
**Methods for sampling and analysis of fire
effluents**

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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 first edition of ISO 19701 cancels and replaces the first edition of ISO/TR 9122-3:1993, which has been technically revised.

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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 atmosphere may be laden with solid and liquid particulates and the gas phase itself can contain many corrosive, toxic and irritant 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 Clauses 3, 4 and 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 (see C.13) have been taken from NF X 70-100-1^[1].

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 colorimetric end point. In these cases, it is assumed that best practice by qualified personnel is applied.

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This International Standard is structured as follows.

- Clause 2 describes methods of sampling.
- Clause 3 describes analytical methods for the so-called “narcotic” (asphyxiant) gases in fire atmospheres: carbon monoxide, carbon dioxide, and hydrogen cyanide. Oxygen is also included.
- Clause 4 describes analytical methods for important irritant gases in the fire atmosphere.
- Clause 5 covers the analysis of particulates, although detailed methodologies for quantifying particle mass, number, density and particle size will be provided in a separate document.
- Annex A provides brief guidance for the analysis of several other species of interest in fire atmospheres where well-documented methods are often not available.
- 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.

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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.

2 Methods of sampling

2.1 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.

The units of concentration of gases used should be volume fraction, e.g. volume percent or volume percent $\times 10^{-4}$ [volume percent $\times 10^{-4}$ = parts per million (ppm), which is a deprecated unit], rather than weight/volume (e.g. milligrams/cubic meter). Ideal gas behaviour is assumed for the gases and concentrations encountered. The temperature of the gases should be measured at the sampling point to allow a correction to be applied to the volume sampled. Suitable and efficient filtering should be maintained in order to protect the measuring equipment.

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.

2.2 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, on-line 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 on-line 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) and hydrogen cyanide (HCN), 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 these 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.

2.3 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 Equation (1):

$$\rho_G = \frac{\rho_S \times V \times H \times (m_G/m_S) \times 10^6}{q \times t} \quad (1)$$

where

- ρ_G is the gas concentration, expressed in micrograms per litre (volume fraction $\times 10^{-6}$)¹;
- ρ_S is the solution concentration, expressed in grams per litre or moles per litre (see H for consistent units);
- V is the volume, expressed in litres, of solution;
- H is a gas constant representing the gaseous volume occupied by 1 g or 1 mol of species. The value of 1 mol occupying 22,4 l at 0 °C and 101,325 Pa²) pressure must be corrected for the ambient temperature and pressure during sampling using the gas laws;
- m_G/m_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.

EXAMPLE If the measured solution concentration of chloride (Cl) is 0,006 g/l in 0,025 l of solution at 20 °C and a pressure of 101,325 Pa, and flow of gas is 0,25 l/min for 2 min, then

$$\begin{aligned} \rho_G &= \frac{0,006 \times 0,025 \times 0,0659 \times (36,5/35,5) \times 10^6}{0,25 \times 2} \\ &= 203 \mu\text{g/l HCl} \end{aligned}$$

- 1) Volume fraction $\times 10^{-6}$ equals parts per million (ppm), a deprecated unit.
- 2) 101,325 Pa = 1 atm, a deprecated unit of pressure.

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 Equation (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 midjet 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. Precautions for filtration of combustion atmospheres are discussed in 2.2. 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.

2.4 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, flowmeters 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 [1], [2] 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 [3] and HCN [4]. Tubes containing flake sodium hydroxide for the absorption of acid gases have also been described [5]. 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 [4].

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.

2.5 Sampling for spectrometric or spectrophotometric analysis

The use of spectrometric analysis [direct mass spectrometry (MS)] and spectrophotometric analysis [both non-dispersive infra-red (NDIR) and Fourier transform infra-red (FTIR)] have become quite widespread in recent years. FTIR techniques in particular are becoming more prominent [6], [7], [8]. The continuous measurement by means of NDIR analysis (e.g. for CO and CO₂) 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 GMF150³) 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

3) 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.

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.

2.6 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 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)	Colorimetry (Chloramine T) Colorimetry (picric acid) HPIC	solution solution solution
Hydrogen chloride (HCl) Hydrogen bromide (HBr)	ISE HPIC	solution solution
Hydrogen fluoride (HF)	ISE HPIC On-line ISE	solution solution solution
Nitrogen oxide (NO _x)	Chemiluminescence	gas
Nitrogen dioxide (NO ₂)	HPIC	solution
Acrolein	Colorimetry HPLC	solution solution
Formaldehyde	Colorimetry HPLC	solution solution
Total aldehydes	Colorimetry	solution
Sulfur dioxide (SO ₂)	HPIC	solution
Ammonia (NH ₃)	Colorimetry HPIC	solution solution
Antimony compounds	AAS or ICP	solution
Arsenic compounds	AAS or ICP	solution
Phosphorus	ICP	solution
Phosphates	Colorimetry HPIC	solution solution

3 Analytical methods for “narcotic” (asphyxiant) gases

3.1 Carbon monoxide by non-dispersive infra-red spectroscopy (NDIR)

3.1.1 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.

3.1.2 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.

3.1.3 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.

3.1.4 Analysis principles

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NDIR instruments operate by passing a beam of infra-red (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.

3.1.5 Procedure

See Clause 2 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 3.1.6 to 3.1.9 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) have sufficient resolution for the chosen range.

3.1.6 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.

3.1.7 Analysis

There is no requirement for additional analytical procedures.

3.1.8 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.

3.1.9 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 non-linear 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.

3.2 Carbon dioxide by non dispersive infra-red spectroscopy (NDIR)

3.2.1 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.

3.2.2 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.

3.2.3 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.

3.2.4 Analysis principles

NDIR instruments operate by passing a beam of infra-red (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.

3.2.5 Procedure

See Clause 2 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 3.2.6 to 3.2.9 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.

3.2.6 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.

3.2.7 Analysis

There is no requirement for additional analytical procedures.

3.2.8 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 than 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.

3.2.9 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 non-linear 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.

3.3 Oxygen by paramagnetism

3.3.1 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.

3.3.2 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.

3.3.3 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.