined above. Control readings are not necessary for the calibration procedure. A linear calibration is obtained with an absorbance of approximately 0,8 corresponding to 200 μg P_2O_5 in the test solution. Calibration standards should be included with each set of analyses.

5.19.1.9 Calculations

Compare the absorbance of the test solution, α_{P}, and the control solution, α_0, with that obtained for the calibration standards and calculate atmospheric concentrations using Formula (30):

$$\rho_{\text{P}_2\text{O}_5} = \frac{\rho_{\text{ts}} \times V_{\text{as}}}{V_{\text{ta}} \times e} \tag{30}$$

where

$\rho_{\text{P}_2\text{O}_5}$	is the concentration of the P_2O_5, expressed in grams per litre of the atmosphere;
ρ_{ts}	is the concentration, expressed in grams per litre, of the P_2O_5 in the absorbing solution;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere.
e	is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.19.1.10 Repeatability and reproducibility

No data has been collected yet.

5.19.2 Phosphates by high performance ion chromatography (HPIC)

5.19.2.1 Application and limitations

See 5.19.2.2 and 5.19.2.3.

5.19.2.2 Sensitivity and selectivity

This technique is capable of measuring concentrations of HPO_4^{2-} ions in solution within the range of 0,5 µg/ml to 20 µg/ml. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to phosphate ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions can also be analysed at the same time.

5.19.2.3 Other considerations

None.

5.19.2.4 Analysis principles

The separation is carried out on an anion-exchange column followed by conductimetric detection. Chemical suppression shall be used. Post-column colourimetric reaction followed by UV-visible detection may be also suitable.

5.19.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of phosphates by HPIC, the specific information in 5.19.2.6 to 5.19.2.10 is relevant:

5.19.2.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere at 2 l/min for 20 min through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of 0,1 M sodium hydroxide and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.19.2.7 Analysis

5.19.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.19.2.7.1.1 Absorbing solution, 0,1 M sodium hydroxide

5.19.2.7.1.2 Eluents, 0,001 7 mol/l sodium hydrogen carbonate and 0,001 8 mol/l sodium carbonate

5.19.2.7.1.3 Stock phosphate solution, approximately 1 000 μg/ml HPO_4^{2-}

Dissolve 0,142 g dry potassium dihydrogen phosphate in 100 ml distilled water.

5.19.2.7.1.4 Standard phosphate solutions

Dilute stock solution in distilled water contained in volumetric flasks and make up to volume in order to obtain several calibration solutions. Prepare freshly each day.

5.19.2.7.2 Protocol

Flow rate should be set at 2 ml/min.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 μl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.19.2.8 Calibration

Standard solutions of phosphate are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each of the standard solutions. A calibration is then prepared.

5.19.2.9 Calculations

Compare the peak area of the test solution corresponding to phosphate ions with those obtained for the calibration curve and calculate atmospheric concentrations, expressed as phosphoric acid (H_3PO_4), using Formula (31):

$$\rho_{H_3PO_4} = \frac{\rho_{HPO_4^{2-}} \times V_{as} \times 1{,}021}{V_{ta} \times e} \qquad (31)$$

where

$\rho_{H_3PO_4}$	is the phosphoric acid concentration, expressed in grams per litre of atmosphere;
$\rho_{HPO_4^{2-}}$	is the phosphate ions concentration in the absorbing solution, expressed in grams of phosphate ions per litre of the solution;
1,021	is the conversion factor from HPO_4^{2-} to H_3PO_4, equal to 98/96;
V_{as}	is the total volume, expressed in litres, of absorbing solution;
V_{ta}	is the volume, expressed in litres, of the test atmosphere sampled;
e	is the collection efficiency of the trapping system, experimentally determined using a train of two traps.

5.19.2.10 Repeatability and reproducibility

No data has been collected yet.

5.20 Phenol

5.20.1 Phenol by high performance liquid chromatography (HPLC)

5.20.1.1 Application and limitations

See 5.20.1.2 and 5.20.1.3.

5.20.1.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of phenol in solution.

No known interference except with possible co-elutants.

5.20.1.3 Other considerations

This method permits the analysis of several other organic species at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

The method uses methanol/water solution for trapping. Ensure that smoke coming into impinger is less than 60°C during the entire test.

5.20.1.4 Analysis principles

Phenol is trapped into a solution of methanol/water. The solution is filtered, then analysed. The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.20.1.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of phenol by HPLC, the specific information in 5.20.1.6 to 5.20.1.10 is relevant.

5.20.1.6 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of Methanol/water solution, in proportion 60/40, at 2 l/min for 20 min and record the total volume sampled.

5.20.1.7 Analysis

5.20.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.20.1.7.1.1 Absorbing solution and Eluent, methanol/water, 60/40.

5.20.1.7.1.2 Phenol stock solution, approximately 500 μg/ml in methanol, commercially available.

5.20.1.7.1.3 Standard solutions

Dilute stock solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 100 mg/l. Prepare freshly every day.

5.20.1.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 271 nm. The sample injection volume is 20 μl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.20.1.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.20.1.9 Calculations

Compare the peak area of the test solution corresponding to phenol with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (32):

$$\rho_{\mathrm{ph}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \quad (32)$$

where

ρ_{ph} is the concentration of phenol, expressed in grams per litre of the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of phenol in the test solution;

V_{as} is the volume, expressed in litres, of the absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.20.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in a solution issued from trapping fire effluents from a material in Methanol/Water (60/40) solution.[2] For concentration around 69 mg/l, repeatability has been estimated as 8 % and reproducibility has been estimated as 10 %.

5.20.2 Phenol by GC-MS

5.20.2.1 Application and limitations

Phenol is collected in liquid phase, then analysed by GC-MS. Phenol is particularly prone to condensation on the walls of gas collection bags, leading to false low tests results. Therefore, the analysis of phenol in the gas phase is prohibited.

5.20.2.2 Sensitivity and selectivity

The limit of detection is 3 µl/l of phenol in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in other organic compounds.

5.20.2.3 Analysis principles

Phenol is trapped into a solution of methanol/water. The solution is filtered, then analysed. The separation is carried out on a capillary column followed by a MS “quadrupole” mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.20.2.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of Methanol/water solution, in proportion 60/40, at 2 l/min for 20 min and record the total volume sampled.

5.20.2.5 Analysis

5.20.2.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.20.2.5.1.1 GC separation

- Liquid injection, volume of the loop of 50 µl found suitable.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.20.2.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s on the fragments obtained after screening from 25 m/z to 200 m/z.

5.20.2.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of solutions with a known quantity of phenol (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.

5.20.2.6 Calibration

Standard solutions containing phenol are prepared, diluting commercially available solutions (see 5.20.1.7.1.2) in methanol/water (60/40) solution.

5.20.2.7 Calculations

Compare the peak area of the test solution corresponding to phenol with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (34) as stated in 5.20.1.9.

5.20.2.8 Repeatability and reproducibility

No data has been collected yet.

5.21 Benzene

5.21.1 Benzene by high performance liquid chromatography (HPLC)

5.21.1.1 Application and limitations

See 5.21.1.2 and 5.21.1.3.

5.21.1.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of benzene in solution.

No known interference except with possible co-elutants.

5.21.1.3 Other considerations

This method permits the analysis of several other organic species at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

The method uses methanol/water solution for trapping. Ensure that smoke coming into impinger is under 60°C during all the test.

5.21.1.4 Analysis principles

Benzene is trapped into a solution of methanol/water. The solution is filtered, then analysed. The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.21.1.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of benzene by HPLC, the specific information in 5.21.1.6 to 5.21.1.10 is relevant.

5.21.1.6 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of Methanol/water solution, in proportion 60/40, at 2 l/min for 20 min and record the total volume sampled.

5.21.1.7 Analysis

5.21.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.21.1.7.1.1 Absorbing solution and Eluent, methanol/water, 60/40.

5.21.1.7.1.2 Standard solutions

Dilute benzene solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 100 mg/l. Prepare freshly every day.

5.21.1.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 271 nm. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.21.1.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.21.1.9 Calculations

Compare the peak area of the test solution corresponding to benzene with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (33):

$$\rho_{\mathrm{bz}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \tag{33}$$

where

ρ_{bz} is the concentration of benzene, expressed in grams per litre of atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of benzene in the test solution;

V_{as} is the volume, expressed in litres, of the absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.21.1.10 Repeatability and reproducibility

No data has been collected yet.

5.21.2 Benzene by GC-MS in gas phase

5.21.2.1 Application and limitations

Benzene is collected in gas phase, and then analysed by GC-MS.

5.21.2.2 Sensitivity and selectivity

The limit of detection is 2 µl/l of benzene in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in acrolein, carbon disulphide, toluene, xylene, styrene, acrylonitrile, formaldehyde and acetaldehyde.

5.21.2.3 Analysis principles

Benzene is collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS “quadrupole” mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.21.2.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.21.2.5 Analysis

5.21.2.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.21.2.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with an stainless steel loop of 0.5 ml.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.21.2.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.21.2.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of a known quantity of benzene (liquid) in a 40-l 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. Fragmentation of benzene is described in the following table:

Table 8 — Fragmentation of benzene in analytical conditions proposed

Compound	Principal peak (parent) at m/z (normalized 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)
benzene	78	No other important fragments	7,7	78

5.21.2.6 Calibration

Standard gas mixtures are prepared by injecting benzene into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid benzene and samples are then taken from the bag for analysis in the GC-MS.

Benzene is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below:

Table 9 — Preparation of gas standards of benzene

Reagent	**Volume of benzene introduced** µl								
	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L								
Mass of benzene introduced in gas bag (mg)	1.77	4.42	8.83	17.7	22.1	44.2	88.3	177	221
Concentration of benzene (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	44.2	110	221	442	552	1104	2208	4415	5519

If other gases are analysed at the same time, it is often needed to prepare them in separate standards because of the immiscibility of some compounds

5.21.2.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.21.2.8 Repeatability and reproducibility

Data are available in Reference [12] for AFAP-3 fire model.[2]

5.22 Toluene (Methylbenzene)

5.22.1 Toluene by high performance liquid chromatography (HPLC)

5.22.1.1 Application and limitations

See 5.22.1.2 and 5.22.1.3.

