BRITISH STANDARD

Implementation of
ISO/TR 9122-3:1993

Toxicity testing of fire effluents —

Part 3: Methods for the analysis of gases and vapours in fire effluents

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee FSH/16, upon which the following bodies were represented:

British Cable Makers Confederation

British Electrical Systems Association (BEAMA Ltd.)

British Plastics Federation

British Railways Board

British Rigid Urethane Foam Manufacturers' Association

British Rubber Manufacturers Association Ltd.

British Textile Technology Group

Chemical Industries Association

Chief and Assistant Chief Fire Officers Association

Consumer Policy Committee of BSI

Department of Health

Department of the Environment (Building Research Establishment)

Department of Trade and Industry (Consumer Safety Unit, CA Division)

International Wool Secretariat

Loss Prevention Council

Queen Mary and Westfield College

RAPRA Technology Ltd.

Warrington Fire Research Centre

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Contents

National foreword

This British Standard reproduces verbatim ISO/TR 9122-3:1993 and implements it as the UK national standard. It is related to PD 6503-1:1990 which is the UK adoption of ISO/TR 9122-1:1989. When ISO/TR 9122-1 is revised, it is intended that it will be implemented as the UK national standard.

The Technical Committee had earlier decided not to implement ISO/TR 9122-2 as the UK national standard but to publish a national document (PD 6503-2) instead. PD 6503-2:1988 remains current until the 1990 edition of ISO/TR 9122-2 is revised when it is envisaged that the new edition of ISO/TR 9122-2 will be implemented as a British Standard.

To avoid any further confusion, the decision has been made to implement all the remaining Parts of the ISO/TR 9122 series as British Standards rather than producing national documents as further Parts of PD 6503.

This British Standard is published under the direction of the Consumer Products and Services Sector Board whose Technical Committee FSH/16 has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international committee any enquiries on interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

NOTE   International and European Standards, as well as overseas standards, are available from Customer Services, BSI, 389 Chiswick High Road, London W4 4AL.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the ISO title page, pages ii to iv, pages 1 to 34 and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

TECHNICAL
REPORT

ISO

TR 9122-3

Toxicity testing of fire effluents —

Part 3:
Methods for the analysis of gases and vapours in fire effluents

Essais de toxicité des effluents du feu —

Partie 3: Méthodes d'analyse des gaz et des vapeurs dans les effluents du feu

Contents

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.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into international Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 9122-3, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 92, *Fire tests on building materials, components and structures,* Sub-Committee SC 3, *Toxic hazards in fire.*

ISO/TR 9122 consists of the following parts, under the general title *Toxicity testing of fire effluents*:

— *Part 1: General*;

— *Part 2: Guidelines for biological assays to determine the acute inhalation toxicity of fire effluents (basic principles, criteria and methodology)*;

— *Part 3: Methods for the analysis of gases and vapours in fire effluents*;

— *Part 4: The fire model (furnaces and combustion apparatus used in small-scale testing)*;

— *Part 5: Prediction of toxic effects of fire effluents*.

Annexes A, B, C and D of this part of ISO/TR 9122 are for information only.

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Introduction

During recent years, analytical techniques have been used widely for the measurement of the concentrations of specific volatiles generated during both laboratory studies and fires. These measurements are necessary for those involved with research and testing of materials and composites, particularly in the toxicological and related fields of interest.

The analysis of gases in fire effluents, whilst occasionally needing to rely upon methods perfected in other fields (e.g. atmospheric pollution), represents a very specialized field of study due to the complexity and reactivity of the gas mixtures and the possibility of a rapid change in concentration with time. This has led a number of scientists from different countries to develop new, or adapt existing methods of analysing the gases present during combustion, in accordance with their own requirements.

In some cases, common lines of analysis have emerged, and there is now sufficient expertise and experience to define standard methods for analysing selected gases.

This part of ISO/TR 9122 is therefore produced to aid all those involved with the analysis of fire gases in research or testing fields to proceed along common, agreed lines. It primarily covers methods of analysis, but also recommends the best state of the art knowledge in sampling methods.

This part of ISO/TR 9122 includes analytical methods for nine common gases. References are also included to other gases of interest where, so far, experience does not permit a standardization of methods.

In each case, specific details of the analytical methods are given. However, with chromatography (reference method for carbon monoxide, carbon dioxide and oxygen), considerable experience exists and different but acceptable techniques are in widespread use internationally.

In these cases, analysis is based on performance requirements with a recommended (i.e. non-mandatory) method of analysis.

In ISO/TR 9122-1, great emphasis was directed towards the need to address the problem of total toxic hazard rather than toxicity *per se* and to attempt to integrate toxicity and combustibility information (and not to use toxicity information by itself as a basis for decisions on control of materials).

Specific methods are presented in this part of ISO/TR 9122 for the analyses of airborne concentrations of carbon monoxide, carbon dioxide, oxygen, hydrogen cyanide, hydrogen chloride, hydrogen bromide, hydrogen fluoride, oxides of nitrogen, and acrolein. Details of several analytical methods are presented for each gas, along with a commentary on the scope, sensitivity, calibration methodology and advantages/disadvantages of the procedures. Chromatography methods are in widespread use internationally and were, therefore, selected to be the "recommended" methods for most gases.

Its purpose is also to identify the role of analytical techniques, i.e. solely to measure/define/identify atmospheres in terms of specific standard gases. It does not give directions on how the atmosphere is created, which is integral to the evaluation of toxic hazard.

Proper use of the analytical methods in this part of ISO/TR 9122 implies that

the analysis of sampled gases has been carried out in accordance with standardized procedures;

the sampling procedure is in accordance with the general recommendations given, and with due consideration to the reactive nature of the species analysed.

A list of additional compounds is also given in this part of ISO/TR 9122 which are known to be of interest in fire effluents, together with literature references for methods of analysis which are given for information only.

The methods cited are generally applicable to the analysis of effluents arising from fires ranging from small-scale laboratory combustion tests to full-scale fires. However, sampling techniques may vary, depending upon the size of the fire and the rate of fire growth. Since sampling is often the most critical part of a procedure for the analysis of gases in fire effluents, considerable attention must be given to sampling techniques. This part of ISO/TR 9122 provides guidelines for such consideration.

The primary purpose of the analytical methods described in this part of ISO/TR 9122 is to measure the concentration of toxic species to aid in

a) the characterization of fire models;

b) setting the conditions for exposure in biological studies;

c) monitoring of biological studies;

d) the interpretation of biological studies.

The methods are also generally applicable to the analysis of fire effluents in many situations including large-scale fires.

It is not technically valid and, therefore, not recommended

> to use chemical analyses alone as a basis for a general toxicity test for materials in fire (because of the possible presence of unknown species);

> to use either chemically or biologically derived toxicity data as direct criteria for fire safety acceptability of materials in specifications or regulations. It is emphasized that the use of these data without knowledge and integration of other material flammability characteristics imparts a serious risk of reaching faulty conclusions, which would be counter-productive to safety objectives.

1 Scope

This part of ISO/TR 9122 specifies methods for the individual analysis of airborne concentrations of carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), hydrogen cyanide (HCN), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen fluoride (HF), oxides of nitrogen (NO_x), and acrolein (CH_2CHCHO) in fire effluents.

2 General

In some cases, experience has led to several different methods of analysis being used internationally with acceptable results. In these cases, several methods are given in this part of ISO/TR 9122 with one method identified as the reference method to be used in the event of apparent disagreements in analytical results (e.g. between laboratories). However, it should be noted that the reference method cited need not necessarily be the ideal method for day-to-day operations. Also, newer methods may be developed which are equally suitable.

The analysis of gases in fire effluents is very complex due to the great number of different organic and inorganic chemicals which representative atmospheres can contain.

Compliance with this part of ISO/TR 9122 implies that

— the analysis of sampled gases has been carried out by standardized procedures;

— the sampling procedure is in accordance with the general recommendations noted in clause **3**, and with the nature of the species.

A second list of chemicals is also given which are known to be of interest in fire effluents, together with literature references for methods of analysis (see annex B). Analysis of any one of these chemicals by any literature method does not form part of this part of ISO/TR 9122.

It should be noted that the list of chemicals is not exhaustive.

Gas concentrations should be expressed as volume/volume ratios [e.g. % (*V/V*) or parts per million] rather than mass/volume ratios (e.g. milligrams per cubic metre) for calculation purposes.

3 Sampling

3.1 General requirements and recommendations

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

3.1.2 The sample presented to the analyser shall be as representative as possible of the test atmosphere, without any change caused by the sampling system.

3.1.3 The sampling procedure should influence the test atmosphere as little as possible (e.g. by depletion of the test volume).

3.1.4 The sampling procedure should be as uncomplicated as possible, while incorporating all of the necessary features detailed herein.

3.1.5 The sampling procedure shall be capable of operating without blockage in the sampling lines, melting or other disruption of the probes, condensation of moisture, etc. for the duration of the sampling period.

3.1.6 Ideal gas behaviour is assumed for the gases and concentrations encountered. The temperature of the gases should be measured at the sampling point.

3.1.7 Suitable and efficient filtering should be maintained in order to protect the measuring equipment.

3.2 Special considerations

There are many factors (e.g. range of analyte concentrations anticipated, limit of analyte detectability, presence of analyte interferences, peak versus average analyte concentration values, etc.) which will have a direct influence on the specific type of sample analysis system selected. Sampling of the extremely complex atmosphere produced during combustion requires a very thorough evaluation and assessment of all potential factors which 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 an accurate identification and quantification of component combustion products. The selected sampling procedure will depend on the instrumentation and analytical procedures available for the specific analyte being examined. Sampling may involve either continuous on-line analysis (e.g. non-dispersive infrared analysis) or non-continuous batch sampling (e.g. evacuated flask or bubbler samples followed by analysis). Batch-type sampling can be further sub-divided into two categories:

a) instantaneous or grab;

b) average or integrated.

Although there is no sharp distinction between the categories, it is generally understood that grab samples relate to samples taken over a short time period, usually less than 1 min; whereas integrated samples are usually taken over a longer time period.

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

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

Test fires may be roughly classified as "small" (laboratory size), "intermediate" or "large" (usually full scale). The sampled gases can be hot or near room temperature. Gases generally need to be extracted from the test atmosphere along 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 should be heated to above 110 °C. Most analytical methods require a dry, particulate-free sample. Glass wool may be used (in most instances) as a particulate filter, with a further trap of a drying agent (e.g. calcium sulfate) 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 will dictate flow requirements and the necessity for moisture removal. Precautions should be taken to minimize the volume of filtering systems to reduce sampling time.

Acid gases (other than hydrogen fluoride) and hydrogen cyanide should be sampled using glass or epoxy-lined tubes to minimize losses due to reactivity and condensation on surfaces. For hydrogen fluoride, tubes lined with polytetrafluoroethylene (PTFE) should be used (glass and glass-lined tubes are unsuitable). Moisture and particulate traps should be avoided prior to the sampling medium (i.e. impinger or absorption tubes, see **3.3** and **3.4**). For these species, sampling lines should be as short as possible and should be heated to 130 °C ± 10 °C. The acid gases are particularly susceptible to loss on to the surfaces of sampling lines.

For organic materials (e.g. acrolein), unlined stainless steel tubing is suitable. Heated lines are necessary to avoid condensation and moisture. Particulate traps should be avoided unless necessary for the instrumentation.

The location of sampling probes is influenced by the size of the test apparatus and the requirements placed on the analytical system. For example, in small-scale toxicity test chambers, it may be desirable to sample near the noses of the animals, however, it should be noted that this procedure might detect a higher than normal carbon dioxide concentration due to the animals' exhalation. The possibility of stratification of gases in chambers without good mixing must be considered. Also, sampling too near the walls should be avoided.

Calibration of the entire sampling and analysis system is recommended in order to ensure that there is no loss of the gases of interest. This may be done with calibrated mixed gases 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 hydrogen chloride and hydrogen fluoride. The concentration of these species will change with time, even in a closed cylinder. The "calibration gas" should be introduced at the sampling inlet and allowed to travel the same course as a test gas, through filters and traps if present, to the analyser or sampling medium.

3.3 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 principles. The test atmosphere is drawn or pushed through the absorbing medium 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. chloride ion for absorption of hydrogen chloride gas in water). Assuming 100 % efficiency (see below), the concentration of the species measured in solution can be calculated. A typical equation is as follows:

$$G = \frac{S \times V \times H \times g/s \times 10^{-6}}{R \times T}$$

where

G is the gas concentration in parts per million (V/V);

S is the solution concentration in grams per litre or moles per litre (see H for consistent units);

V is the volume of solution, in litres;

H is the gas constant at the particular temperature and pressure, in litres per gram or litres per mole (see S for units);

g/s is the ratio of atomic or molecular weights for the gaseous species (g) and solution species (s), if different (e.g. hydrogen chloride/chloride);

R is the rate of flow of gas through an impinger, in litres per minute;

T is the time of gas flow, in minutes.

For example, if the measured solution concentration of chloride (Cl^-) was 0,006 g/l in 25 cm^3 of solution (0,025 l) at 20 °C and 1 atmosphere pressure, and flow of gas was 0,25 l/min for 2 min

$$G = \frac{6 \times 0,025 \times 0,659 \times \frac{(36,5)}{(35,5)} \times 10^{-6}}{0,25 \times 2}$$

G = 203 ppm of hydrogen chloride

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, smaller solution volume and/or larger gas volume sampled will produce higher solution concentrations. The choice of sampling conditions will be 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 a liquid is affected by

a) the solubility of the gas in the solution;

b) the physical characteristics of the absorber;

c) the 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 "breakthrough" from the first impinger (i.e. whatever is collected in the other traps). Another check on the efficiency of a given flow/impinger system would be to conduct a series of experiments with a known concentration of gas, using different impingers and various flow rates. In practice, however, one is often limited in the choice of apparatus and must then choose gas flow rates and solution volumes based on the equation above, with knowledge of the possible gas concentration and limitations of the analytical measurement.

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 liquid. 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 bubbles size (which increases relative surface contact). The spiral or helical absorbers are built in specialized shapes to allow long contact time. Flow rate in these bubblers is limited because of solution overflow. The 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 glass 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). Caution should be exercised in using such bubblers so that frothing does not occur and coalescence of the fine bubbles does not defeat the purpose of the frit. Also, smoky atmospheres (containing particulates or liquid aerosols) shall be filtered before drawing through a fritted bubbler in order to prevent clogging of the frit (which occurs very easily). Precautions on filtration of combustion atmospheres have been presented elsewhere (see **3.2**). Certain gas species (e.g. hydrogen chloride) may be absorbed on to a filter, especially once it has collected soot particulates.

3.4 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 analysis is performed similarly 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 last advantage can have dramatic consequences in the measurement of hydrogen fluoride, hydrogen chloride and hydrogen bromide 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, there is no need for any sampling line ahead of the sorption tube itself. All associated hardware (valves, rotameters and pumps) may 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.

Sorption tubes have been used for many years for atmosphere sampling and for staff monitoring in the workplace. Only recently have similar tubes been re-examined for potential use in sampling fire effluents. Two studies[1 and 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 firemen who were actually fighting the fires. Tubes of similar design, containing activated charcoal, have been used to sample hydrogen fluoride[3] and, with soda lime, for sampling hydrogen chloride[3 and 4] and hydrogen cyanide[4]. Tubes containing flake sodium hydroxide for absorption of acid gases have also been described[5]. A procedure for sampling tubes at one location in succession (e.g. every 3 min or 5 min) without removing or replacing tubes has been described for sampling gases in full-scale fires[4].

Calculation of the original gas concentration (e.g. hydrogen chloride) from that in the desorbent solution (e.g. chloride ions) is the same as that described for solution absorbers, except that the solution volume is the volume of the desorbent liquor. In practice, a small aliquot of the desorbent solution is often used, rather than the entire solution, so this factor must be taken into account.

The same consideration for solution absorbers relative to inefficient absorption, breakthrough and the relationship of volume sampled to gas and solution concentration also applies to the use of solid sorbents. Instead of bubble size, one must be concerned with the particulate size of the absorbent (large particles offer less surface area per unit volume and more opportunity for channelling, small particles can cause the tube to plug when sampling moist gas). The tubes are small enough (typically 10 cm long, Ø ext. 0.6 cm) that two tubes can easily be placed in series to reduce the possibility of breakthrough.

Solid sorption tubes are subject to plugging due to soot collection. This is easily observed during a test by a decrease in flow. 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. Loose packing of a glass-fibre plug in the inlet end of the tube will reduce the tendency to blocking from soot collection.

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

4 Analytical methods for carbon monoxide

4.1 General

The methods in this clause cover the analysis of carbon monoxide (CO) at concentrations between 50 ppm and 10 % in air, or in an oxygen-depleted atmosphere. The reference method is gas chromatography (batch method); an alternative method is non-dispersive infrared analysis (continuous).

Because gas chromatography is now a common laboratory tool, compliance with this part of ISO/TR 9122 is based primarily on performance specifications so that various methods can be employed. Details are given of recommended methods. Use of these methods is not mandatory if the performance of other methods can be shown to be within the desired accuracy range.

4.2 Gas chromatography

4.2.1 *Performance requirements*

Gas chromatography is an ideal batch method for analysing carbon monoxide in combustion gases[6 to 11]. For concentrations of 500 ppm to 10 %, direct chromatography is used with thermal conductivity detection. For concentrations of 50 ppm to 500 ppm, the carbon monoxide is reduced to methane for flame ionization detection.

The analysis shall be carried out within a calibrated range of operation suitable for the experiment. This calibrated range shall be set up with a minimum of three pure gas injections of known gas concentration covering the lower, middle and upper end of the range so that interpolations of any "unknown" gas concentration can be achieved. If this is not possible with a linear interpolation then a calibration curve may be drawn but a minimum of five separate calibration points are required. It may not be necessary to set up the full calibration range at frequent intervals, but regular checks are necessary to ensure that the instrument is operating within the defined range.

4.2.2 *Sampling and procedure*

Sample the gases from the apparatus using a suitable probe and inert collection vessel to ensure that the sample is representative of the atmosphere under test and that a sufficient volume is available for analysis. Ensure that the sample is adequately sealed and does not leak or lose contents by diffusion through the walls.

Transfer the sample to the gas sampling valve to ensure full purging, or take a syringe sample as appropriate.

Analyse gas and report.

4.2.3 *Isothermal method*

4.2.3.1 *Apparatus*

4.2.3.1.1 *Gas chromatograph,* comprising column and oven (temperature control better than ± 2 °C), with flow regulators to control carrier gas. Helium should be used as the carrier gas.

4.2.3.1.2 *Bypass injector (gas sampling valve),* capable of injecting a sample volume ranging from 0,1 ml to 5 ml in stainless steel or PTFE, or conventional injection point for precision syringe injection.

4.2.3.1.3 *Thermal conductivity detector,* capable of being separately heated and controlled. Suitable potentiometric recorder or integrator.

4.2.3.2 *Column*

Molecular sieve 5A or 13X (0,5 m, Ø int. 5 mm).

4.2.3.3 *Operating conditions*

The test shall be carried out under the following conditions:

Carrier gas flow:	about 30 ml/min
Oven temperature:	about 40 °C to 70 °C
Detector temperature:	about 120 °C

4.2.4 *Temperature-programmed method*

4.2.4.1 *Apparatus*

4.2.4.1.1 *Temperature-programmed gas chromatograph,* with thermal conductivity detector, column and oven capable of temperature programme from 20 °C to 200 °C at a rate of 10 °C/min to 35 °C/min. Other details as for isothermal method.

4.2.4.2 *Column*

Molecular sieve 5A, Carbosieve S-II or Carbosieve G.

For examples, see annex A

4.2.4.3 *Operating conditions*

These should be chosen to give the best chromatographic peak for carbon monoxide.

Detector temperature should be 200 °C to 275 °C.

4.2.5 *Calibration*

Use carbon monoxide or calibration gases of carbon monoxide in air to give the required performance requirement (see **4.2.1**) using peak height or peak area by integration. Ensure that carbon monoxide is fully separated from other peaks. A typical chromatogram is shown in annex A.

4.2.6 *Interference and limitations*

Since molecular sieves 5A and 13X readily absorb water, the column will gradually be deactivated, reducing the quality of the permanent gas analysis. As water from samples (or the carrier gas) accumulates in the column, both retention times and peak separations decrease.

Molecular sieve columns totally absorb chlorine, hydrogen chloride, hydrogen sulfide and sulfur dioxide and other corrosive gases. Hydrocarbons heavier than methane are either absorbed by these packings or have excessively long retention times. Absorption of any of these materials will generally deactivate the column and reduce performance. Reactivation can normally be achieved by heating to 150 °C with carrier gas flowing. However, hydrogen chloride and other acidic gases can even destroy molecular sieves, making column replacement necessary.

Carbosieves S-II and G are high purity carbon packings with large surface areas and, therefore, do not permanently absorb sample components as conventional carbons do. Carbosieves can trap contaminants from the air, and consequently should not be exposed to the atmosphere for long periods of time.

Oxidation of Carbosieve S-II or G will alter the surface, causing sample component peaks to tail. To avoid oxidizing these packings, do not heat the column above 200 °C in the presence of air oxygen-contaminated carrier gas.

When temperature programming a carbosieve column, while using a thermal conductivity detector, the carrier gas must be dry. Otherwise, as the temperature rises, water in the gas will cause an irregular baseline and a broad water peak will elute in the vicinity of the carbon monoxide peak. [This problem does not occur with a flame ionization detector (FID) because it does not respond to water.] Use a molecular sieve 5A trap to remove water from the carrier gas.

4.2.7 *Two-column system*

Methods of analysis exist where two-column systems can be used to assist analysis of permanent gases in fire effluents.

4.2.7.1 *Summary of method*

Mixtures of permanent gases hydrogen, oxygen, argon, nitrogen, carbon monoxide and carbon dioxide) and methane can be separated isothermally using a two-column system (e.g. Chromosorb R102 and molecular sieves 5A or 13X).

The system is built up with two columns in series and a switching device that allows the second column to be bypassed.

The first column, e.g. Chromosorb R102, silica gel or Porapak Q separates carbon dioxide from the rest of components; otherwise carbon dioxide will be absorbed on the molecular sieve column.

The molecular sieve column separates hydrogen, oxygen, argon, nitrogen, methane and carbon monoxide in that order (see annex A).

4.2.8 *Interference and limitations*

Chromosorb R102 (styrene divinylbenzene polymer) is a solid absorbent, but its chromatographic characteristics are similar to those of conventionally coated packing. Column efficiency with Chromosorb R102 is directly related to particle size — the smaller the particles the more efficient the column. However, column back pressure increases as particle size decreases. At the same time, since column efficiency is directly related to flow rate, operating the column below optimum flow rate will seriously reduce its efficiency. (Operating above the optimum flow rate is not as harmful.) These characteristics must be kept in mind because Chromosorb R102 swells as the column temperature is increased, reducing flow and increasing back pressure.

4.2.9 *Measurements of carbon monoxide by reduction to methane*

This method is most suitable for measurements of low concentrations of carbon monoxide.

4.2.9.1 *Summary of method*

An aliquot of the air sample is introduced into a pre-chromatographic or stripper column which removes hydrocarbons other than methane and carbon monoxide. Methane and carbon monoxide are passed quantitatively through the analytical column where they are separated. The carbon monoxide is eluted first and is passed unchanged through the catalytic reduction tube where it is reduced to methane before passing through the flame ionization detector.

4.2.9.2 *Apparatus*

4.2.9.2.1 *Gas chromatograph,* with a hydrogen flame ionization detector.

4.2.9.2.2 *Stripper column,* suitable for eluting the air, carbon monoxide and methane, capable of removing hydrocarbons or species other than methane, carbon dioxide and water, and capable of being back flushed.

Columns giving satisfactory results are 30,5 cm long stainless steel tube, 6,35 mm outside diameter packed with 12,7 cm of 10 % Carbowax on 60/80 mesh Chromosorb WHP; 12,7 cm of 60/80 mesh silica gel, and 5,1 cm of Mallcosorb 8/20 mesh; or 15,2 cm of Porapak Q 50/60 mesh in 3,18 mm outside diameter stainless steel tubing.

4.2.9.2.3 *Analytical or gas chromatographic column,* suitable for giving baseline resolution between carbon monoxide and methane.

4.2.9.2.4 *Catalytic reactors,* 15,2 cm long, stainless steel tubing, outside diameter same as analytical column, packed with 10 % nickel on 42/60 mesh C-22 firebrick encased in a heating element for operation at elevated temperatures.

4.2.9.2.5 *Program,* capable of automatically controlling the sequence of measurement of methane and carbon monoxide. This is preferred to manual control but an override switch should be provided for manual activation.

4.2.9.2.6 *Oven or ovens,* capable of controlling the temperature of the housing of the stripper and chromatographic columns, multiport injection valves and detector.

4.2.9.2.7 *Detector,* hydrogen flame ionization type.

4.2.9.2.8 *Suitable potentiometric recorder or integrator.*

4.2.9.3 *Test requirements and operating conditions*

The carrier gas shall be helium or hydrogen with less than 1 000 ppm impurity.