5.22.1.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of toluene in solution.

No known interference except with possible co-elutants.

5.22.1.3 Other considerations

This method permits the analysis of several other organic species at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

The method uses methanol/water solution for trapping. Ensure that smoke coming into impinger is less than 60°C during the entire test.

5.22.1.4 Analysis principles

Toluene is trapped into a solution of methanol/water. The solution is filtered, then analysed. The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.22.1.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of toluene by HPLC, the specific information in 5.22.1.6 to 5.22.1.10 is relevant.

5.22.1.6 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of Methanol/water solution, in proportion 60/40, at 2 l/min for 20 min and record the total volume sampled.

5.22.1.7 Analysis

5.22.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.22.1.7.1.1 Absorbing solution and Eluent, methanol/water, 60/40.

5.22.1.7.1.2 Standard solutions

Dilute toluene solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 100 mg/l. Prepare freshly every day.

5.22.1.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 271 nm. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.22.1.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.22.1.9 Calculations

Compare the peak area of the test solution corresponding to toluene with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (34):

$$\rho_{\mathrm{to}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \tag{34}$$

where

ρ_{to} is the concentration, expressed in grams per litre, of toluene in the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of toluene in the test solution;

V_{as} is the volume, expressed in litres, of the absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.22.1.10 Repeatability and reproducibility

No data has been collected yet.

5.22.2 Toluene by GC-MS in gas phase

5.22.2.1 Application and limitations

Toluene is collected in gas phase, and then analysed by GC-MS.

5.22.2.2 Sensitivity and selectivity

The limit of detection is 5 µl/l of toluene in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in acrolein, carbon disulphide, benzene, xylene, styrene, acrylonitrile, formaldehyde and acetaldehyde.

5.22.2.3 Analysis principles

Toluene is collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS "quadrupole" mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.22.2.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.22.2.5 Analysis

5.22.2.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.22.2.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with an stainless steel loop of 0.5 ml,
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.22.2.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.22.2.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of a known quantity of toluene (liquid) in a 40-l 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. Fragmentation of toluene is described in the following table:

Table 10 — Fragmentation of toluene in analytical conditions proposed

Compound	Principal peak (parent) at m/z (normalized 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)
toluene	92	1 fragment 92 (70 %) = molar	10	92

5.22.2.6 Calibration

Standard gas mixtures are prepared by injecting toluene into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid toluene and samples are then taken from the bag for analysis in the GC-MS.

Toluene is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below:

Table 11 — Preparation of gas standards of toluene

Reagent	**Volume of toluene introduced** µl								
	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L								
Mass of toluene introduced in gas bag (mg)	1.72	4.30	8.60	17.2	21.5	43.0	86.0	172	215
Concentration of toluene (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	43.0	108	215	430	538	1075	2150	4300	5375

If other gases are analysed at the same time, it is often needed to prepare them in separate standards because of the immiscibility of some compounds

5.22.2.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.22.2.8 Repeatability and reproducibility

Data are available in Reference [12] for AFAP-3 fire model.[2]

5.23 Styrene (Phenylethene)

5.23.1 Styrene by high performance liquid chromatography (HPLC)

5.23.1.1 Application and limitations

See 5.23.1.2 and 5.23.1.3.

5.23.1.2 Sensitivity and selectivity

The limit of detection is 10 µg/ml of styrene in solution.

No known interference except with possible co-elutants.

5.23.1.3 Other considerations

This method permits the analysis of several other organic species at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

The method uses methanol/water solution for trapping. Ensure that smoke coming into impinger is under 60°C during all the test.

5.23.1.4 Analysis principles

Styrene is trapped into a solution of methanol/water. The solution is filtered, then analysed. The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.23.1.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of styrene by HPLC, the specific information in 5.23.1.6 to 5.23.1.10 is relevant.

5.23.1.6 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of Methanol/water solution, in proportion 60/40, at 2 l/min for 20 min and record the total volume sampled.

5.23.1.7 Analysis

5.23.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.23.1.7.1.1 Absorbing solution and Eluent, methanol/water, 60/40

5.23.1.7.1.2 Standard solutions

Dilute styrene solution contained in volumetric flasks with eluent and make up to volume in order to obtain several standard solutions between 0,1 mg/l and 100 mg/l. Prepare freshly every day.

5.23.1.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at 271 nm. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.23.1.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.23.1.9 Calculations

Compare the peak area of the test solution corresponding to styrene with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (35):

$$\rho_{\mathrm{st}} = \frac{\rho_{\mathrm{ts}} \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \tag{35}$$

where

ρ_{st} is the concentration, expressed in grams per litre, of styrene in the atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of styrene in the test solution;

V_{as} is the volume, expressed in litres, of the absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.23.1.10 Repeatability and reproducibility

No data has been collected yet.

5.23.2 Styrene by GC-MS in gas phase

5.23.2.1 Application and limitations

Styrene can be analysed by gas chromatography and mass spectrometry.[39],[40] Styrene is collected in gas phase, then analysed by GC-MS.

5.23.2.2 Sensitivity and selectivity

The limit of detection is 10 µl/l of styrene in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in acrolein, carbon disulphide, benzene, toluene, xylene, acrylonitrile, formaldehyde and acetaldehyde.

5.23.2.3 Analysis principles

Styrene is collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS “quadrupole” mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.23.2.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.23.2.5 Analysis

5.23.2.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.23.2.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with an stainless steel loop of 0.5 ml.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.23.2.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.23.2.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of a known quantity of styrene (liquid) in a 40 l 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. Fragmentation of styrene is described in the following table:

Table 12 — Fragmentation of styrene in analytical conditions proposed

Compound	Principal peak (parent) at m/z (normalized 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)
styrene	104	No other important fragments	12,4	104

5.23.2.6 Calibration

Standard gas mixtures are prepared by injecting styrene into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid styrene and samples are then taken from the bag for analysis in the GC-MS.

Styrene is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below:

Table 13 — Preparation of gas standards of styrene

Reagent	**Volume of styrene introduced** µl								
	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L								
Mass of styrene introduced in gas bag (mg)	1.81	4.53	9.06	18.1	22.7	45.3	90.6	181	227
Concentration of styrene (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	45.3	113	227	453	566	1133	2265	4530	5663

If other gases are analysed at the same time, it is often needed to prepare them in separate standards because of the immiscibility of some compounds

5.23.2.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.23.2.8 Repeatability and reproducibility

Data are available in Reference[12] for AFAP-3 fire model.[2]

5.24 Acrylonitrile and other nitriles by GC-MS in gas phase

5.24.1 Application and limitations

These compounds can be analysed by gas chromatography and mass spectrometry.[39],[41] Acrylonitrile and other nitriles are collected in gas phase, then analysed by GC-MS. GC/FID has been found suitable too.[2]

5.24.2 Sensitivity and selectivity

The limit of detection is 4 µl/l of acrylonitrile in gas phase.[2]

No known interference.

The method is also adapted to determine concentrations in acrolein, carbon disulphide, benzene, toluene, xylene, styrene, formaldehyde and acetaldehyde.

5.24.3 Analysis principles

Acrylonitrile and other nitriles are collected in suitable gas bag, then analysed in gas phase. The separation is carried out on a capillary column followed by a MS "quadrupole" mass selective detector used in Electronic Impact mode; see References [2],[27],[28]. Quantification is performed with analysis of total ionic current (TIC) obtained on fragments.

5.24.4 Sampling

The following procedure has been found suitable. Pump the fire atmosphere in a gas bag at 2 l/min for 20 min and record the total volume sampled. These sampling parameters may to be varied if necessary.

5.24.5 Analysis

5.24.5.1 Analytical conditions

The conditions proposed hereunder have been found suitable for such analysis. These parameters may to be varied if necessary.

5.24.5.1.1 GC separation

- Splitless injection in pulsed mode of the volume of gas with an automatic valve equipped with a stainless steel loop of 0.5 ml.
- Gas vector: helium (1 ml/minute), flow of gas vector 3 ml/min at the injection for 12 s followed by a flow rate of gas vector of 1 ml/minute.
- Capillary column, stationary phase: 5 % methylphenylsilicone or equivalent, Length 30 m at least, 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, then to elute the gases with high boiling points and to eliminate other heavy compounds from the column.

5.24.5.1.2 MS detection

Detection is ensured by a MS detector type quadrupole mass selective detector in Electronic impact (fragmentation). The time interval selected is one spectrum every 1.5 s 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.

5.24.5.1.3 Quantification

Analysis is done using Total Ionic current (TIC). Libraries such as NIST library are used for qualitative recognition of compounds. A standard containing the required gas is prepared by injection of a known quantity of acrylonitrile (liquid) in a 40 l 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. Fragmentation of acrylonitrile is described in the following table:

Table 14 — Fragmentation of acrylonitrile in analytical conditions proposed

Compound	Principal peak (parent) at m/z (Normalized 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)
acrylonitrile	53	2 fragments 26 (85 %) 52 (79 %)	3,2	53

5.24.6 Calibration

Standard gas mixtures are prepared by injecting acrylonitrile into a gas collection bag containing 40 l of air. Analytical grade chemicals are used and purity is considered in calculation of final concentrations. The bag is then warmed to ensure evaporation of the liquid acrylonitrile and samples are then taken from the bag for analysis in the GC-MS.

Acrylonitrile is injected in gas bags using a syringe to prepare a range of concentration as shown in the table below:

Table 15 — Preparation of gas standards of acrylonitrile

Reagent	**Volume of acrylonitrile introduced** µl								
	2,0	5,0	10,0	20,0	25,0	50,0	100,0	200,0	250,0
	Volume of gas bag: 40 L								
Mass of acrylonitrile introduced in gas bag (mg)	1.61	4.03	8.06	16.1	20.2	40.3	80.6	161	202
Concentration of acrylonitrile (mg/m^3) (assuming a perfect gas at 20°C, 101 325 Pa)	40.3	101	202	403	504	1008	2015	4030	5038

If other gases are analysed at the same time, it is often needed to prepare them in separate standards because of the immiscibility of some compounds

5.24.7 Calculations

No further calculation is required. The method compares directly TIC from samples to standards expressed in mg/m^3.