The fuel shall be hydrogen or a hydrogen-inert gas mixture. When ordering specify "electrolytic-grade hydrogen".

The calibration gas mixtures shall be moisture-free and shall contain a known percentage of the components in the range expected to be found. These known percentages should be traceable to an acceptable standard.

The zero-gas shall be a gas containing no more than 0,1 ppm of the component to be measured.

The operating conditions should be chosen to give the best chromatographic peak for carbon monoxide.

4.2.9.4 *Calibration*

Introduce the zero-gas and adjust the various zero controls to the concentrations of carbon monoxide, methane, or total hydrocarbons in the zero-gas (if any). Some commercial instruments have the capability for automatically setting zero without using a zero-gas.

Introduce the calibration gas and adjust the span control to indicate the proper value on the recorder scale.

To determine the linearity of the instrument, proceed as follows:

a) With the instrument maintained under its recommended operating conditions, introduce a sample of each of the four calibration gas mixtures corresponding to 10 %, 20 %, 40 % and 80 % of full scale. If the gases are under pressure, bypass the pump.

b) With the calibration gas mixtures, determine the linearity of the detector response for methane, carbon monoxide, and total hydrocarbons using peak height or peak area.

c) From the data obtained, prepare calibration curves if instrument non-linearity is greater than ± 2,0 % of full-scale response.

4.2.9.5 *Interferences*

Although hydrocarbons, carbon dioxide and water, which interfere with the methane and carbon monoxide separation, have been removed, anything which coelutes with the methane is considered an interferent.

4.3 Other method [non-dispersive infrared (NDIR)]

The non-dispersive infrared technique is the preferred method for continuous measurement of carbon monoxide[12].

4.3.1 *Summary of method*

Instruments based on NDIR utilize the fact that gases or vapours, whose molecules consist of two or more dissimilar atoms, absorb radiation in the infrared region and possess a unique absorption spectrum.

Most available instruments have a limited range of measurement, but it is possible to combine several units to cover ranges from 0 ppm to 100 ppm up to 100 %. Continuous analysis is possible, and as the method is non-destructive, sample gases may be returned to the test environment.

4.3.2 *Apparatus, reagents and materials*

Several types of commercial instruments may be suitable.

A typical instrument should have the following approximate specifications:

Reproducibility:	within 1 % full-scale deflection (f.s.d.)
Noise levels:	typically less than 0,5 % f.s.d. Maximum 1 %. f.s.d. on most sensitive range
Stability:	within 1 % f.s.d. over 24 h for ambient temperatures in the range 10 °C to 25 °C
Linearity:	within 1 % f.s.d.
Response time:	90 % of reading within 10 s using full-length analysis cell (maximum sensitivity) and sample flow rate of 1 l/min [down to 2 s (90 % of reading) for high concentrations]
Sample flow:	up to 2 l/min

4.3.2.1 *Calibration mixtures*

The zero-gas shall be pure nitrogen containing less than 0,1 mg/m^3 carbon monoxide (0,09 ppm) held in a pressurized cylinder having a regulated flow supply. Where expected concentrations of carbon monoxide are greater than 500 ppm, ambient air may be used as zero-gas. This also allows for background errors.

The up-scale span gas shall be a mixture consisting of carbon monoxide in air corresponding to 80 % of full scale held in a pressurized cylinder. A regulated flow system shall be provided.

The calibration gases should contain concentrations of carbon monoxide in air corresponding to the instrument operating range. In order to establish a calibration curve, carbon monoxide in amounts of 10 %, 20 %, 40 % and 80 % of full scale are needed. The gases shall be contained in pressurized cylinders with regulated flow control.

4.3.3 *Procedure*

Place the analyser in an enclosure with the temperature control within the range of stability requirements.

As the measurements will be affected by the pressure within the analyser cell, both calibrations and measurements shall be carried out either by pressure or suction feed of the sample.

Record the temperature and pressure of the atmosphere sample. After proper calibration has been established, check all analyser system operating parameters and set the sample flow rate.

When the analyser output has stabilized, take the recorder readout and determine the concentration of carbon monoxide directly from the calibration curve in parts per million.

4.3.4 *Calibration*

4.3.4.1 *Frequency of calibration*

A multipoint calibration shall be carried out when

— the analyser is first purchased;

— the analyser has undergone maintenance that could affect its response characteristics;

— the analyser shows drift in excess of specifications as determined when the zero and span calibration is performed.

A zero and span calibration shall be performed before and after each sampling period.

The flowmeter should be calibrated in accordance with an appropriate method such as ASTM D3195 at the following times:

— when the analyser is purchased;

— when the flowmeter is cleaned; and

— when it shows signs of erratic behaviour.

If a sample cell pressure gauge is present it should be calibrated as follows:

— when the analyser is purchased;

— at six-monthly intervals.

4.3.5 *Interference and limitation*

The degree of interference varies among individual instruments.

The primary interferent is water vapour. With no correction, the error may be as high as 11 mg/m^3 (10 ppm) of carbon monoxide.

5 Analytical methods for carbon dioxide

5.1 General

The methods in this clause cover the analysis of carbon dioxide (CO_2) between 5 ppm and 40 % in air and in an oxygen-depleted atmosphere. The reference method is gas chromatography (batch method). An alternative method is non-dispersive infrared analysis (continuous).

Because gas chromatography is now a common laboratory tool, compliance with this part of ISO/TR 9122 is based primarily on performance specifications so that various methods can be employed. Details are given of recommended methods. Use of these methods is not mandatory if the performance of other chromatographic methods can be shown to be within the desired accuracy range.

5.2 Gas chromatography

5.2.1 *Performance requirement*

The analysis shall be carried out within a calibrated range of operation suitable for the experiment. This calibrated range shall be set up with a minimum of three pure gas injections of known gas concentrations covering the lower, middle and upper end of the range so that interpolations of any "unknown" gas concentration in the calibration range can be analysed to within 2 % of the real concentration. If this is not possible with a linear interpolation then a calibration curve may be drawn but a minimum of five separate calibration points are required. It may not be necessary to set up the full calibration range at frequent intervals, but regular checks are necessary to ensure that the instrument is operating within the defined range.

5.2.2 *Methods*

The isothermal and temperature-programmed methods described for carbon monoxide (see **4.2.3** and **4.2.4**) may be used for carbon dioxide with respect to

— operating conditions;

— calibration;

— sampling procedures.

The apparatus specified for the two methods may also be used except that the column should be Chromosorb R102 (isothermal), Carbosieve S-II (temperature-programmed) or Carbosieve G (temperature-programmed).

For examples of chromatograms, see annex A.

5.2.3 *Limitations*

See **4.2.6**.

5.3 Other method [non-dispersive infrared (NDIR)]

As for **4.3** but with instrument designed for carbon dioxide.

6 Analytical methods for oxygen

6.1 General

These methods cover the analysis of oxygen (O_2) between 0,1 % and 21 %. The reference method is gas chromatography (batch method). An alternative method is the paramagnetic (continuous) technique.

Because gas chromatography is now a common laboratory tool, compliance with this part of ISO/TR 9122 is based primarily on performance specifications so that various methods can be employed. Details are given of recommended methods. Use of these methods is not mandatory if the performance of other methods can be shown to be within the desired accuracy range[6,13 and 14].

6.2 Gas chromatography

6.2.1 *Performance requirements*

The analysis shall be carried out within a calibrated range suitable for the experiment. This calibrated range needs to be set up with a minimum of three pure gas injections of known gas concentrations covering the lower, middle and upper end of the range so that interpolation of any "unknown" gas concentration in the calibrated range can be analysed to ± 2 % of the real concentration. If this is not possible with a linear interpolation then a calibration curve may be drawn but a minimum of five separate calibration points are required. It may not be necessary so set up the full calibration range at frequent intervals, but regular checks are necessary to ensure that the instrument is operating within the defined range.

6.2.2 *Methods*

The isothermal method (see **3.2**) is normally employed for oxygen although the analysis can be extended by subsequent temperature programming for other permanent gases with respect to

— operating conditions;

— calibration;

— sampling procedures.

The apparatus specified for the isothermal method may be used except that the column should be molecular sieve 5A, Carbosieve S-II, Carbosieve G or Chromosorb R102.

For examples, see annex A.

6.2.3 *Limitations*

See **4.2.6**.

6.3 Paramagnetic method

This method is suitable for continuous measurement of oxygen[15].

6.3.1 *Summary of method*

The paramagnetic susceptibility of oxygen is much higher than other common gases. When oxygen is present in a magnetic field, the oxygen tends to concentrate the lines of force of the magnetic field. The instrument measures the total magnetic susceptibility of the sample. This total is almost entirely due to the oxygen present, so the measurement is an accurate indication of oxygen content.

6.3.2 *Apparatus requirements*

The instrument shall have the following specifications:

Span:	within the range 0 % to 25 % oxygen (minimum concentration 0,1 %)
Accuracy:	2 % of measured value
Response time:	10 s, 90 % of full scale
Operating temperature:	ambient to 50 °C

6.3.3 *Procedure*

Connect two different gas bottles having oxygen concentrations at least 2 percentage points apart (for example, 15 % and 17 %) to a selector valve at the inlet analyser.

Connect the electrical power and let the analyser warm up for 24 h with one of the test gases flowing through it.

Connect a strip chart recorder to the output of the analyser. Quickly switch from the first bottle to the second bottle. Take data for 20 min.

Determine the drift by passing a best-fit linear trend line through the last 19 min of data. Extrapolate the line back through the first minute. Record the 20 min drift in terms of parts per million of oxygen.

Determine the noise by computing the standard deviation of the excursions around the linear trend line. Record the noise in terms of parts per million of oxygen.

The analyser is suitable for use in general-purpose fire testing if the sum of drift and the noise terms is less than or equal to 50 ppm oxygen.

6.3.4 *Interference and limitations*

Cooling and filtration of fire gases are necessary due to temperature problems. Fire gases may often have a corrosive effect on the instruments.

A paramagnetic oxygen analyser is directly sensitive to barometric pressure changes at its outlet port and to flow rate fluctuations in the sample supply stream. It is essential that the flow rate of the supply steam be regulated by either a mechanical diaphragm type flow rate regulator or by an electronic mass flow rate controller. To guard against errors due to changes in barometric pressure it is possible either

   a) to control the back-pressure to the analyser with an absolute-pressure type back pressure regulator; or

   b) to measure the actual pressure at the detector element electrically and provide a signal correction to the analyser's output.

Other gases can be present which have a paramagnetic effect and can affect the reading.

7 Analytical methods for hydrogen cyanide

7.1 General

These methods cover the analysis of cyanide ions in solution. It is a common analytical procedure. The uncertainty in measuring hydrogen cyanide (HCN) in fire gas effluents is primarily in the sampling techniques. Hydrogen cyanide, when in the gas phase, is easily lost by sorption and condensation on any surface such as syringe walls, sampling bottles, soot particles and water droplets. It is recommended that clause **3** on sampling be studied prior to using the analytical procedures described here. Four techniques will be described for hydrogen cyanide. The gas chromatographic method may be used to analyse hydrogen cyanide directly in the gas phase. The ion-selective electrode (ISE), colorimetric analysis and high performance ion chromatography (HPIC) techniques require that the hydrogen cyanide be dissolved in aqueous solution prior to analysis. HPIC is the reference method.

7.2 Gas chromatographic methods

7.2.1 *Performance requirements*

The nitrogen phosphorus specific detector (NPD) can detect nitrogen compounds down to 10^{-13} g of nitrogen per second to 10^{-14} g of nitrogen per second. The range of detection of hydrogen cyanide in one study was 5 ppm to 400 ppm. The minimum detection level was of the order of picograms (1 ppm in a 50 µl injection).

7.2.2 *Sampling and procedure*

Gas chromatography (GC) is a useful technique for analysing hydrogen cyanide gas directly. Several of the common detectors will respond to hydrogen cyanide. However, only the alkali flame or nitrogen-phosphorus specific detector is recommended for fire effluents (see **7.2.5** for the reasons that only the NPD is being recommended).

Standard chromatographic techniques may be used for analysis of hydrogen cyanide in fire gases. A column of Porapak Q at 110 °C (200 °C injection temperature) has been used successfully[16]. Injection volume was generally 50 µl. The detector is operated in the "N-mode" with a hydrogen/air mixture as the detector gas. However, unlike most other GC procedures, the column must be conditioned with repeated injections of hydrogen cyanide in order to prevent erratic results.

7.2.3 *Calibration*

Analysed, compressed gas mixtures (hydrogen cyanide in nitrogen) are used for calibration of the GC system. However, even analysed mixtures shall be checked by one of the techniques listed below. The gas is bubbled into an impinger and the resultant (cyanide ions) in solution are measured. Gas mixtures of hydrogen cyanide can change with time and shall be checked periodically if used for calibration purposes.

7.2.4 *Interferences and limitations*

With the NPD, the only interferences are possibly from other nitrogen-containing gases. Under proper column conditions, hydrogen cyanide is adequately separated from other nitrogen compounds which can be present in fire gases. The NPD is approximately 10 000 times more sensitive to nitrogen-containing compounds than to hydrocarbons without nitrogen.

7.2.5 *Advantages and disadvantages*

The NPD can be a more difficult detector to operate than the simpler flame-ionization detector (FID) or thermal conductivity detector (TCD). However, the sensitivity to hydrogen cyanide outweighs its disadvantages. The FID is equally sensitive to nitrogen-containing and non-nitrogen-containing hydrocarbons. Therefore, although the FID may be used for analysis of relatively pure hydrogen cyanide atmospheres, it shall not be used for other fire gas samples. The TCD has been used for analysis of hydrogen cyanide in fire gases; however its detection limit is much higher than that of the NPD. Hydrogen cyanide concentrations of 10 ppm to 15 ppm were achieved with a 2 ml sample using a TCD.

7.3 Ion-selective electrode (ISE) techniques

7.3.1 *Performance requirements*

The cyanide ion electrode is reportedly sensitive to cyanide ions in the range of 0,03 mg/l to 260 mg/l. The repeatability of measurements probably depends more on the output meter than on the electrode. For example, a digital meter may be considered to be accurate to plus or minus the last digit (e.g. 10 mg/l ± 0,1 mg/l). When electrodes have been contaminated (e.g. by oils or by sulfide) their response can become slow and/or erratic. The response time of an electrode is also dependent on concentration. Low concentrations take longer to equilibrate.

7.3.2 *Sampling and procedure*

In order to analyse cyanide ions using an ion-selective electrode, a gas-solution impinger or bubbler must absorb the hydrogen cyanide from the gas-phase (see description of gas-solution absorbers in **3.3**). A two-electrode system is employed, a cyanide-selective electrode and a reference electrode. This system is recommended over that using the silver ion/sulfide ion electrode for determination of cyanide, for the reasons given in **7.3.4**.

The impinger should be filled with approximately 0,1 mol/l sodium hydroxide solution. The volume of solution and rate of flow of gas for the particular application must be determined empirically, keeping in mind the cautions and considerations expressed in clause **3**. Likewise, one must decide whether or not to have a filter prior to the impinger. The equation relating gas and solution concentrations is also given in clause **3**.

Gas sampling using an impinger is carried out over some time interval which may be as short as 1 min to 2 min or as long as 20 min to 30 min. The analysis of the solution, therefore, results in a bar-graph plot of concentration *vs.* time. The time interval selected is dependent on the concentration of hydrogen cyanide in the gas, the gas flow rate, and the solution volume (see **3.3**).

The measurement of cyanide ions in solution is performed after the sampling; however, researchers have experimented with continuous methods of analysis whereby the electrode is in the impinger during the course of the sampling[17]. Care must be taken to ensure that any oils present in the impinger solution (from combustion products) do not contaminate the electrode. If necessary, the oils should be removed prior to analysis using an appropriate non-reactive filtering medium. Solutions to be analysed by ISE must have the proper background ionic strength. If necessary, an ionic-strength adjustment may be made in accordance with recommendations for use of the cyanide electrode. Stirring speed can be an important factor in analysis of ions by ion-selective electrodes. It should be maintained as constant as possible for calibration and for test solutions.

There are various meters suitable for reading the output of ion-selective electrodes. Simple analogue meters are suitable for many applications; however, modern digital instruments are extremely easy to operate and allow rapid checks of calibration standards. Output from meters are in the millivolt (mV) range.

7.3.3 *Calibration*

Calibration of the electrode response should be carried out periodically using solutions of cyanide ions, properly adjusted to the required ionic strength. As the meter needs to be adjusted often, the standards should be checked frequently. If the slope of the millivolt-concentration limit is non-linear, concentration measurements should not be taken, unless numerous standard solutions have been tested to chart the response and repeatability of the electrode for that concentration range.

The entire sampling and analysis system should be calibrated when it is first commissioned, using analysed compressed gas standards (although these should be checked occasionally using another analysis technique), or by the use of a gas permeation device. The efficiency of the sampling impinger train may be determined using this technique.

NOTE 1 Because this procedure is dangerous with gases it is advisable to use liquid standards wherever possible and follow safety raquirements for these types of products.

7.3.4 *Interferences and limitations*

The major interference in the determination of cyanide ions using the cyanide ISE is the sulfide ion. This not only interferes with the analysis, but fouls the electrode so that cleaning is required. Sulfide may be removed from the solution by adding a drop of a saturated solution of lead acetate.

Other interfering species are chloride, bromide and iodide; however, the interference is not significant at low levels. At high concentrations of cyanide ions, the life of the electrode is limited.

Compared to other solution measurements of cyanide, the ISE technique is simpler and quicker; however, it is subject to certain interferences. The method is generally repeatable but reproducibility is poor. Since little sample preparation is required, confirmatory analysis of cyanide ions could be performed using titration or ion-chromatography.

The silver ion/sulfide ion electrode for cyanide is useful for a wider range of concentrations than the cyanide ion selective electrode. However, it requires measurement of free silver ion in equilibrium with the silver cyanide complex ion and calculation of the free cyanide ion concentration. This entails more extensive preparation of the impinger solution and, possibly, analysis of the solutions for silver ions prior to exposure to hydrogen cyanide.

7.4 Colorimetric analysis techniques

7.4.1 *Performance requirements*

This technique is capable of measuring 0,01 g of cyanide ions in the aliquot taken.

7.4.2 *Procedure*

The colorimetric analysis techniques for hydrogen cyanide require the cyanide ion to be in solution. This may be accomplished by using either gas-solution impingers (see **3.3**) or the aqueous extract of dry absorption tubes (see **3.4**). The procedure for the impingers is the same as described in **7.3.2**. The procedure for absorption tubes is given below. In either case, the aqueous solution containing cyanide ions is treated with a reagent to produce a coloured product which is then measured on a spectrometer.

The recognized technique using either pyridine-pyrazolone or pyridine-barbituric acid is based on a standard method for measurement of cyanide[18]. An aliquot is mixed in a 50 ml Erlenmeyer flask with enough 0,12 mol/l potassium hydroxide to make up a 5 ml solution. 2 ml of freshly prepared chloramine T/sodium dihydrogen phosphate buffer solution are added; the solution is swirled for a few seconds and allowed to stand for 2 min. 2,5 ml of 0,1 mol/l potassium hydroxide is then added, followed by 0,5 ml of the colour producing reagent (pyridine-barbituric acid is recommended). This total solution volume of 10 ml is left standing for 10 min to allow the colour to develop. The absorbance of the solution is measured at 578 nm (for pyridine-barbituric acid) on a spectrometer.

The pyridine-barbituric acid is preferred for this method because of its greater stability after preparation and prior to use. However, pyridine-pyrazolone can also be used. A longer standing time (25 min) is required after addition of the reagent and the colour is read at a different wavelength (620 nm).

7.4.3 *Calibration*

Standard solutions are prepared exactly like the test samples, using reagent grade sodium or potassium cyanide. Analysis of standard solutions is also performed in an identical manner (see **7.4.2**). Standard curves are prepared frequently, plotting absorbance at the particular wavelength *vs.* concentration of cyanide ions. Unknown solutions are read directly (as grams of cyanide ions) from the standard curve.

7.4.4 *Interference and limitations*

Known interferences are sulfide or thiocyanate ions in solution.

The colorimetric methods are relatively time consuming. Also, colour development is a function of time and the "standing time" can influence the accuracy of the results. On the other hand, the method is less subject to interferences than either the ISE or the GC methods. This method is suitable for analysis of cyanide sampled by soda lime absorption tubes; whereas the other methods are not applicable to this sampling technique.

7.5 Hydrogen cyanide ion chromatography

7.5.1 *Performance requirement*

The technique is capable of measuring within the range 10 ppb to 1 ppm in solution. For measurement of higher concentrations, accurate dilution of the sample solution is necessary.

7.5.2 *Sampling and procedure*

A gaseous sample of hydrogen cyanide is collected in an evacuated glass bottle (a 270 ml bottle has been used), containing 20 ml of deionized water. Once the glass bottle is opened to the fire atmosphere and the sample is taken, the hydrogen cyanide is present in aqueous solution. Direct analysis of this solution can then be carried out. The analysis technique involves separation of the cyanide from other dissolved gases and its detection using an ion chromatograph. The sample injection volume is normally 50 μl and it is advisable to inject at least 10 times the volume to fill the sample loop completely. The separation is carried out on an anion exchange column followed by amperometric detection with a silver working electrode. There is a silver chloride reference and a stainless steel counter electrode fitted in the cell. The applied voltage setting for hydrogen cyanide analysis is zero volts and the eluent used is a mixture of 0,001 mol/l sodium carbonate, 0,01 mol/l sodium hydrogenborate, and 0,015 mol/l ethylene diamine at a flow rate of 2,5 ml/min.

7.5.3 *Calibration*

A 0,5 ppm solution of cyanide is injected into the system and the detector response is monitored by a chart recorder or integrator. The peak height monitored is directly related to the concentration of the 0,5 ppm calibration solution. The response for the unknown cyanide solution can be measured and its concentration calculated.

7.5.4 *Interference and limitations*

The technique is specific to cyanide ions in aqueous solution. A basic eluent shall always be used for separation and detection to ensure the cyanide exists in the anionic form. 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. A number of samples can be taken over a period of time to provide a concentration-time profile for cyanide in a fire effluent.

8 Analytical methods for hydrogen chloride and hydrogen bromide

8.1 General

Hydrogen chloride (HCl) and hydrogen bromide (HBr) may be analysed by many techniques, once they have been collected in a suitable medium (such as water). Techniques and precautions relating to the sampling of these gases have been presented in clause **3**. The reference method is titrimetry, with ion chromatography as an alternative method. These are batch sampling procedures. A continuous analysis scheme is also presented[19 to 22].

8.2 Analysis by titrimetry

8.2.1 *Procedure and sampling*

Combustion gases are collected in a series of aqueous impingers. The halide concentration is then measured by potentiometric titration. This procedure is limited to batch sampling over a specific time increment.

Sampling and transfer of acid gases have to avoid the following special problems:

    a) Reaction of gaseous products with materials used in sampling lines and equipment, which could lead to loss of samples; to avoid it use glass or PTFE;

    b) Absorption or condensation of hydrogen chloride and hydrogen bromide in the sampling system or on trapped particulates; use a short and heated (about 130 °C ± 10 °C) sample line and avoid filtering the smoke before the sampling tube or impinger.

Within the limitations given in clause **2** there is wide variation in the flow of gas and the solution volumes that can be used. However, both the gas volume and the final solution volume must be precisely measured. As an example, three impingers in series, each containing 100 cm^3 of neutral, distilled water may be used with a gas flow rate of 120 dm^3/h. The contents of the impingers are then combined and transferred to a volumetric flask.

Halide concentrations are measured by potentiometric titration with silver nitrate (0,1 mol/l) using a silver electrode and a reference electrode.

The end point of the titration is marked by a sharp increase in electrode potential indicating excess silver ions present in solution.

The quantity of halide ion collected (in grams) can be determined by the following equations:

$$\text{Cl}^- = \frac{V}{E} \times n \times 35{,}5$$

and

$$Br^- = \frac{V}{E} \times n \times 79,9$$

where

V	is the volume of impinger solutions combined, in cubic centimetres;
E	is the aliquot taken for analysis, in cubic centimetres;
n	is the number of moles of silver ions used (molarity × litres of titrant);
35,5	is the atomic mass of chlorine;
79,9	is the atomic mass of bromine.

The concentration of hydrogen chloride or hydrogen bromide gas can be calculated using the equations in clause **3**.

8.2.2 *Calibration*

Calibration entails using silver nitrate solutions of known molarity. Gas calibration standards may be used which have been carefully and recently analysed to determine the efficiency of the sampling system (halogen acid gas mixtures change with time).

8.2.3 *Interferences and limitations*

This method is specific at high concentrations of chloride and bromide; however sulfides, cyanides and thiocyanates (SCN^-) can interfere at low concentrations.

When bromide and chloride are present together there is adequate separation of the two halides for a ratio of chloride and bromide ions of

$$0,1 < \frac{Cl^-}{Br^-} < 5$$

For other ratios the error can be more than 10 % because of the co-precipitation of both halides.