5.24.8 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model,[2] in GC with a combination between MS and FID detection techniques.[12] For yield around 0,4 mg/g, repeatability has been estimated as 12 % and reproducibility has been estimated as 294 %. For yield around 1,9 mg/g, repeatability has been estimated as 44 % and reproducibility has been estimated as 97 %. For yield around 2,9 mg/g, repeatability has been estimated as 39 % and reproducibility has been estimated as 85 %.

5.25 Formic acid

5.25.1 Formic acid by high performance ion chromatography (HPIC)

5.25.1.1 Application and limitations

See 5.25.1.2 and 5.25.1.3.

5.25.1.2 Sensitivity and selectivity

This technique is capable of measuring concentrations of formiate ions in solution within the range of 0,5 µg/ml to 20 µg/ml. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

This technique is specific to formiate ions in aqueous solution. Co-elutants can interfere with the accuracy of the results.

Other anions can also be analysed at the same time.

5.25.1.3 Other considerations

None.

5.25.1.4 Analysis principles

The separation is carried out on an anion-exchange column followed by conductimetric detection, without chemical suppression.

5.25.1.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.2 for general principles of the method. However, for the analysis of phosphates by HPIC, the specific information in 5.25.1.6 to 5.25.1.10 is relevant:

5.25.1.6 Sampling

The following procedure has been found suitable; see AFNOR NF X70-100-1[1] and AFNOR NF X70-100-2.[15] Pump the fire atmosphere at 2 l/min for 20 min through a non-fritted then a fritted impinger, containing 75 ml and 150 ml, respectively, of water and record the total volume sampled. These sampling parameters may be varied if necessary to suit conditions.

5.25.1.7 Analysis

5.25.1.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.25.1.7.1.1 Absorbing solution, deionized water.

5.25.1.7.1.2 Eluents, 0,001 7 mol/l sodium hydrogen carbonate and 0,001 8 mol/l sodium carbonate.

5.25.1.7.1.3 Standard formiate solutions

Dilute formic acid solution in distilled water contained in volumetric flasks and make up to volume in order to obtain several calibration solutions. Prepare freshly each day.

5.25.1.7.2 Protocol

Flow rate should be set at 2 ml/min.

Direct analysis of the unknown solution can be carried out. The sample injection volume is 25 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.25.1.8 Calibration

Standard solutions of formiate are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each of the standard solutions. A calibration is then prepared.

5.25.1.9 Calculations

Compare the peak area of the test solution corresponding to formiate ions with those obtained for the calibration curve and calculate atmospheric concentrations, expressed as formic acid (HCOOH), using Formula (36) :

$$\rho_{\mathrm{HCOOH}} = \frac{\rho_{\mathrm{ts}} \times 1{,}022 \times V_{\mathrm{as}}}{V_{\mathrm{ta}} \times e} \tag{36}$$

where

ρ_{HCOOH} is the concentration, expressed in grams per litre, of the formic acid in atmosphere;

ρ_{ts} is the concentration, expressed in grams per litre, of formiate ions in the test solution;

1,022 is the conversion factor from formiates to formic acid equal to 46/45;

V_{as} is the volume, expressed in litres, of the absorbing solution;

V_{ta} is the volume, expressed in litres, of the test atmosphere;

e is the collection efficiency of the trapping system experimentally determined using a train of two traps.

5.25.1.10 Repeatability and reproducibility

Repeatability and reproducibility were estimated in fire effluents from various materials, considering AFAP-3 fire model,[2] in a combination between HPIC and FTIR techniques.[12] For yield around 2,1 mg/g, repeatability has been estimated as 12 % and reproducibility has been estimated as 228 %. For yield around 3,2 mg/g, repeatability has been estimated as 34 % and reproducibility has been estimated as 263 %. For yield around 13,9 mg/g, repeatability has been estimated as 24 % and reproducibility has been estimated as 267 %.

5.25.2 **Formic acid by high performance liquid chromatography** (HPLC)

5.25.2.1 Application and limitations

See 5.25.2.2 and 5.25.2.3.

5.25.2.2 Sensitivity and selectivity

The limit of detection is 0,01 µg/ml of formiates in solution.

No known interference except with possible co-elutants.

5.25.2.3 Other considerations

This method permits the analysis of several other organic acids at the same time. A sufficient running time is necessary to ensure all the peaks have been eluted (about 30 min).

5.25.2.4 Analysis principles

Formic acid is trapped as formiate ions into a solution of water. The solution is filtred, then analysed. The separation is carried out on a reverse-phase column (for example C18) followed by ultraviolet detection; see References [22],[23],[24],[25].

5.25.2.5 Procedure

See Clause 4 for principles of sampling and C.5.1 and C.5.3 for general principles of the method. However, for the analysis of formiates by HPLC, the specific information in 5.25.2.6 to 5.25.2.10 is relevant.

5.25.2.6 Sampling

The following procedure has been found suitable. Pump the fire atmosphere through two non-fritted impingers, containing 250 ml of water solution, at 2 l/min for 20 min and record the total volume sampled.

5.25.2.7 Analysis

5.25.2.7.1 Reagents

Liquid chromatography grade reagents should be used where possible.

5.25.2.7.1.1 Absorbing solution, deionized water.

5.25.2.7.1.2 Eluent, methanol/water (60/40).

5.25.2.7.1.3 Standard solutions

Dilute formic acid solution in eluent contained in volumetric flasks and make up to volume in order to obtain several calibration solutions between 0,1 mg/l and 100 mg/l. Prepare freshly each day.

5.25.2.7.2 Protocol

Flow rate should be set at about 1 ml/min (depending on the column) and detection is carried out at maximum wavelength determined on a preliminary spectral analysis. The sample injection volume is 20 µl and it is advisable to inject at least 10 times the volume to fill the sample loop completely.

5.25.2.8 Calibration

Standard solutions are injected into the system and a chart recorder or an integrator monitors the detector response. The peak area monitored is directly related to the concentration of each standard solution. A calibration curve is then obtained.

5.25.2.9 Calculations

Compare the peak area of the test solution corresponding to formiates with those obtained for the calibration curve and calculate atmospheric concentrations using Formula (42) as stated in 5.25.1.9.

5.25.2.10 Repeatability and reproducibility

No data has been collected yet.

5.26 Total hydrocarbons by FID

The term “total hydrocarbons” is very misleading because it is defined only by the response of the detector, e.g. flame ionization or catalytic detectors, which is an indication of the concentration of combustible gases or vapours in an atmosphere. These detectors can also react to oxygenated species (alcohols, aldehydes, ketones), nitriles, and amines that are present in fire effluents [39],[42],[43],.[44]

The range of molecular weights of “total hydrocarbons” cannot easily be defined because hydrocarbons and other combustible species are in both vapour and/or condensed form.

For these two major reasons, it is not considered possible to obtain a true measurement of “total hydrocarbons”.

Some of the FID systems are equipped with a catalytic furnace, which allows determination of methane released.

5.27 Isocyanates

Isocyanates are very reactive species and analysis is normally based on derivatization followed by high-performance liquid chromatography (HPLC). Sensitized paper detectors are available but can suffer from a lack of specificity. Also, the isocyanates can readily dimerize and trimerize and care is required if a particular species is required. Errors can arise through interferences from water and amines. Differences between laboratory methods and realistic fires can result in wide differences in isocyanate analysis results.[45]

5.28 Oxygenated organic species

A range of oxygenated organic species is important as irritant compounds. Techniques such as gas chromatography (see C.5.4) often coupled with mass spectrometry (see C.6) have been used to measure these compounds.

Annex A
(informative)

Species and measurement techniques currently deemed unsuitable in fire effluents

A.1 General criteria for selection of species and measurement techniques.

Although it is clear that the sampling and analytical techniques provided in the Normative clauses of this Standard may have limitations when used for particular species, these may usually be overcome (or allowed for) by using the methodology described in each case. However there are some analytical techniques that are now deemed unsuitable for use with some fire effluents, even if they are commonly used for gas analyses outside the field of fire effluents (and in some cases for fire effluents). There are also compounds or groups of compounds which although may be present in fire effluents are normally regarded primarily as environmental pollutants and not particularly important for the acute toxicity and short-term life threat normally associated with fire effluents. It should also be noted that the specific use of FTIR is covered in ISO 19702[4] and the analysis of solid and liquid phase components of fire effluents (i.e. aerosols) is currently the subject of a draft International Standard ISO 29904.[3]

Based on practical experience, as many of the following criteria should be met when choosing a sampling and analytical method for a specific species in fire effluent. The method chosen should:

a) Be specific for the species required with no cross sensitivity to other species unless these can be allowed for in the method.

b) Have a limit of detection and limit of quantification below those required.

c) Be capable of allowing for and quantifying losses (e.g. absorption and condensation) between the sampled atmosphere and up to (and within) the analytical instrument.

d) Utilize existing and proven technology which has also been shown to be robust and durable when dealing with fire effluents.

e) Not require frequent extensive and/or expensive maintenance.

f) Be capable of operation by a laboratory technician with minimal suitable training.

g) Be non invasive and not significantly alter the nature of the sampled fire atmosphere.

h) Not require the sample to be stored for extended periods.

i) Minimize further chemical reaction after sampling.

A.2 Methodology and species, which do not adequately meet the criteria in A.1 and a brief summary of reasons

A.2.1 SO_2 by UV-fluorescence

The technique is widely used in combustion analysis (e.g. flue gases and diesel engine exhaust). It presents severe cross sensitivity and interference to the basic fluorescent mechanism, particularly from NO, CO_2 and O_2.[46]

A.2.2 O_2 by electrochemical detector

Electrochemical technique is widely used in process analysis and control, and flues and engine exhaust gases. Nevertheless, it presents severe cross sensitivity to many reducible species in fire effluents and Sulphide-containing species such like SO_2 or H_2S deteriorates the sensor.

A.2.3 Non-dispersive IR techniques for hydrogen halides and sulfur dioxide

The technique is often used in various gases composition. Nevertheless, it has strong cross sensitivity to H_2O, NO_2 and other IR active components. With fire effluents, it is not possible to eliminate these interferents, such as water, without strongly affecting the concentration in the measured species, as they are hygroscopic.

A.2.4 Dioxins, halogenated bi-phenyls, furans and related species

Normally considered as environmental pollutants, particularly from soil and watercourses but also from combustion (e.g. from incinerator stack emissions) the methodology is covered in detail in other Standards.[47] Due to the highly labile nature of these species in a fire effluent plume and the highly specialized sampling and analytical methods required together with their environmental impact within the scope of a future standard under development, they are not considered within the scope of this International Standard.

A.2.5 Polycyclic aromatic hydrocarbons (PAH)

These compounds are a generic group which have a varying toxicity across the individual species. They are mainly regarded as an environmental pollutant and while methods are available for individual species, specific analysis of these will be within the scope of a future standard under development. They are not considered within the scope of this International Standard.

Annex B
(informative)

Colour-change chemical detection tubes

This method involves passing the fire atmosphere through glass tubes packed with chemical reagent. The proprietary tubes are designed to be specific for a particular chemical species but in many cases there can be interference or "cross sensitivity" from other species. Manufacturers' data and warnings should be carefully noted and observed. A fixed volume of fire atmosphere is drawn through the tube resulting in a colour change in the chemical reagent. The length of colour change as shown from graduation marks on the glass tube gives a direct reading of concentration. There are, however, important limitations to the method as applied to fire gas analysis, in addition to the cross sensitivity to other compounds. These are connected with the relatively long sampling time required to obtain a reading, compared to the duration of the fire test itself; and also the fact that gases are at relatively high temperatures when they enter the tubes can affect the degree of colour change. It is also important to appreciate that correct interpretation can be difficult/impossible for operators who have some form of colour blindness. It is recommended that operators undergo colour vision tests.

Despite these limitations these devices can provide valuable information (mainly qualitative) on the chemical makeup of fire atmospheres when other techniques are not available and allowance can be made for interferences and cross sensitivities.

Annex C
(informative)

Quantitative instrumental methods

C.1 General

This annex provides a brief outline of the main instrumental methods available for fire gas analysis. It excludes a description of colour-change detector tubes. While these are valuable for obtaining a guide to specific compounds in fire atmospheres, the cross sensitivity and extended sampling time normally required make them of limited use in tenability assessment as applied to fire test gases. They are summarized briefly in Annex B.

C.2 Non dispersive infrared spectroscopy (NDIR)

C.2.1 Principle of operation and instrumentation

The molecules of many chemical species of interest in fire gas analysis will possess an electrical dipole that will interact with infrared (IR) radiation, predominantly due to the vibration of the molecule. Different species will absorb IR radiation at different frequencies and an IR absorption spectrum is usually obtained by sweeping the (usually pure) sample with all frequencies of interest using optical dispersion methods. The pattern of absorptions that results is used to identify and quantify the chemical species present. However, for some species (e.g. carbon monoxide and carbon dioxide), it is possible to use a fixed frequency of IR radiation that is absorbed strongly by the species of interest but not by other species.

Instruments using this technique are, therefore, designed to produce IR radiation over a relatively narrow band of wavelengths (hence the term “non-dispersive infra-red”) chosen to provide maximum absorption of the target compound with minimum absorption of the interfering compounds. To improve selectivity and to compensate for a range of variables, double-beam techniques can be used with a “reference” beam not passing through the sample and the sample beam itself.

C.2.2 Advantages and limitations

NDIR instruments are commonly used for oxides of carbon but have been developed for several other gases, including water and a range of organic compounds. They are obviously not applicable to compounds which are infrared inactive. The instruments usually need a “clean” sample and do not tolerate hot, acidic, moisture- and particle-laden samples.

Their overriding value is through their ability to provide a continuous analysis of the species of interest with minimal servicing and consumable requirements.

C.3 Paramagnetism

C.3.1 Principle of operation and instrumentation

Paramagnetism is a phenomenon whereby a paramagnetic material will be attracted by a magnetic field rather than repelled by it (this latter is known as diamagnetism and is present to a degree in all compounds). Essentially the magnetic properties of materials are brought about by the presence of electrons, which are both spinning on their own axis and moving around the nucleus of their parent atom in orbitals. Whenever unpaired electrons arise, whether in ions, atoms or molecules, there is a tendency for that species to exhibit paramagnetism. However, the classical valency theory of bonding does not always predict the presence of unpaired electrons which can, nevertheless, arise through further electron-sharing characteristics as predicted by the molecular orbital theory of bonding. Oxygen and nitric oxide are typical compounds exhibiting paramagnetism.

Instrumentation to exploit paramagnetism generally provides for a diamagnetic material to be suspended in a magnetic field, producing a turning moment. When a paramagnetic substance is interposed between the magnetic field and the diamagnetic material, the effect of the field on the latter is reduced and the turning moment diminishes. This can be measured as a rotation of the diamagnetic body and converted to a signal representative of the quantity of the paramagnetic material present.

C.3.2 Advantages and limitations

It is difficult to provide complete selectivity in such instruments, as a number of chemical species in the fire atmosphere will exhibit paramagnetism. However, it is now used almost universally for oxygen analysis, due to the high concentrations involved and the strong signal provided by this compound over the other potential interfering compounds.

Its main advantages are the relative selectivity of the method, the fact that it will monitor continuously and that although a “clean” sample is required from the fire or combustion atmosphere, sample clean-up procedures will not normally reduce the oxygen content significantly.

C.4 Colourimetry

C.4.1 Principle of operation and instrumentation

Colourimetry is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light of the substance in solution with respect to a known concentration of the substance; see Reference [48].

The colour can be due to the formation of a coloured compound by the addition of an appropriate reagent, or it may be inherent in the desired constituent itself. The coloured species usually has an optimum wavelength at which the absorbance is measured.

In visual colourimetry, natural or artificial white light is used as a light source and determinations made using a simple colour comparator or colourimeter. The intensity of the colour is judged visually by comparison with prepared standard solutions or coloured glass standards.

When estimation by the human eye is replaced with measurement by a photoelectric cell, the instrument is termed a photoelectric colourimeter. The light source usually consists of a comparatively narrow range of wavelengths obtained by passing white light through filters made from coloured glass, gelatin, etc., which transmit a limited spectral region. This instrument is sometimes termed a filter photometer.

More sophisticated instruments use light of a definite wavelength, not exceeding about 10 Å, in bandwidth, produced by directing white light through a prism or grating monochromator. This type of instrument is known as a spectrophotometer and usually extends into the ultraviolet region of the spectrum (i.e. where the wavelengths of the light are less than 400 nm).

Filter-photometers and spectrophotometers give the greatest precision and are most suitable for combustion studies. Colour comparators may have a use in some applications.

In practise, a known volume of gas or vapour is trapped in a suitable absorbing solution that is then analysed using colour-forming reagents specific to the species being analysed. The depth of colour produced is measured spectrophotometrically and compared with calibration standards prepared in a similar manner.

C.4.2 Advantages and limitations

C.4.2.1 The advantages of colourimetry include the following:

- instrumentation/apparatus are well proven and not prone to malfunction;

- allows the analysis of multiple samples and is not excessively time consuming;
- capable of quantifying more than one species in one test solution;
- wide range of concentrations can be measured;
- reasonably specific for most species, interferences can be accounted for.

C.4.2.2 The limitations of colourimetry include the following:

- can suffer interference with some species;
- hazardous chemicals used sometimes;
- analysis within a few hours of sampling can be required;
- usually measures time-integrated concentrations only; continuous monitoring is difficult and can miss or “damp” large changes in concentration.

C.5 Chromatography

C.5.1 General principles

Extensive literature exists describing chromatography in all its forms and applications. Only a brief outline is presented here. Chromatography can be generally described as a chemical analysis method, based on the separation of the different components in a mixture followed by their detection/recording. The separation is achieved by the “partitioning” of the components of the mixture between a mobile phase (the “carrier gas” in gas chromatography or the “eluent” in liquid chromatography), and a stationary phase all contained in a tube or “column”. Choice of detection method (of which there are many) depends on factors associated with the particular chromatographic method and the type of sample analysed. Output from a chromatograph is termed a chromatogram, typically consisting of a number of peaks separated in time, ideally with each peak representing a different component of the original mixture. In practice, however, complete separation of all components is difficult to achieve.

Two of the essential parameters for all chromatography are the following:

- retention time, which is the time between injection of the mixture into the chromatograph column and detection of the component (top of the peak as recorded by the detector). For a given component, retention time depends on the nature of the mobile and the stationary phases. Retention time, or a derivative of it, can be used as the basis of identification of the chemical species giving rise to a peak;
- peak area, which is the area under a peak ideally for a single component that can be used as the basis for quantifying the component.

Detector data are usually recorded and displayed electronically, often with sophisticated computing techniques to manipulate and quantify (through integration of the component peak areas) the chromatogram.

In practice, for quantification, a calibration plot is usually obtained for each species of interest by injection of a range of known quantities of the species.

A brief description of the main chromatographic methods is given below.

C.5.2 High performance ion chromatography (HPIC)

C.5.2.1 Principle of operation and instrumentation

In HPIC, the stationary phase is an ion-exchange resin contained in an inert tube (the “column”) and the mobile phase is an ionic solution. Samples are those which give rise to ionized species in solution and are often obtained by trapping the species in alkaline solution using metering “bubblers”.

Instruments contain a sample-injection system for the liquid mixture, a high-pressure pumping system for forcing the sample and eluent through the ion-exchange resin, and a detector coupled with a suitable readout device.

The following are important detection methods:

- Conductivity detection: based on the ability of an ionic solution to conduct a current when placed between two electrodes. Conductivity of the solution is directly related to concentration of the analysed component.

Species detected by conductivity are ionic, so this method requires a mobile phase containing strong electrolytes. Consequently, ionic analytes and ions of mobile phase can be detected. In order to avoid a loss of sensitivity of the detector due to the large quantity of ions from a mobile phase, chemical suppression can be used. There are different systems, but they all provide a lower baseline shift, a lower detection limit and elimination of interferences from cations (in case of anions analysis).

- Amperometry detection: based on the measurement of the current generated by oxidation or reduction of a component on the surface of a working electrode. This current is proportional to the concentration of the analysed component.