If

$$\frac{Cl^-}{Br^-} > 5$$

we may neglect the bromide and give the result expressed as chloride.

If

$$\frac{Cl^-}{Br^-} < 0,1$$

the chloride may be neglected and the result expressed as bromide.

Cyanide can be a significant interferent due to its high concentration in certain combustion atmospheres. Under these circumstances, cyanide must be removed (usually by oxidation with a peroxide compound or complexing with nickel).

8.2.4 *Reproducibility*

Reproducibility between different laboratories is about 20 %.

8.3 Ion chromatography

8.3.1 *Procedure*

Collect a gas sample in an evacuated flask. Using a syringe, inject a small quantity of deionized water into the flask. Shake the flask so that gases are absorbed in the water and remove the resulting solution for analysis. As an example, some studies have used a 5 000 cm^3 flask with 25 cm^3 of water. Other volumes may be used.

To remove organic materials, treat the solution with a short separating column. Flush the column with 20 cm^3 of deionized water and add to the sample solution.

Apply a volume of 0,5 cm^3 of the solution to an ion exchange column using the following:

Mobile phase:	4 mol/l *o*-phthalic acid aqueous solution buffered at pH 4,5 with borax (flow rate 2 $cm^{3} \cdot min^{-1}$)
Separation column:	ion exchange column
Detector:	conductivity detector

8.3.2 *Calibration*

Calibration should be carried out with a solution containing a calculated amount of sodium chloride and sodium bromide, accurately weighed.

8.3.3 *Interferences and limitations*

This method (ion chromatography) is very specific to bromide and chloride anions in aqueous solution and it permits simultaneous analysis of other anions. Coelutants can interfere with the accuracy of the results.

The detection limit is as low as a microgram per injection. Ion chromatographic analysis is very specific for the compounds of interest (chloride or bromide in this case). It may be used in conjunction with sampling procedures other than those presented in this clause (i.e. impingers). This technique provides a concentration at the particular sampling time. Repetitive sampling can be performed to yield a concentration-time curve.

8.4 Continuous analysis (on-line)

8.4.1 *Procedure*

Pass combustion products through a dilute solution of nitric acid in which gaseous halides are absorbed. Maintain the solution potential at a value near the equivalence point where halide ions are titrated by silver nitrate.

Maintain this value by continuous addition of silver nitrate.

Record the consumption curve of silver nitrate as a function of time. When both bromides and chlorides are present, maintain the solution potential at the equivalence point of chloride titration. In the other cases it corresponds to the equivalence point of chloride or bromide titration, depending on the ions present.

Gases are absorbed in a titration cell (500 cm³) with an accurately measured flow of 30 dm³/h (see Figure 1).

The absorbing solution shall be nitric acid (pH = 1). Potential shall be measured by a silver electrode and a reference electrode (mercury sulfate).

From the consumption curve of silver nitrate, it is possible to calculate at any given time the slope which can give the theoretical rate of evolution of hydrogen halide and its concentration in the gaseous mixture.

The concentration $C_{m/V}$, expressed in milligrams per millilitre, is given by

$$C_{m/V} = \frac{v \times 10^3}{n \, T/T_0}$$

and the concentration $C_{V/V}$ expressed in parts per million gas phase, is given by

$$C_{V/V} = \frac{22{,}4 \, v \times 10^3}{n \cdot M}$$

where

- T is the test temperature, in kelvin;
- T_0 = 273 K;
- n is the volume, in cubic decimetres, of gas sampled during 60 s;
- v is the rate of evolution of gas, in milligrams per minute, calculated from the silver nitrate consumption curve;
- M is the molecular mass of determined species.

8.4.2 *Calibration*

This technique using a liquid impinger permits the use of halide solutions for calibration. However, gaseous calibration standards may be used under the same conditions as the test to determine the efficiency of the absorption and time response of the analyser system.

8.4.3 *Interference and limitations*

This method is specific to chlorides or bromides when they are not present together. Sulfides, cyanides and thiocyanate can interfere at low concentrations of halogen.

This procedure allows detection of concentrations of about 2 mg m^{-3}, but the results are only significant for concentrations of 5 mg m^{-3} or more.

This technique yields a continuous analysis of halide. However, the speed and accuracy of response has not been demonstrated. Combustion gases shall be filtered to prevent smoke from fouling the electrodes. The possible loss of hydrogen chloride (or hydrogen bromide) shall be accounted for during filtration and in the sampling line (see clause **3** and in bibliographic reference [23]). The same procedure with somewhat modified apparatus is described in a published report[24].

8.5 Gas filter correlation analyser

8.5.1 *Procedure*

The gas filter correlation analyser (GFCA)[22] is a non-dispersive infrared analyser (NDIR) which provides a continuous record of the hydrogen chloride concentration. This continuous monitoring of hydrogen chloride is a significant advantage of this method since the hydrogen chloride concentration changes rapidly in combustion experiments where hydrogen chloride is produced. The multiple pass optical system measuring cell provides high sensitivity and hydrogen chloride in the concentration range of 0 ppm to 5 000 ppm can be measured. The GFCA is an instrumental method of analysis and provides a direct, instantaneous readout of the hydrogen chloride concentration without any additional sample handling or workup. The sampling system used with the GFCA analyser has the following essential features:

a) a filter to remove particulate matter;

b) a gas dryer;

c) all segments of the sampling system ahead of the dryer are heated to prevent water vapour condensation anywhere in the sampling system or the analyser.

This last feature is necessary since hydrogen chloride dissolves very readily in condensed water, resulting in losses and analytical errors.
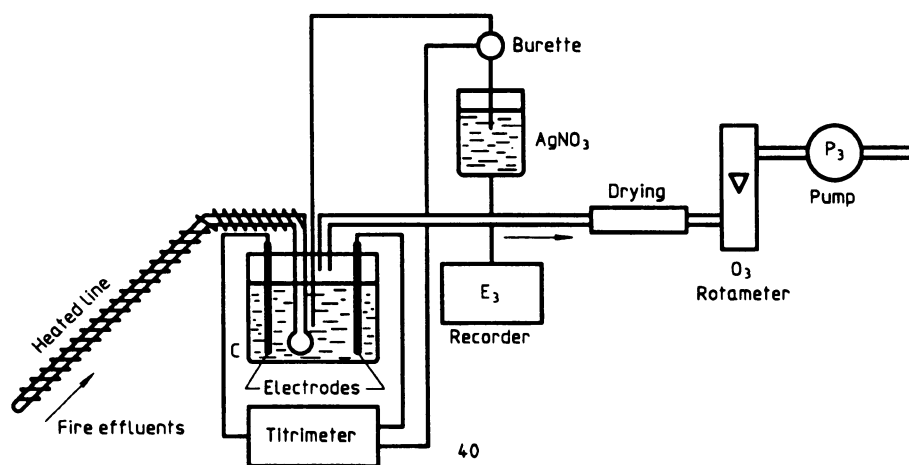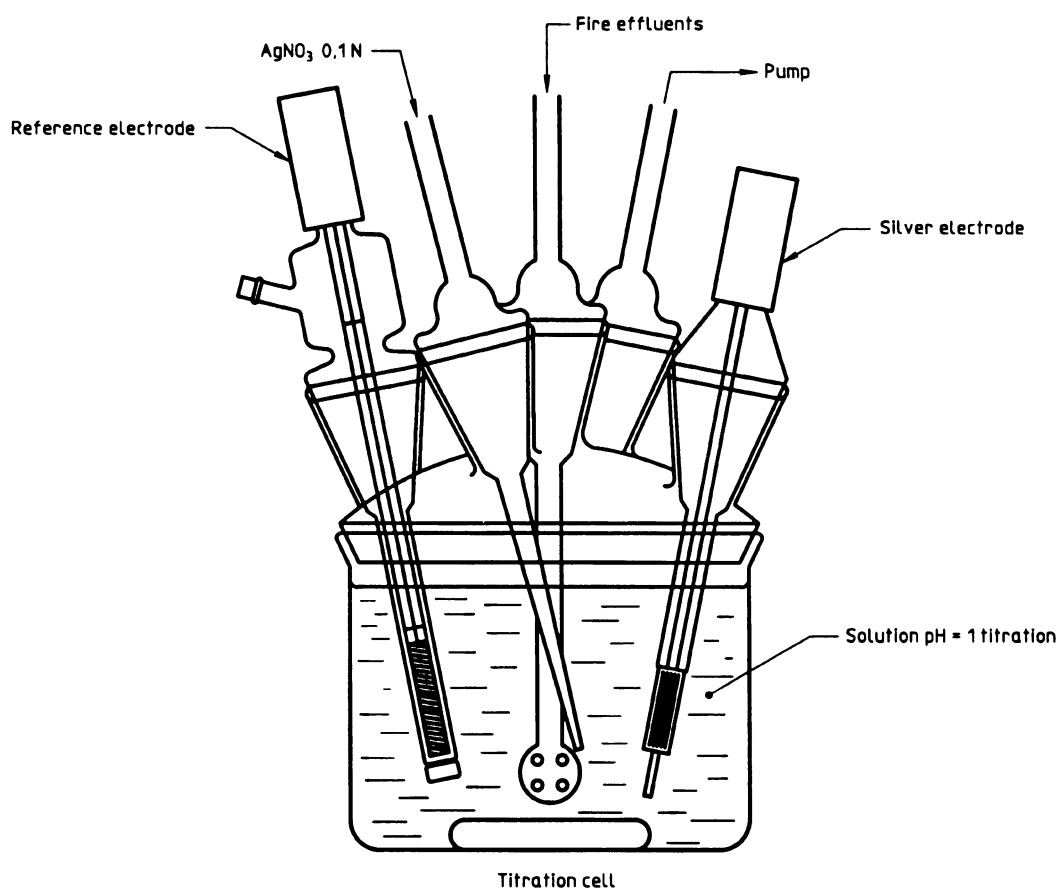
Figure 1 — On-line analysis of hydrogen chloride and hydrogen bromide

8.5.2 *Calibration*

Gaseous calibration standards of known concentration shall be used. Through proper selection of the gas cylinder lining materials, stable mixtures of hydrogen chloride in nitrogen can be obtained and maintained.

8.5.3 *Interferences and limitations*

The gas filter correlation modification of the NDIR principle eliminates the interference of carbon monoxide and water vapour that would otherwise exist. The observed concentration-time profile is about 30 s behind the true profile. The observed peak concentration is lower than the true peak concentration by about 10 %. In many cases these differences are not a problem; however, the extent of these differences can be determined by off-line data analysis techniques. The system is well suited for measurements of the total yield of hydrogen chloride.

9 Analytical methods for hydrogen fluoride

9.1 General

Analysis of hydrogen fluoride (HF) may be performed by an ion-selective electrode once the hydrogen fluoride has been absorbed into aqueous solution[25 to 27]. The other technique is ion chromatography[28].

Techniques and precautions relating to the sampling of reactive gases such as hydrogen fluoride have been presented (see clause **3**). The reference method is the ion-selective electrode.

9.2 Analysis by ion-selective electrode

9.2.1 *Procedure and sampling*

Sampling and transfer of hydrogen fluoride have to avoid the following special problems:

a) Reaction of gaseous products with material used in sampling lines and equipment which could lead to loss of samples. It is necessary to use tubes, probes and interior parts of devices (pumps, valves, etc.) coated with PTFE. Glass shall not be used.

b) Absorption or condensation of hydrogen fluoride in the sampling system or on trapped particulates; use a short and heated sampling line (above the dew point) and avoid filtering the smoke before the sampling tube or impinger.

c) PTFE probes should not be heated above 250 °C because their physical properties can be affected.

A measured volume of fire effluent is drawn through a series of aqueous alkali impingers. The hydrogen fluoride is absorbed in the solution and the fluoride ion is measured using an ion-selective electrode.

Two impingers may be used in series. The selection and use of various types of gas-solution absorbers is discussed in **3.3**. After absorption, transfer the contents of the impingers to a volumetric flask and make up to the mark with a buffer/ionic strength adjuster solution as recommended by the manufacturer of the electrode. One such solution consists of 200 g sodium acetate, 200 cm^3 sodium hydroxide and 36 g Titriplex IV (cyclohexylene-1,2-dinitrotetracetic acid) made up to 1 000 cm^3 total volume in distilled water.

An aliquot of the final test solution is analysed for fluoride ions directly by use of a fluoride ion-selective electrode, reference electrode, and suitable ion meter. A potentiometer may be used to read the millivolt potential from the electrodes and this is then compared to a calibration curve prepared from sodium fluoride standard solutions (which are buffered similarly to the test solutions).