C.5.2.2 Advantages and limitations

C.5.2.2.1 The advantages of HPIC include the following:

- allows analysis of multiple samples and is not excessively time-consuming;
- capable of quantifying more than one species per test solution;
- wide range of concentrations can be measured;
- high sensitivity for many elements;
- very specific for most species (except with possible co-elutants);
- continuous monitoring possible.

C.5.2.2.2 The limitation of HPIC is that a relatively high level of technical expertise is required.

C.5.3 High performance liquid chromatography (HPLC)

C.5.3.1 Principle of operation and instrumentation

In HPLC, two chromatographic systems can be used:

- reversed-phase chromatography: the mobile phase is polar and the stationary phase non-polar (for example, an MeOH/H_2O eluent with a C18-greffed silica column);
- normal phase chromatography: the mobile phase is non- (or very low-) polar and the stationary phase is polar (for example, a $CHCl_3$ eluent with a silica column).

Samples are typically collected by trapping in aspirated bubblers and injected as liquids into the HPLC instrument.

Samples are injected in a similar way to HPIC with a high-pressure liquid pump. This can be an isocratic pump (fixed mobile phase composition) or a gradient pump (variable mobile phase composition). Typically, an ultraviolet (UV) absorption spectrometer detector is used. This is based on the principle that different compounds will absorb UV light at different wavelengths. The degree of absorption is dependent on the concentration of the compound in solution and the wavelength of the light.

C.5.3.2 Advantages and limitations

C.5.3.2.1 The advantages of HPLC include the following:

- allows the analysis of multiple samples and not excessively time-consuming;
- capable of quantifying more than one species in one test solution;
- wide range of concentrations can be measured;
- high sensitivity for many elements;
- very specific for most species (except with possible co-elutants);
- continuous monitoring possible.

C.5.3.2.2 The limitation of HPLC is that a relatively high level of technical expertise is required.

C.5.4 Gas chromatography

C.5.4.1 Principle of operation and instrumentation

The separating column is present either as a packed or lined tube. The tube can be relatively short (e.g. approximately 1 m) and wide (e.g. Two mm to 5 mm ID) or relatively long (e.g. many metres) and thin (e.g. < 1 mm), the latter being known as a capillary column.

The column packing or lining (the so-called stationary phase) can be one of a large variety of materials, depending on the separation required. The sample can be injected onto the separating column in a variety of ways, from a simple liquid syringe to a sophisticated gas sampling valve.

The sample in the gas phase (achieved if necessary by a heated injection port to vaporize the mixture) is forced through the column by an inert carrier gas, often helium, with the combined sample and carrier gas being known as the mobile phase. During passage of the mixture through the column, various chemical and physical forces act on it, with differing effects on the mixture components. This has the effect of separating the mixture components along the column and they emerge (elute) separately at the end. The components can then be detected in a variety of ways, but most commonly in fire gas analysis this will be either a flame ionization detector (where the eluted components are combusted in a small hydrogen flame and the ionic activity sensed and amplified), or a hot-wire detector (where cooling of the wire by passage of an elutant is measured by the change of electrical resistance of the wire).

The technique is primarily a quantitative one, although there are many examples of the use of gas chromatography to identify compounds. Sensitivities of between microgram and picogram levels are possible. Instrumentation has reached high levels of sophistication and automation, although the technology of the basic instrument is relatively simple.

C.5.4.2 Advantages and limitations

The main advantage of gas chromatography is its ability to separate and analyse an enormous number of chemical species, often with one instrument configuration and often with little operator intervention. Detectors can be highly sensitive and in some cases selective, to aid identification of individual species. The main disadvantage is that a typical analysis of fire gases can take up to one hour to complete, resulting in the need to take several samples during the course of a fire test, for example if the changing yields of many compounds are required during the course of the fire. Coupled with mass spectrometry, gas chromatography is probably the most powerful and comprehensive method for fire gas analysis. The equipment is expensive and requires a reasonable level of chemical analytical competence.

C.6 Mass spectrometry

C.6.1 Operating principles and instrumentation

Mass spectrometry provides chemical identification of species introduced (usually singly) into an instrument. In a typical “electron ionization/scanning magnetic sector” instrument, the sample, which can be a gas (from a gas chromatograph or a vaporizable liquid or solid) is introduced into a high-vacuum chamber (the ion-source) where it is bombarded by a high-energy electron stream. This both fragments the molecules of the sample compound and gives them a positive charge. The charged particles are accelerated from the ion-source and along a curved path between the poles of a powerful magnet. Particles of different momentum (i.e. through differing masses and velocity) are deviated by different amounts in the field. By scanning the field strength, the different particles can be focused on an electron multiplier tube, the signal amplified and the series of peaks representing the particles detected in one scan (i.e. the mass spectrum) displayed and/or recorded. Compounds have characteristic fragmentation patterns and their identity can be deduced by reference to library spectra produced from many materials.

Several other techniques exist, both to generate the ions and to separate them, in order to provide a mass-spectrum, but the desired result is an unambiguous identification of the sample compound.

The technique has proved particularly useful when combined with gas chromatography, the latter providing the single components of a mixture required by the mass spectrometer.

Mass spectrometry is primarily an identification technique, but it can be used in the quantitative mode. Microgram and picogram sensitivities are routinely achievable with absolute sensitivities of less than a femtogram. Some important species, e.g. carbon monoxide, cannot be readily measured by mass spectrometry, due to the strong similarity of their fragmentation patterns with those of other species.

C.6.2 Advantages and limitations

Mass spectrometry is a powerful tool for the identification of most species to be found in fire gases. When combined with gas chromatography (or in some cases liquid chromatography), it can be considered the best reference method for most compounds of interest. Typically, a mass spectrometer by itself can deal with only one compound at a time, although techniques exist to enable mixtures to be analysed. It tends to require a fairly high degree of technical expertise for operation (although this is changing with new automated running and library-searching techniques). A quadrupole MS, operating at a low electron energy (e.g. near the highest expected species ionization potential), can deal successfully with mixtures. However, the signal strength decreases sharply with electron energy.

C.7 Ion-selective electrodes (ISE)

C.7.1 Principle of operation and instrumentation

Ion-selective electrodes (ISEs) or membrane electrodes operate on the principle that a solution containing ions will register an electrical potential via an electrode immersed in the solution, with respect to a second defined potential. This can be used as a basis for detecting and quantifying the ionic species in solution. Selectivity becomes possible as different ionic species exhibit different potentials. The potential generated is described by the Nernst Formula (C.1):

$$x\,\mathrm{Ox} + n\,e^{-} \leftrightarrow y\,\mathrm{Red}$$

$$E = E^{0} - \frac{RT}{nF}\ln\left(\frac{a_{\mathrm{Red}}^{y}}{a_{\mathrm{Ox}}^{x}}\right) \tag{C.1}$$

where

E is the potential of measured solution;

E^{0} is the standard electrode potential;

R is the universal gas constant (8,314570 $\mathrm{J.mol^{-1}.K^{-1}}$);

T is the absolute temperature;

n is the number of electrons involved in the relevant reaction;

F is the Faraday constant (96 485 $\mathrm{C.mol^{-1}}$ = 1 F);

a_{Red}^{y} is the total chemical activity of reductant species;

a_{Ox}^{x} is the total chemical activity of oxidant species.

Many ISEs are able to operate without the need for a reference electrode, however, for some ions, their use is required; reference to manufacturer’s data are necessary.

The types of ISEs that are commercially available include sensing electrodes such as the following:

— solid-state electrodes (sse), constructed with a uniform or homogeneous solid substance, which is used as the ion-sensing area;

— glass electrodes (g) act as a membrane electrode for cation exchange;

—membrane. The potential is developed by the ion exchanging across this membrane;

— gas-sensing electrodes (gse) are able to detect dissolved gases in aqueous solutions. The detection is by an internal pH electrode which detects the pH change in an internal buffer, brought about by the gas reaction with the buffer;

— combinations (c) constructed from a combination of materials to provide a desired operating potential with given ions.

The choice of ISE is determined by the species to be measured, the speed and accuracy required, the sample concentration, whether the sample is dry or aqueous, the instrumentation available to operate the ISE and whether the sampling is in the field or the laboratory.

Some commercially available ISEs, their uses and some important interfering species, are shown in Table C.1.

Table C.1 — ion selective electrodes

Electrode	Type	Principle interferences	Concentration range M (µl/l)
Ammonia (NH_3)	gse	Volatile amines	1 M to 10^{-6} M (0,02 µl/l)
Bromide (Br^-)	sse	CN^-, I^-, NH_3, Cl^-, $S^=$, Hg^{2+}(must be absent), OH^-, NH_3, S_2O^{3-}	1 M to 5 × 10^{-6} M (0,04 µl/l)
Carbon dioxide (CO_2)	gse	NO_2, SO^-, CH_2O	10^{-4} (4,04 µl/l) to 10^{-2M} (440 µl/l)
Chloride (Cl^-)	g sse c	ClO_4^-, I^-, NO_3^-, OH^-, $SO_4^=$, Br^-, F^-, CN^-, NH_3, $S_2O_3^-$ $S^=$, Hg^{2+} (must be absent)	1 M to 5 × 10^{-5} M (0,18 µl/l) 1 M to 5 × 10^{-5} M (1,77µl/l) 1 M to 5 × 10^{-5} M (1,77µl/l)
Cyanide (CN^-)	sse	10^{-1} I^-, 5 × $10^3$$Br^-$, 10^6 Cl^-, $S^=$	10^{-2} to 10^{-6}M (0,03 µl/l)
Fluoride (F^-)	sse c	F^-, OH^-	10^{-6} M (0,02 µl/l) to saturated 10^{-6} M (0,02 µl/l) to saturated
Sulfide ($S^=$)	sse	$H_g^{2+} < 10^{-7}$M	1 M to 10^{-7} M (3,20 ppb)
Nitrogen oxides (NO_x) **Nitrite** NO_2^-	gse	NO_2, SO_2, pyruvic, lactic, formic, acetic	4 × 10^{-6} M (0,18 µl/l) to 5 × 10^{-3} M (220 µl/l)

C.7.2 Advantages and limitations

The instrumentation is robust, rugged, relatively cheap and easy to operate without particular expertise. A high sensitivity is possible but this advantage is normally offset in fire gas analysis by the cross sensitivity to other compounds in addition to the compound of interest.