Since the fluoride concentration is read directly, no calculation is required. Equations for converting fluoride ions in solution to hydrogen fluoride in the gas phase have been presented (see **3.3**).

9.2.2 *Calibration*

This technique, using a liquid impinger, permits the use of fluoride solutions for calibrations. However, gaseous calibration standards may be used to determine when absorption of hydrogen fluoride is complete. Mixed gases containing hydrogen fluoride shall be analysed frequently since they can change with time.

9.2.3 *Interference and limitations*

The nature of the fluoride-selective electrode and the buffer solution (which complexes some metallic ions) make this method very specific for hydrogen fluoride analysis of fire effluents.

The fluoride-selective electrode permits detection of hydrogen fluoride concentrations in the absorbing solution below 0,1 mg/l (i.e. 120 ppm). Caution must be exercised in the analysis of solutions of low fluoride concentration which can be in the non-linear portion of the calibration curve.

This technique yields a time-integrated analysis of hydrogen fluoride. With proper selection of solution volumes and gas flow rates the time of sampling can be adjusted to fit the requirements of the test.

Solutions of fire effluent can require treatment prior to analysis by ion-selective electrode so that the electrode does not become poisoned or fouled due to organic compounds. Filtration of the gases prior to the impingers is not recommended (see clause **3**).

9.3 Ion chromatography

9.3.1 *Procedure*

A volume of fire effluent is absorbed in alkali aqueous impingers as described in **9.2.1**. Midget impingers with 10 cm^3 volume are used.

Transfer the contents of the impingers into a 25 cm^3 volumetric flask and make up to the mark with distilled water. Withdraw 0,1 cm^3 of this solution and apply to an ion exchange column.

The following chromatographic conditions are typical of those used to analyse for fluoride ions:

— Mobile phase: 0,002 mol/l sulfuric acid (aqueous solution), flow rate: 0,8 cm^3 min^{-1}.

— Separation column: anion exclusion column.

— Detector: conductivity detector.

— Time of elution: 11 min.

Record the peak corresponding to fluoride ions in the solution and integrate in order to calculate the quantity of fluoride ions for this injection. Calculate the hydrogen fluoride concentration in the fire effluent as described in clause **3**.

9.3.2 *Calibration*

This technique permits the use of fluoride solutions for calibration, the ion chromatograph shall be calibrated with accurate fluoride solutions. Gaseous calibration standards may be used to determine if absorption of hydrogen fluoride is complete.

9.3.3 *Interference and limitations*

This method using ion chromatography is very specific for fluoride anions (F$^-$) in aqueous solution; and it also permits simultaneous analysis of other anions such as chloride and bromide.

Ion chromatography permits fluoride detection at concentrations lower than 0,1 mg l^{-1} in aqueous solutions.

This technique yields a time-integrated analysis of hydrogen fluoride. If frequent samples are taken, a concentration-time graph can be developed. Analysis by ion chromatography is relatively slow and time-consuming; however, the accuracy and lack of interference can justify its use over other possible methods.

9.4 Continuous analysis (on-line)

9.4.1 *Principle*

A sample of fire effluent is drawn into an aqueous solution; it is then automatically transferred into a measuring cell containing a fluoride-selective electrode. The electrode potential is amplified and recorded (or the concentration recorded directly).

9.4.2 *Test requirements*

Figure 2 is a schematic diagram of the apparatus. The flow rate of the solution through the measuring cell shall be 1,5 cm$^3 \cdot$ min^{-1} and its volume shall be 1 cm^3. Cell solution is extracted automatically in order to keep pH = 2,2.

Composition of the cell solution shall be

Phosphoric acid:	0,14 mol/l
Sodium hydroxide:	0,17 mol/l
Potassium chloride:	2 mol/l
Sodium fluoride:	2×10^{-7} mol/l

Response time shall be less than 2 s.

9.4.3 *Calibration*

This technique permits the use of fluoride solutions for calibration. However, it is desirable to use gaseous calibration standards to determine the extent of absorption of hydrogen fluoride.

9.4.4 *Interference and limitations*

This electrode is specific for fluoride ions and the pH of the absorbing solution (2,2) does not obstruct hydrogen fluoride dissociation. Some cations such as iron(III) ions and aluminium ions can complex with fluoride and interfere with the determination.

This device permits detection of hydrogen fluoride concentrations lower than 0,5 mg m^{-3} (i.e. 0,6 ppm).

There are numerous problems associated with continuous analysers which rely on dissolutions 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. Also, the electrode response (such as used in this analyser) is not immediate. The special problems for determining acid gases in fire effluents (as discussed in clause **3**) are even more critical in a continuous analysis device.

10 Analytical methods for oxides of nitrogen

10.1 General

These methods cover the analysis of oxides of nitrogen (NO$_x$) between 0,01 ppm and 1 000 ppm in air or in an oxygen-depleted atmosphere. The reference method is chemiluminescence. An alternative uses a chemical colorimetric method.
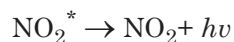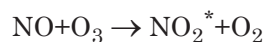
10.2 Chemiluminescence

10.2.1 *Principle*

The method is based on measurement of the chemiluminescence (600 nm to 3 000 nm with maximum at 1 200 nm) generated in the reaction between nitrogen monoxide and ozone[29 to 32]. Therefore, the method is primarily applicable to nitrogen monoxide (NO) only. For nitrogen dioxide measurement, the nitrogen dioxide must be converted into nitrogen monoxide and nitrogen dioxide is recorded as the difference between the nitrogen monoxide and oxides of nitrogen measurements.

The reactions involved are

$$NO + O_3 \rightarrow NO_2{}^* + O_2$$

$$NO_2{}^* \rightarrow NO_2 + h\upsilon$$

where $h\upsilon$ is the radiation energy (υ being the frequency, in hertz, and h being Planck's constant).

When nitrogen monoxide and ozone react, the sub-sequent chemiluminescent reaction produces light emission that is directly proportional to the concentration of nitrogen monoxide. This emission is measured by a photomultiplier tube and associated electronic circuitry. The analytical range is about 0,01 ppm to 4 000 ppm.
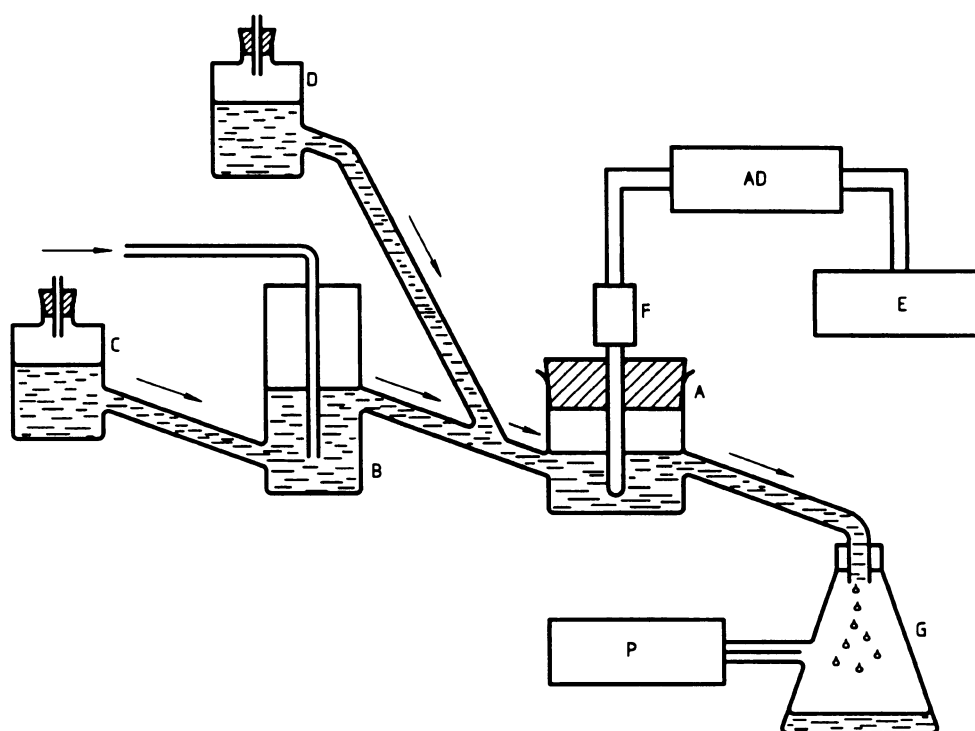
A	Measuring cell
B	Gas washing bottle
C	Alkaline reagent
D	Acid reagent
E	Recorder
F	Combination fluoride electrode
G	Collector
P	Pump
AD	Differential amplifier

Figure 2 — Sampling for measurement of hydrogen fluoride (on-line)

Two basic types of converters available for the nitrogen dioxide to nitrogen monoxide transformation are the catalytic (stainless steel) and chemically reactive (molybdenum or carbon-based) converters. Using the stainless steel converter at high temperatures (650 °C to 800 °C) can lead to substantial errors in oxides of nitrogen measurement since it can also convert low molecular weight nitrogen-containing species such as hydrogen cyanide and ammonia to nitrogen monoxide. Using the reactive converter reduces the possibility of interferences, e.g. at low temperatures (375 °C to 400 °C) the molybdenum does not react with hydrogen cyanide. The reactive converters however, have a finite lifetime and shall be periodically rejuvenated or replaced.

10.2.2 *Sampling*

The sampling line shall be constructed of materials that will not react with nitrogen monoxide or nitrogen dioxide. It is recommended to use glass or PTFE.

The gas sample for analysis of the combustion effluents can be taken either

— without dilution, directly from the stream of combustion effluents;

— after cooling and dilution with air of the combustion effluents.

The fire effluents are initially hot and have high humidity. At a distance from the fire the effluents are cooled and the humidity decreases. This change can cause considerable differences in concentration depending on which analytical procedure is being used. This problem must be considered when deciding the method of sampling.

The gas sampling line is mounted in the stream of fire effluent gases in such a way that an appropriate sample is obtained. The sampling line should contain a glass filter (G0-G2) or PTFE filter to separate particulates from the gas stream, the filter being heated to a temperature above that on the sampling inlet. The sample is sucked into the line by means of a pump. The temperature of the sample should be measured, first, as close as possible to the pump and second, at the spot at which the sample is introduced into the sampling line. Depending on the analytical procedure the sampling train can differ after the filter for particulates.

10.2.3 *Procedure*

The sampling rate of the analytical instrument is usually in the range of 1 l/min. Thus the sample is taken from the fire effluent gases at approximately that rate.

Depending on the state of the switches (3 and 5 in Figure 3), the instrument will read nitrogen monoxide or oxides of nitrogen. The response of the instrument is normally very quick (10 s to 20 s). After calibration, the recorder gives the concentration of nitrogen monoxide or oxides of nitrogen. An approximate value of nitrogen dioxide can be obtained by taking the difference between oxides of nitrogen and nitrogen monoxide. (Normally, the instruments are single-channel models and nitrogen monoxide and oxides of nitrogen cannot be read simultaneously unless two channels are available).

10.2.4 *Calibration*

Let instrument warm up for the recommended time (normally 1 h).

Set range switch to appropriate range.

Follow recommended procedure in accordance with the manufacturer's instrument manual.

For calibration procedures and measurements, follow the recommendations given in ISO 7996.

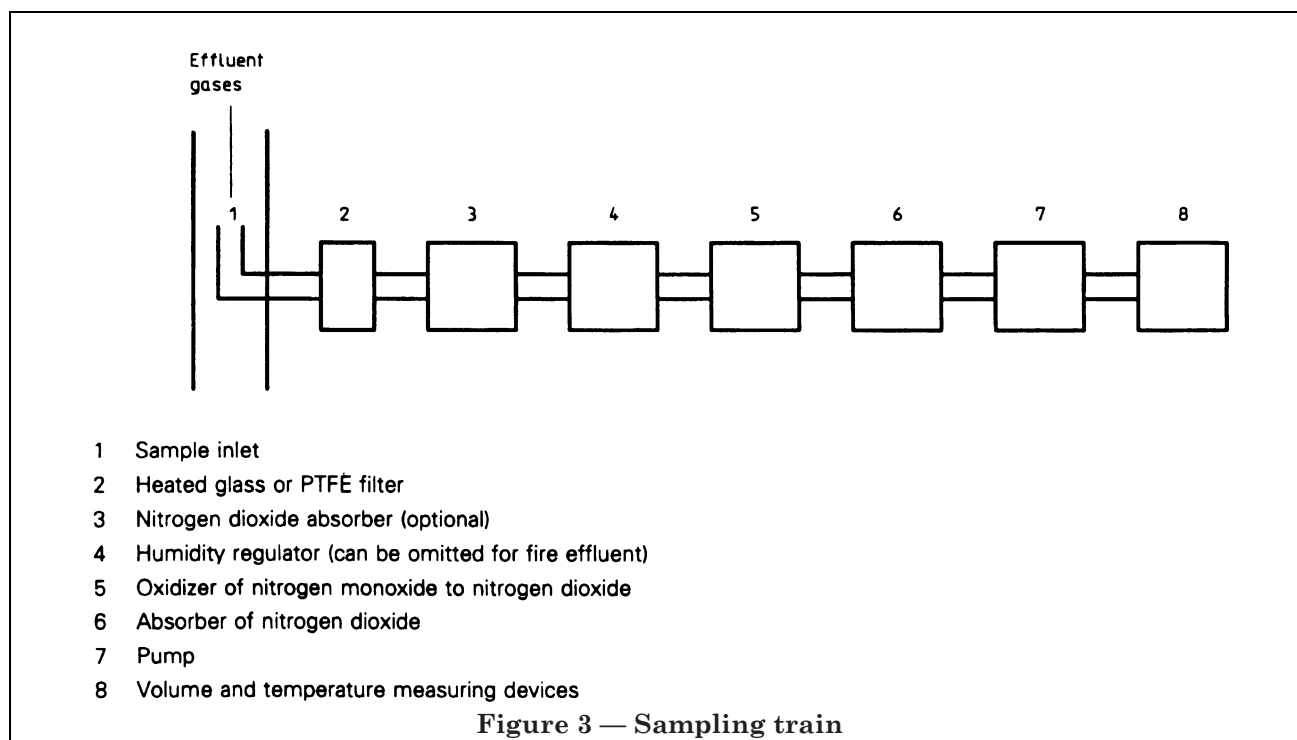### 10.2.5 *Interference and limitations*

Water is the major interferent since it reduces the production of nitrogen dioxide by reducing the number of collisions between nitrogen monoxide and ozone (O_3).

The reaction for nitrogen monoxide with ozone is highly specific. Normally, gases in fire effluents do not interfere with the above reaction. At very low concentrations of nitrogen monoxide, high concentrations of ozone have been observed to quench the reaction leading to low readings of nitrogen monoxide[31]. This is normally no problem in investigating combustion products.

For oxides of nitrogen determination, interferences exist depending on the kind of converter for oxides of nitrogen being used.

Interferences from ammonia have been reported with molybdenum and copper converters. Conversions to nitrogen monoxide being in the range of 2 % and 0,2 % respectively of the concentration of ammonia.

The chemiluminescence method of analysis for nitric oxide provides a linear relationship over an extremely wide concentration range, from 0,004 ppm to more than 1 000 ppm. Accuracy depends on the instrument and the set range on the instrument. It is therefore difficult to state a single value. The method is considered to be very accurate.

Effluent
gases

1 Sample inlet
2 Heated glass or PTFE filter
3 Nitrogen dioxide absorber (optional)
4 Humidity regulator (can be omitted for fire effluent)
5 Oxidizer of nitrogen monoxide to nitrogen dioxide
6 Absorber of nitrogen dioxide
7 Pump
8 Volume and temperature measuring devices

Figure 3 — Sampling train

10.3 Colorimetric method for determination of oxides of nitrogen

10.3.1 *Principle*

Fire effluent gases are collected on a solid sorbent and later brought into solution and analysed. The colorimetric reaction is specific for nitrogen dioxide. Nitrogen monoxide is oxidized to nitrogen dioxide before absorption. Quantitative oxidation of nitrogen monoxide in the gas phase can be accomplished using chromic oxide. It is then analysed with a colorimetric method based on an established procedure[32].

Analysis of nitrogen monoxide can be achieved by adsorbing nitrogen dioxide on a precolumn. This precolumn can be included or omitted. In this description the precolumn is included.

10.3.2 *Procedure*

10.3.2.1 *Sampling*

Assemble a sampling train (see Figure 3) comprising, in order, a nitrogen dioxide absorber (optional), a humidity regulator, an oxidizer, a nitrogen dioxide absorber and a pump. Draw in the sample at a rate of 0,2 l/min. Record the total volume sampled, as well as the temperature and pressure.

The combined train can be used for at least 800 h/ppm nitrogen dioxide and shall be changed whenever it becomes visibly wet or discoloured.

10.3.2.2 *Colour development*

Transfer the nitrogen dioxide absorbent pellets and glass wool plugs from the second nitrogen dioxide absorber in the train to a 50 ml test tube. Wash the tube with about 10 ml of water and add washings to the test tube. Ignore the volume occupied by the pellets and the glass wool. Dilute to 50 ml with diluting reagent. Cap and shake vigorously for about 1 min. Set aside and shake again after 10 min. Allow the solids to settle and transfer 10 ml to a 25 ml graduated cylinder. Similarly treat an unexposed nitrogen dioxide absorber as a blank. To each sample, add 10 ml of the sulfanilamide solution and 1 ml of NEDA (see **10.3.4**) solution, mix well and dilute to 25 ml with distilled water. Allow the colour to develop for 15 min and read the absorbance at 500 nm.

10.3.3 *Apparatus*

10.3.3.1 *Pump,* approved and calibrated, whose flow can be determined accurately at 0,2 l/min[34].

10.3.3.2 *Nitrogen dioxide absorber,* comprising a 50 mm long polyethylene tube of internal diameter 20 mm with connecting caps at both ends, filled with pellets of nitrogen dioxide absorbent. The pellets are held in place with glass wool plugs.

10.3.3.3 *Humidity regulator,* capable of maintaining a steady 40 % to 70 % relative humidity control over the efficient working range of the chromic oxide, typically a 50 mm long polyethylene tube of internal diameter 20 mm filled with constant humidity buffer mixture[35].

10.3.3.4 *Oxidizer,* comprising a glass tube of 15 mm internal diameter with connecting ends filled with oxidizing pellets to a length of 10 cm between two glass wool plugs[29, 30 and 36].

10.3.4 Reagents and materials

Use only reagents of recognized analytical grade[37], and distilled or demineralized water or water of equivalent purity.

10.3.4.1 *Nitrogen dioxide absorbent*[29, 36 and 38]

1,5 mm pellets of 10 mesh to 20 mesh size porous inert material, such as firebrick, alumina, zeolites, etc., are soaked for 30 min in 20 % aqueous triethanolamine, drained, extended on a wide petri dish, and dried for 30 min to 60 min at 95 °C. The pellets should be free-flowing.

CAUTION — Soda lime should not be used as an absorbent[30].

10.3.4.2 *Constant humidity grains*

These consist of a 50/50 anhydrous and hydrous sodium acetate mixture. Stir slowly and add dropwise 13 ml of water into a beaker containing 40 g of anhydrous sodium acetate in order to obtain a coarse-grained crystal pellet.

10.3.4.3 *Oxidizer*[29, 30 and 36]

Soak glass, firebrick or alumina, 15 mesh to 40 mesh size in a solution containing 17 g of chromium trioxide in 100 ml of water for 30 min. Then drain, dry in an oven at 105 °C to 115 °C and condition to 70 % relative humidity. Conditioning can be done by exposing a thin layer of pellets, contained in a petri dish, to a saturated solution of sodium acetate in a desiccator. The reddish colour changes to orange when conditioning is complete.

CAUTION — Protect eyes and skin when handling this reagent.

10.3.4.4 *Diluting reagent*

Add 15 g of triethanolamine to approximately 500 ml of water; then add 3 ml of butan-1-ol which acts as a surfactant. If excessive foaming occurs during sampling, the amount added of butan-1-ol should be decreased. The reagent is stable for two months if kept in a brown bottle, preferably in the refrigerator.

10.3.4.5 *Sulfanilamide solution*

Dissolve 10 g of sulfanilamide in 400 ml of water, then add 25 ml of concentrated phosphoric acid (85 %). Make up to 500 ml. This solution is stable for several months if stored in a brown bottle and up to one year in the refrigerator.

10.3.4.6 *N-(1-naphthyl)ethylenediamine dihydrochloride (NEDA)*

Dissolve 0,1 g of NEDA in 100 ml of water. The solution is stable for one month if kept in a brown bottle in the refrigerator.

10.3.4.7 *Stock nitrite solution (1,77g/l)*

Before preparing this solution it is desirable to assay the solid reagent, especially if it is old. The stock solution is stable for 90 d at room temperature and for a year in a brown bottle under refrigeration.

10.3.5 Calibration and standards

The method may be calibrated with nitrite solutions[39] or with known gas mixtures. In the latter case, stoichiometric and efficiency factors need not be used in the calculation.

Calibration references are also given in ISO 6142 and ISO 6349.

10.3.5.1 *Calibration with nitrite solutions*[31]

By assuming a quantitative conversion of nitrogen(II) oxide to nitrogen dioxide, the method can be calibrated as described in bibliographic reference [42] (see annex D).

Calibration with nitrite solution is based upon the empirical observation that 0,63 mol of sodium nitrite produces the same colour as 1 mol of nitrogen dioxide[43], and this gas is obtained in a quantitative yield during oxidation of nitrogen monoxide[29 and 30]. Nitrite solution equivalent to 10 µl nitrogen monoxide per millilitre contains

$$\frac{10^5 \text{ NO} \times 0,63 \times 69 \times 1\,000}{24,47}$$

$$= 1,77 \times 10^{-2} = 0,017\,7 \text{ g/l of NaNO}_2$$

where

    69   is the molecular mass of sodium nitrite;

    0,63   is the efficiency factor nitrogen monoxide/nitrogen dioxide;

    24,47 is the molar volume, in litres, at 0,1 kPa and 25 °C;

    1 000 is the conversion from millilitres to litres.

This solution is prepared fresh just before use from a stronger stock solution containing 1,77 g of sodium nitrite per litre[34 and 36].

Construct the calibration curve by adding graduated amounts of dilute nitrite solution, equivalent to the concentration expected to be sampled, to a series of 25 ml volumetric flasks. Plot the absorbencies against microlitres of nitrogen monoxide added to the 25 ml final solution. If preferred, transmittances in percent may be plotted on the logarithmic scale *vs.* nitrogen monoxide concentration on the linear coordinate on semilog graph paper. The plot follows Beer's law up to absorbance unity (or 10 % transmittance).

10.3.5.2 *Dynamic calibration method*

Known quantities of nitrogen monoxide in air may be prepared by the method outlined below. The known gas mixture is sampled using the sampling train described in **10.3.3**. From the known concentration of nitrogen monoxide a calibration curve is constructed of absorbance *vs.* concentration of nitrogen monoxide in air. This should be made to cover the expected concentration in the sampled atmosphere. The dynamic calibration method enables the entire sampling system to be calibrated and eliminates the need to know the efficiency factor of nitrite to the initial nitrogen monoxide present in the air sample.

Nitrogen monoxide in argon or nitrogen is obtained from a special gas supplier and is certified as to nitrogen monoxide concentration either by the supplier or by independent analysis. The high-pressure cylinder should contain at least 200 ppm of nitrogen monoxide for calibration of the sampling system over the full range of 100 ppm to 2 ppm. Concentration of nitrogen monoxide in the dilution system, c_{NO}, expressed in parts per million can be calculated as follows:

$$c_{NO} = \frac{cF_1}{F_1 + F_2}$$

where

c is the concentration of nitrogen monoxide in the cylinder, in parts per million;

F_1 is the flow rate of cylinder gas;

F_2 is the flow rate of dilution air.

The dilution air flow rate F_2, should be at least twice as large as the cylinder gas flow rate F_1 in order to approximate ambient air. The greater the ratio of F_2 to F_1 the more the composition of the dynamic system corresponds to the major constituents of air. The dilution air should be humidified before mixing the nitrogen monoxide cylinder gas into the stream and the relative humidity should approximate to the sampling conditions.

10.3.6 *Interferences and limitations*

Oxidizing vapours that are known to interfere with the nitrogen dioxide measurement part of this method cannot coexist with nitrogen monoxide at significant concentrations because of their rapid gas phase reaction with nitrogen monoxide[32]. Therefore, no significant interferences are expected from such vapours.

Nitrogen dioxide interferes by being partially converted (3 % to 4 %) into nitrogen monoxide in the nitrogen dioxide absorbers[38].

Sulfur dioxide is removed by the oxidizer[44] and ordinarily produces no interference. However, if present at very high concentrations, it depletes the oxidizer rapidly and requires more frequent oxidizer changes. The oxidizer will indicate depletion by a change from orange to a brownish colour.

Relative humidity higher than 70 % (at room temperature) can reduce the efficiency of the oxidizer[36].

This method is intended for the manual determination of nitrogen monoxide in the atmosphere in the range of 2 ppm to 100 ppm by volume, or 2 mg/m^3 to 123 mg/m^3.