C.8 Chemiluminescence

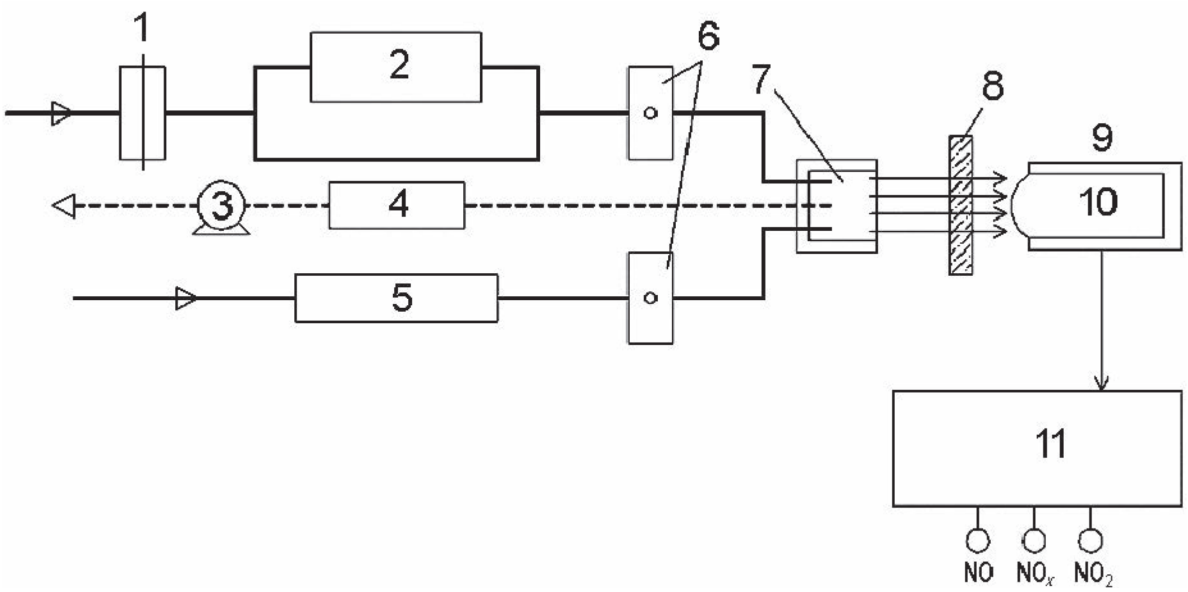
C.8.1 Principle of operation and instrumentation

The term chemiluminescence is generally used for chemical reactions that proceed with the evolution of light either within or outside the visible range of wavelengths. In the case of nitric oxide (NO), its reaction with ozone can be represented thus:

$$NO + O_3 = NO_2 + O_2 \tag{C.2}$$

A small proportion of the NO_2 produced is in an electronically excited state which, on decay, emits light of wavelengths in the regions of 0,6 µm and 3,0 µm. The intensity of the emitted light is proportional to the concentration of NO. In practical instruments, the light intensity is measured by a sensitive photomultiplier tube/amplifier to give a direct readout of NO.

Three main types of chemiluminescence analysers are available (see Figures C.1 to C.3):

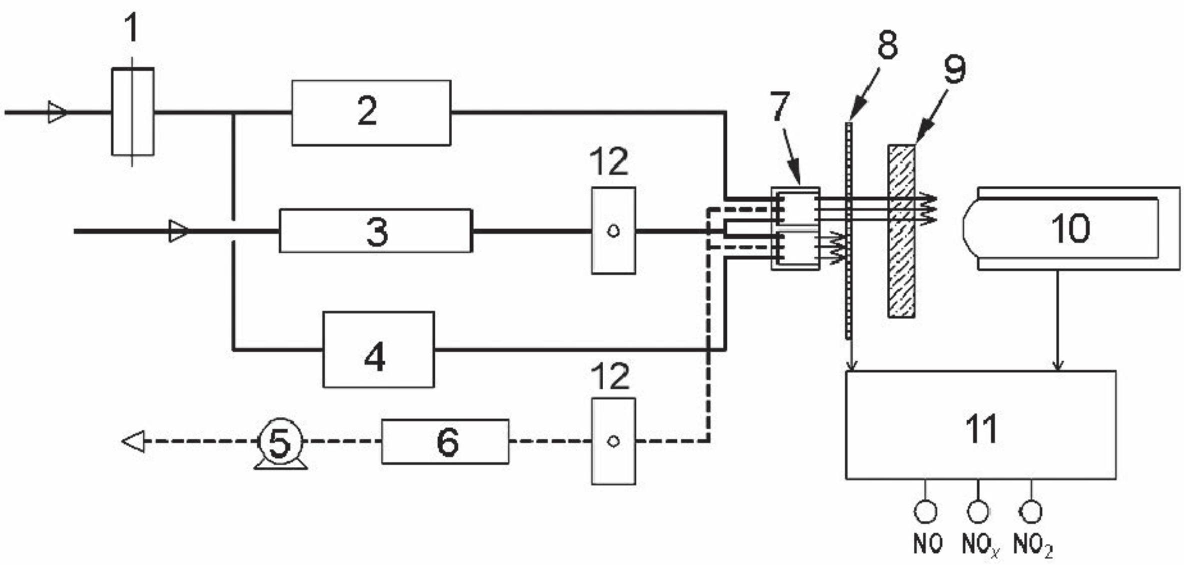


Key

1	initial sample filter
2	NO_2 to NO converter
3	pump
4	ozone elimination filter
5	ozone-generating system
6	sample flow control
7	reaction chamber
8	optical filter
9	refrigerated enclosure
10	photomultiplier tube
11	control and regulation of NO/NO_x cycle

Figure C.1 — Type 1: One reaction chamber and one photomultiplier tube

With these instruments, simultaneous analysis of NO and NO_x is not possible. A “commutation system” in the analysis line (with or without the converter) allows the analysis of NO or NO_x. The photomultiplier tube then records a response for NO or NO_x at a given frequency. This design of instrument is usually used with a system where the fire effluents have been diluted.

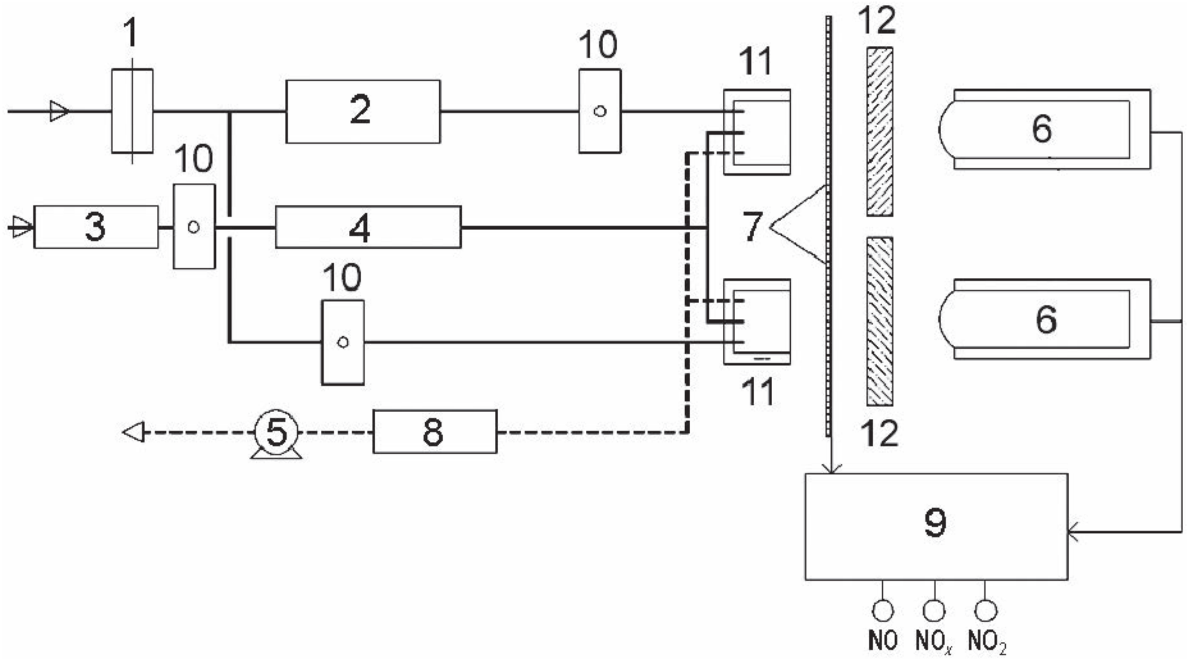


Key

1	initial sample filter
2	NO_2 to NO converter
3	ozone-generating system
4	equivalent volume
5	pump
6	ozone elimination filter
7	double reaction chamber
8	modulating system
9	optical filter
10	photomultiplier tube
11	synchronized electronic control and regulation system
12	sample flow control

Figure C.2 — Type 2: Two reaction chambers and one photomultiplier tube

Simultaneous analysis of NO and NO_x is possible. A modulating system allows detection by the photomultiplier tube of the response to NO or NO_x. The frequency of the modulation has to be high enough to provide a good evaluation of the released gases. This design of instrument is usually used with a system where the fire effluents have been diluted.



Key

1	initial sample filter
2	NO_2 to NO converter
3	drying system
4	ozone-generating system
5	pump
6	twin photomultiplier tubes
7	modulating system
8	ozone elimination filter
9	synchronized electronic control and regulation system
10	sample flow control
11	reaction chambers
12	optical filters

Figure C.3 — Type 3: Two reaction chambers and two photomultiplier tubes

Simultaneous analysis of NO and NO_x is possible. The use of two photomultiplier tubes can cause some problems, insofar as the adjustment on the two analysis lines has to be exactly the same. This design of instrument is usually used without previous dilution of the fire effluents.

The ozone is generated *in situ* using air or oxygen in a corona discharge unit.

As NO_x is mainly determined by the sum of NO and NO_2 released, condensation must be avoided in any trap used as NO_2 is very hydrophilic. The use of a heated sampling line for fire effluents can solve these condensation problems.

In NO_x instruments, the sample stream can be diverted to a converter unit, where it is heated and passed through a reducing medium. This converter uses a molybdenum catalyst and works at about 400 °C. Any NO_2 present in the sample will be converted to NO, which is then measured with the existing NO. Older instruments, which employ carbon converters running at 500 °C to 600 °C, tend to convert other nitrogen-containing species to NO as well, enhancing the “NO_x” signal and making the estimation of NO_2 less precise. For example, with these high temperatures, the chemical bond C = N in HCN can be broken and free nitrogen can react with oxygen and lead to the production of oxides of nitrogen, which are measured by the analyser.

C.8.2 Advantages and limitations

Instruments tend to show a tendency to baseline drift, resulting in the need for frequent resetting of the zero. Calibration is prone to inaccuracy as the standard gas mixtures for NO have a limited lifetime due to reaction between the gas and the container. The method is, however, of great value in providing a continuous analysis of NO_x.

C.9 Titrimetry (potentiometry)

C.9.1 Operating principles and instrumentation

The titrimetric methods use addition of a solution to generate a precipitate with ions to be determined. The precipitation reaction can be followed by electrochemical way. In the majority of cases, reactions of precipitation between chloride and bromide ions with silver ions are used.

The quantity of silver ions introduced (in general with silver nitrate solution) is monitored as function of advancement of precipitation reaction. Advancement is determined using electrodes, because of the dependence of electronegativity of the solution when consuming ions to form precipitate. Commonly, standard Silver/silver chloride reference electrode is used to form a couple with ions present in the solution.

C.9.2 Advantages and limitations

The method is very simple to operate, and don't need any standard of the compound to be determined. It is very sensitive to low concentrations of chloride and bromide, and less sensitive to other anions like cyanide.

Nevertheless, interpretation is subject to caution when multiple ions precipitate. The method can be not enough selective depending on the content of solution to be analysed.

C.10 Atomic absorption spectroscopy

C.10.1 Operating principles and instrumentation

Atomic absorption spectrophotometry is a spectroscopic technique which makes use of the absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by most metallic elements (and some other elements) when in the form of an atomic vapour [49], [50]

The vapour is formed by aspirating a solution containing the element into a flame or by evaporation from an electrically heated surface, and this supplies enough thermal energy to dissociate a proportion of the chemical compounds containing the element of interest, into free atoms. When light of a suitable wavelength impinges on a free, "ground state" atom, it causes the atom to enter an excited state, and the atom absorbs the light in a process known as atomic absorption. The amount of light absorbed is proportional to the population density of the atoms in the flame, i.e. the sample concentration.

Samples are typically collected by passing the fire atmosphere through metered aspirated "bubblers".

Instruments generally consist of three basic components:

— light source:	usually a lamp having a hollow cathode made of the element to be determined;
— sample cell:	burner system or electrically heated furnace or carbon rod;

— means for specific wavelength light measurement: monochromator and photomultiplier detector.

C.10.2 Advantages and limitations

C.10.2.1 AAS has the following advantages:

— very specific, little interference;

- high sensitivity for many elements (0,1 µl/l to 100 µl/l);
- allows the analysis of multiple samples and is not excessively time consuming;
- capable of quantifying more than one element in one test solution.

C.10.2.2 AAS is limited in that it usually measures only time-integrated concentrations; continuous monitoring is difficult.

C.11 Inductively coupled plasma emission spectrophotometry (ICP)

C.11.1 Operating principles and instrumentation

Plasma emission spectrometry is an atomic spectroscopic technique involving the emission of electromagnetic radiation in the visible and ultraviolet region of the spectrum by atoms and ions after electronic excitation in a high-temperature gas plasma. With this particular technique, the plasma source is an inductively coupled plasma torch (ICP).[49]

Argon is used to create a plasma containing high proportions of ions and free electrons at temperatures of 8 000 K to 10 000 K. An aerosol of the sample solution is injected into the plasma and the intense temperature causes the electrons in the atoms to move to a higher energy level. The light emitted when the excited atoms are restored to the "ground state" contains spectra characteristic of the elements present. Individual spectral lines are isolated by a monochromator and their intensities measured by a photomultiplier tube.

Samples are typically obtained by passing the fire gases through metered liquid aspirated "bubblers".

Instruments generally consist of the following components:

- ICP source; an aerosol of the sample solution is injected into the plasma in a stream of argon passing through the central tube of three concentric quartz tubes. A higher flow of argon is injected between the second and outer tubes. The argon plasma is ignited by a high-voltage discharge from a "Tesla" coil and sustained by induction heating from a radio frequency coil at a power level of about 2 kW;
- grating monochromator, to isolate spectral lines characteristic of the element being analysed;
- photomultiplier detection system.

C.11.2 Advantages and limitations

C.11.2.1 ICP has the following advantages:

- very specific, little interference;
- very high sensitivity for many elements (0,01 µl/l to 100 µl/l);
- allows the analysis of multiple samples and is not excessively time consuming;
- capable of quantifying more than one element in one test solution.

C.11.2.2 ICP has the following limitations:

- instrumentation is complex;
- usually measures only time-integrated concentrations. Continuous monitoring is difficult.

C.12 Total organic/hydrocarbon monitors (general notes)

These instruments provide a measure of the “unburnt” fraction in fire gases and several techniques exist to achieve this. Many instruments are based on the flame-ionization principle, in which the gas sample is passed through a small hydrogen flame and the ionization produced is measured by an amplifier. Other instruments depend on the catalysed combustion of the unburnt species on a heated, coated wire that causes a rise in the temperature which is measured as a change in the resistance of the wire which is used to provide the output signal.

Instruments are readily available commercially and have been developed particularly as compact portable units for checking flue gas emissions, etc.

The instruments generally have a variable sensitivity to different organic compounds and can be expected to provide only a semiquantitative indication of concentration. They are particularly insensitive to oxygenated species, which are of high importance in toxicology.

Annex D
(informative)

Hydrogen fluoride by continuous online ion selective electrode

D.1 Application and limitations

This method permits continuous measurement of fluoride ion in solution where a sample flow-through system enables the measurement to be carried out dynamically. There are numerous problems associated with continuous analysers which rely on the dissolution of gaseous species. They often have severe limitations in the range of gas concentrations detected because of equipment constraints on flow rates of gas and liquid. In addition, the electrode response is not immediate. Timing and flow rates are therefore crucial in determining the accuracy of the final analysis.

D.2 Sensitivity and selectivity

This method permits the detection of hydrogen fluoride concentrations lower than 0,5 mg/m^3 (i.e. 0,16 µl/l). It is specific for hydrogen fluoride.

D.3 Other considerations

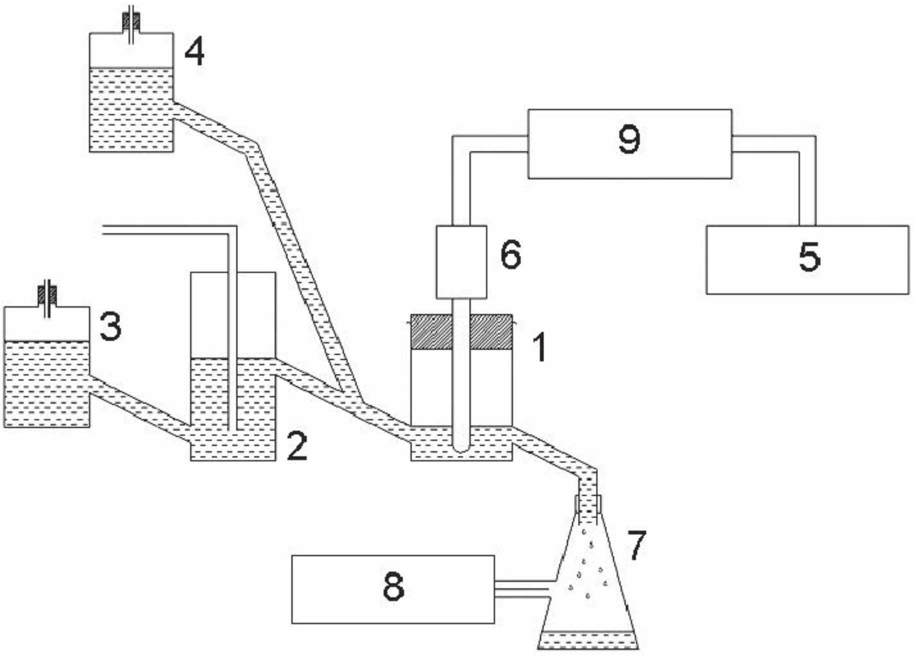
Despite the limitations of this method, it is essentially the only continuous technique available for hydrogen fluoride and is, therefore, included in this document. However, whenever discrete sampling and analysis can be tolerated (e.g. in the “steady-state” conditions of some fires or fire model operations), methods 5.6.1 and 5.6.2 are recommended.

D.4 Analysis principles

A sample of fire effluent is drawn continuously into an aqueous solution and then automatically into a measuring cell containing a proprietary fluoride-ion-selective electrode. The electrode potential is amplified and recorded (or the concentration directly recorded); see Figure D.1.

D.5 Procedure

See Clause 4 for principles of sampling and C.7 for the general principles of the ISE method. However, for the analysis of hydrogen fluoride by a continuous online ion-selective electrode, the specific information in Annex D is relevant.



Key

1	measuring cell
2	gas-washing bottle
3	alkaline reagent
4	acid reagent
5	recorder
6	combination
7	collector
8	pump
9	differential amplifier

Figure D.1 — Schematic of the apparatus for continuous online ion-selective electrode

D.6 Sampling

Because of the reactivity of hydrogen fluoride, sampling lines, probes etc. should be constructed from non-reactive materials (e.g. PTFE). In particular, glass should not be used. Pumping rate from the fire atmosphere will in general be far higher than that required for the apparatus and it will normally be necessary to provide a “tee” connection from the main effluent sampling line.

D.7 Analysis

D.7.1 Reagents

The composition of the cell solution shall be as follows:

— phosphoric acid 0,14 mol/l;

— sodium hydroxide 0,17 mol/l;

— potassium chloride 2,0 mol/l;

— sodium fluoride 2×10^{-7} mol/l.

D.7.2 Protocol

The flow rate of solution through the measuring cell should be 1,5 cm^3/min and its volume 1 cm^3. Cell solution is extracted automatically in order to keep the pH at 2,2 and the response time should be less than 2 sec.

D.8 Calibration

Prepare calibration standard solutions using sodium fluoride.

D.9 Calculations

The “instantaneous” hydrogen fluoride concentration is obtained from Formula (D.1):

$$\rho_{\mathrm{HF}} = \frac{\rho_{\mathrm{F}} \times 1{,}053 \times V_{\mathrm{as}} \times 1{,}22}{V_{\mathrm{ta}}} \tag{D.1}$$

where

ρ_{HF}	is the concentration, expressed in microlitres per litre, of the hydrogen fluoride;
ρ_{F}	is the concentration, expressed in micrograms per litre, of fluoride ion;
1,053	is the conversion factor from F− to HF equal to 20/19;
V_{as}	is the volume, in millilitres, of the absorbing/desorbing solution;
1,22	is the factor converting micrograms per litre (milligrams per cubic metre) to microlitres per litre of atmosphere at 25 °C;
V_{ta}	is the volume, in litres, of the test atmosphere sampled.

Bibliography

[1] AFNOR NF X70-100-1, *Fire tests — Analysis of gaseous effluents — Part 1: Methods for analysing gases stemming from thermal degradation*

[2] AFAP-3 NATO. *Reaction-to-fire tests for materials – Toxicity of fire effluents*, edition 3 (2010)

[3] ISO 29904, *Fire chemistry — Generation and measurement of aerosols*

[4] ISO 19702, *Toxicity testing of fire effluents — Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis*

[5] Grand A.F., Kaplan H. L., Lee G.H.*Investigation of Combustion Atmospheres in Real Building Fires*, Final Report for the Society of the Plastic Industry Incorporated and US Fire Administration by Southwest Research Institute, SWRI Project No 01-. 6067 (USAF Grant No 80027) (May 1981)

[6] Burgess W.A, Treitman R.D, Gold , Awram *Air Contaminants in Structural Firefighting*, Final Report, Harvard School of Public Health, (March 1979)

[7] Kaplan H.L., Grand A.F., Switzer W.G., Gad S.C. Acute Inhalation Toxicity of the Smoke Produced by Five Halogenated Polymers. *J. Fire Sci.* 1984 March/April, **2** pp. 153–172

[8] Grand A.F., Kaplan H.L., Beitel J.J., Switzer W.G., Hartzell G.E.*An Evaluation of Toxic Hazards from Full-Scale Furnished Room Fire Studies*. Fire Safety, Science and Engineering

[9] NT FIRE 047 (May 1993). *Combustible Products: Smoke Gas Concentrations. Continuous FTIR Analysis*

[10] Nyden M.R., & Babrauskas V.*Use of FTIR Spectroscopy for MultiComponent Quantitation in Combustion Technology*, Combined Technical Meetings: Eastern Section, the Combustion Institute, and The Center for Fire Research Annual Conference on Fire Research, Gaithersburg, MD (198, pp. 107-1 to 107-4), 1987

[11] Kallonen R. Smoke Gas Analysis by FTIR Method. Preliminary Investigation. *J. Fire Sci.* 1990, **8** p. 343

[12] Guillaume E., Le Tallec Y., Ayrault M., Saragoza L.Fire behaviour of materials used in military ships – Review report 2002-2005, Ref C670N02 (2005) (Document published only in the framework of NATO STANAG 4602 FRT Group experts)

[13] JIS K-0109:1982, *Methods for determination of hydrogen cyanide in flue gas*

[14] ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

[15] AFNOR NF X70-100-2, *Fire tests — Analysis of gaseous effluents — Part 2: Tubular furnace thermal degradation method*

[16] American Society for Testing and Materials. *Standard guide for measurement of gases present or generated during fires*. ASTM Committee E-5 on Fire Standards, Document E800-81, (1981)

[17] Guillaume E., Athimon N., Saragoza L., Yardin C.*Analysis of HBr, HCl and SO2 produced during thermal degradation of materials - adaptation of standardized method*, in Proceedings of 13th International Metrology Congress, ISBN 2-915416-06-0, Lille 2007

[18] national institute of occupational safety and health. *Fluorides, Aerosol and Gas*. NIOSH Manual of Analytical Methods, 3rd Edition, Publication No. 84 - 100, Method 7902, (1984)

[19] Airbus Industries Specification ABD 0031. *Hydrogen Fluoride (HF) - Potentiometric Measurement*

[20] American Public Health Association. *Tentative Method of Analysis for Acrolein Content of the Atmosphere (Colorimetric)*. Methods of Air Sampling and Analysis 2nd Edition. (Ed M Katz), 43505-01-70T (1977), 297-300

[21] Cophen I.R., & Altshuller A.P. A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and in the Atmosphere. *Anal. Chem.* 1961, **33** pp. 726–733

[22] Guenier J.P, Simon P, Delcourt J, Didierjean M.F, Lefevre C, Muller J.*Air sampling of aldehydes - application to chromatographic determination of formaldehyde and acetaldehyde*, Chromatographia, 18-3 (March 1984), 137-144

[23] Anderson K., Hallgren C., Levin J.O., Nilsson C.A. Chemosorption sampling and analysis of formaldehyde in air - Influence of recovery during simultaneous sampling of formaldehyde, phenol, furfural and furfural alcohol. *Scand. J. Work Environ. Health*. 1981, **7** pp. 282–289

[24] Lipari F., & Swarin S.J. Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4, dinitrophenylhydrazine method. *J. Chromatogr. A*. 1982, **247** pp. 297–306

[25] Lehtonen P., Laakso R., Puputti E. Liquid chromatographic determination of 2- propenal (acrolein) and 2-butanal (crotonaldehyde) from water-ethanol mixtures. *Z. Lebensm. Unters. Forsch.* 1984, **178** pp. 487–489

[26] Schulte-Ladbeck R., Lindalh R., Levin J.O., Karst U. Characterization of chemical interferences in the determination of unsaturated aldehydes using aromatic hydrazine reagents and liquid chromatography. *J. Environ. Monit.* 2001, **3** pp. 306–310

[27] Ramaz M., Weber J., Le Tallec Y.Toxic gases analysis using GC-MS technique, Poster session, Flame Retardants 2002 Conference, London (unpublished)

[28] Fardell P.J., & Guillaume E.*Sampling and measurement of toxic fire effluent*, in Fire Toxicity Handbook, chapter 11, Woodhead Publishing Ltd, ISBN 978-1-84569-502-6

[29] American Public Health Association. *Tentative Method of Analysis for Formaldehyde, Acrolein and Low Molecular Weight Aldehydes in Industrial Emissions on a Single Collection Sample*. Methods of Air Sampling and Analysis 2nd Edition, (Ed M Katz), 43501-02-74T, (1977), 333-335

[30] National Institute for Occupational Safety and Health. *Formaldehyde in Air*. NIOSH Manual of Analytical Methods, 2nd Edition, Part I, Niosh Monitoring Methods 1, Method No PμCAM 125, (1977)

[31] Hauser T.R.*Determination of Aliphatic Aldehydes: 3-Methyl-2-Benzothiazolone Hydrazone Hydrochloride (MBTH) Method. Selected methods for the Measurement of Air Pollutants*. Public Health Service Publication No 999-AP-11, (1965) p. F-1

[32] American Public Health Association. *Tentative method of Analysis for Formaldehyde Content of the Atmosphere (MBTH-Colorimetric Method-Applications to other Aldehydes)*. Methods of Air Sampling and Analysis, 2nd Edition, (Ed. M Katz). 43502-02-70T, (1977), 308-313

[33] Miksch R.R., & Anthon D.W. A Recommendation for Combining the Standard Analytical Methods for the Determination of Formaldehyde and Total Aldehydes in Air. *Am. Ind. Hyg. Assoc. J.* 1982, **43** (May) pp. 362–365

[34] Tsuchiya Y., & Boulanger J.G.*Carbonyl sulfide in fire gases*

[35] National Institute for Occupational Safety and Health. *Ammonia in Air*. NIOSH Manual of Analytical Methods, 2nd Edition, Part 1, Niosh Monitoring Methods 1., Method No. PμCAM 205, (1977)

[36] Fifield F.W., & Kealey D. *Principles and Practice of Analytical Chemistry*. International Textbook Company Ltd, Second Edition, 1983

[37] Beaty R.D. *Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry*. Perkin-Elmer Corporation, 1978

[38] Egan H., Kirk R.S., Sawyer R. *General Chemical Methods, Phosphate. Pearsons Chemical Analysis of Foods*. Churchill Livingston, Eighth Edition , 1981, pp. 29–30.

[39] Mindrup R. The analysis of gases and light hydrocarbons by gas chromatography. *J. Chromatogr. Sci.* 1977, **16** p. 293

[40] Chaigneau M., & Le Moan G. *Study of pyrolysis of polystyrene*. Ann. Pharm. Franc. No, 1970, pp. 41.

[41] Chaigneau M., & Le Moan G. *Analysis and evolution of the compounds formed by pyrolysis and combustion of silk*. *Analysis*. 1979, **7** (3) p. 154

[42] Klimisch H.J. Measurement of concentration of total volatile organic substances in inhalation chamber. *J. Combust. Toxicol.* 1980, **7** p. 257

[43] King W.H. Jr. The monitoring of hydrogen, methane, and hydrocarbons in the atmosphere. *Environ. Sci. Technol.* 1970, **4** (12) p. 1136

[44] Lubeck Detector tube handbook, Draegerwerk A.G. Germany, Fourth Edition, May, 1979

[45] MDHS method 25/3

[46] Mohn J., & Emmenegger L.Determination of Sulphur Dioxide by Pulsed UV-Fluorescence. Swiss Federal Laboratories for Materials Testing and Research (EMPA), Überlandstrasse 129, CH-8600 Dübendorf

[47] BS EN 1948 (all parts), *Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs*

[48] Vogel A.I. *A text book of quantitative inorganic analysis, including elementary instrumental analysis*. Longmans, Green and Co. Ltd, London, Third Edition, 1961

[49] Fifield F.W., & Kealey D. *Principles and Practice of Analytical chemistry*. International Textbook Company Ltd, Second Edition, 1983

[50] Beaty R.D. *Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry*. Perkin-Elmer Corporation, 1978

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