The sensitivity is 0,01 µg nitrogen monoxide per 10 ml of diluting reagent[31].

The precision of the method depends on the conversion efficiency of the oxidizer and other variables such as volume measurement of the sample, sampling efficiency of the solid triethanolamine (TEA) absorber, and absorbance measurement of the colour.

Under normal conditions, the conversion efficiency of the oxidizer varies within a range of 98 % to 100 %[29 and 44].

Accuracy data are not available at present.

The sampling method is simple and permits storage of the absorbed samples for periods of several weeks.

The analytical method has the disadvantages associated with wet chemical methods.

Exposure to light affects the developed colour.

10.3.7 *Calculations*

For convenience, standard conditions are taken as 0,1 kPa and 25 °C, where the molar volume is 24,47 litres. Ordinarily, the correction of the sample volume to these standard conditions is slight and may be omitted. However, if conditions deviate significantly, corrections can be made by means of the ideal gas equation.

From the plot obtained with nitrite solutions, read the amount of nitrogen monoxide or nitrogen dioxide, in microlitres, at the intercept of the calibration curve with absorbance unity or transmission 10 %. This amount can be used as factor K for calculating the concentration, c_{NO}, in parts per million, rather than reading concentrations directly from the graph, from the following equation:

$$c_{NO} = \frac{A \times K \times 10}{V \times 25}$$

where

> A is the absorbance of the sample made up to 10 ml after sampling;
>
> K is the factor as described above;
>
> V is the volume of air sampled, in litres;
>
> 10   is the volume of sampling solution, in millilitres;
>
> 25   is the volume of calibrating solution, in millilitres.

When using the calibration with gaseous mixtures, the sampling shall be made under similar conditions of time and flow rate as the calibration, because the stoichiometric factor varies with incoming concentrations of nitrogen monoxide and hence of nitrogen dioxide[43]. The concentrations of nitrogen monoxide collected are read directly from the calibration curve.

11 Analytical methods for acrolein

11.1 General

The reference method for analysis of acrolein (CH_2CHCHO) is a colorimetric technique following sampling by solution impinger. The alternative method is high performance liquid chromatography after sampling with an evacuated glass vessel.

11.2 Colorimetry

11.2.1 *Principle* [45]

Acrolein is collected in 1 % sodium hydrogen sulfite solution in Greenberg-Smith impingers then measured by the modified mercury(II) chloride/4-hexylresorcinol procedure. Colorimetry can also be used as a continuous method for determining acrolein concentrations[46].

11.2.2 *Procedure*

11.2.2.1 *Collection of samples*

Connect two Greenberg-Smith impingers, each containing 10 ml of 1 % sodium hydrogen sulfite, in series with "Tygon" tubing. Connect downstream of these, an empty impinger (for meter protection), a dry test meter and a source of suction. During sampling, immerse the impingers in an ice bath. Maintain a sampling rate of 14 l/min to 28 l/min. Sampling duration will depend on the concentration of aldehydes in the sample stream; 15 min is adequate for most cases. After sampling is complete, store the impingers in an ice bath or at 6 °C in a refrigerator until analyses are performed. Cold storage is necessary only if the acrolein determination cannot be performed within 4 h of sampling.

11.2.2.2 *Analysis of samples*

Analyse each impinger separately.

If the second impinger contains more than 10 % of the amount found in the first impinger, repeat sample collection for a shorter time period. To a 25 ml graduated tube, add an aliquot of the collected sample in bisulfite containing no more than 30 µg acrolein. Add 1 % sodium bisulfite (if necessary) to give a volume of 4 ml. Add 12 ml of the mercury(II) chloride/4-hexylresorcinol (**11.2.5.1**) and mix. Add 5 ml of trichloroacetic acid (TCAA) (**11.2.5.2**) and mix again. Insert in a boiling water bath for 6 min, remove and set aside until tubes reach room temperature. Centrifuge samples at 1 500 rpm for 5 min to clear slight turbidity. One hour after heating, measure in a spectrometer at 605 nm against a bisulfite blank prepared in the same fashion as the samples[47].

11.2.2.3 *Calculations*

The concentration of acrolein in the sample, c_a, expressed in parts per million, is given by

$$c_a = \frac{m}{2,3V}$$

where

> m is the mass of acrolein, in micrograms;
>
> V is the sample volume, in litres.

11.2.3 *Calibration*

To 250 ml of 1 % sodium bisulfite add 4 µl freshly distilled acrolein. This yields a standard containing 13,4 µg/ml. To a series of tubes add 0,5 ml, 1 ml, 1,5 ml and 2 ml of standard. Adjust the volume to 4 ml with 1 % bisulfite and develop colour as described above. Plot data on semilog paper to give the standard curve.

11.2.4 *Apparatus*

11.2.4.1 *Absorbers.* All glass standard Greenberg-Smith impingers are acceptable. A train of two bubblers in series is used.

11.2.4.2 *Air pump,* capable of drawing at least 28 l/min of air for 15 min through the sampling train.

11.2.4.3 *Air metering device.* Dry test meter or other suitable device.

11.2.4.4 *Spectrometer,* capable of measuring the developed colours at 605 nm and 580 nm. The absorption bands are rather narrow and a lower absorptivity may be expected in a broad-band instrument.

11.2.5 *Reagents*

Use only reagents of recognized analytical grade and only distilled or demineralized water or water of equivalent purity.

11.2.5.1 *Mercury(II) chloride / 4-hexylresorcinol*

0,30 g mercury(II) chloride and 2,5 g 4-hexylresorcinol are dissolved in 50 ml of 95 % ethanol (Remains stable for at least three weeks if kept refrigerated.)

11.2.5.2 *Trichloroacetic acid (TCAA)*

To 450 g of trichloroacetic acid, add 23 ml of water and 25 ml of 95 % ethanol. Mix until all the TCAA has dissolved.

11.2.5.3 *Collection medium*

Sodium bisulfite, 1 % in water.

11.2.6 *Interferences and limitations*

A slight interference occurs from dienes: 1,55 % for 1,3-butadiene and 2 % for 1,3-pentadiene. The red colour produced by some other aldehydes and undetermined materials does not interfere in spectrometric measurement.

When a collected sample is highly darkened by soot, the measurement of the blue-green colour of acrolein-hexylresorcinol reaction products will be affected. The soot may be removed by filtering.

11.2.6.1 *Effect of storage*

After sampling is complete, samples shall be stored in an ice bath or refrigerator at 6 °C. Under cold storage conditions, analysis can be performed within 47 h with no deterioration of collected samples.

11.2.6.2 *Concentration of acrolein*

At a sampling rate of 14 l/min to 28 l/min over a 14 min period, the limiting concentration of 0,1 ppm acrolein can be determined. Shorter sampling periods are permissible for higher concentrations.

11.3 High performance liquid chromatography (HPLC)

11.3.1 *Principle*

Acrolein and other carbonyl compounds are converted to 2,4-dinitrophenylhydrazones which are determined by HPLC.

11.3.2 *Procedure*[48 and 49]

11.3.2.1 *Sampling*

To trap the gas-phase carbonyl, add 200 ml of saturated 2,4-dinitrophenylhydrazine in 2 mol/l hydrogen chloride and 20 ml chloroform to a 1 l gas sampling flask. Then evacuate the flask and take the gas sample.

11.3.2.2 *Detection*

Shake the flask for 30 min to separate the organic layer and adjust to a known volume. Inject 20 µl of hydrazine solution into the HPLC. The mobile phase of the HPLC is methanol/water; use a ratio of 60/40, 65/35 or 70/30 depending on the type of column. Perform detection at 254 nm for the highest sensitivity with a reasonably clean gas sample, or at 350 nm for complex aerosols, resulting in better selectivity and about a 20 % decrease in sensitivity.

11.3.3 *Calibration*

From the 2,4-dinitrophenylhydrazine reagent and freshly distilled acrolein, prepare the hydrazone derivative. Purify the hydrazone to a constant melting point (165 °C) by recrystallization from ethanol. To construct a calibration curve, dissolve varied amounts of the hydrazone in 75/25 methanol/water and inject on the column of the HPLC.

11.3.4 *Apparatus*

11.3.4.1 Commercially available **HPLC equipment**, including a reverse-phase column for the separation. For example, Partisil-10-ODS-2, Zorbax-ODS, and Bio-sil-HP-10 in a standard sized 25 cm × 4,6 mm column.

11.3.4.2 *Ultraviolet detector,* fixed- or variable-wavelength type.

11.3.5 *Interferences and limitations*

The use of HPLC for determining the hydrazones has the advantage of avoiding interferences from other types of organic compounds that are found in fire gases. Several species of carbonyl compounds can be determined at the same time as acrolein. Easy handling of stable hydrazones rather than volatile aldehydes is another advantage.

No known interferences.

For a 1 l gas sample, concentrations of acrolein from 40 ppm to 50 ppm can be determined. A significant factor affecting the minimum detectable limit is the presence of carbonyl compounds in reagents and solvents.

12 Test report

The report shall state that

"Compliance with this part of ISO/TR 9122 implies that

a) the analysis of sampled gases has been carried out to standardized procedures;

b) the sampling procedure has been carried out in accordance with the general recommendations given herein for the particular species."

The report shall state

a) name of laboratory;

b) date of analysis;

c) description of material(s);

d) description of combustion device and location of sampling probes;

e) time and frequency of sampling;

f) temperature and pressure at the sampling point;

g) temperature, pressure and relative humidity of analyser stream;

h) sampling flow rate or total volume (whichever is appropriate);

i) calibration standards used;

j) sampling method used (with reference);

k) for each gas analysed (carbon monoxide, carbon dioxide, oxygen, hydrogen cyanide, hydrogen chloride, hydrogen bromide, hydrogen fluoride, oxides of nitrogen, acrolein):

— concentration or total quantity of gas (whichever is appropriate during each period of sampling);

— if possible, (continuous measurement) curve of concentration *vs.* time;
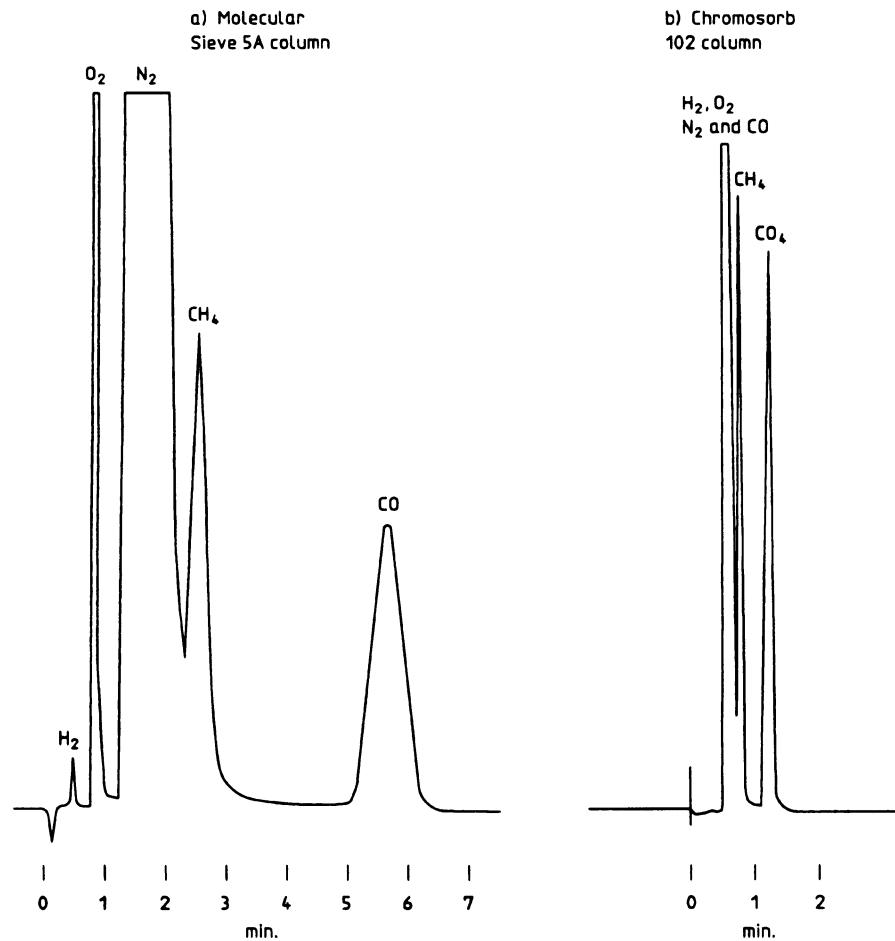
— reference to the analytical methods.

Annex A (informative)
Examples of separation of permanent gases
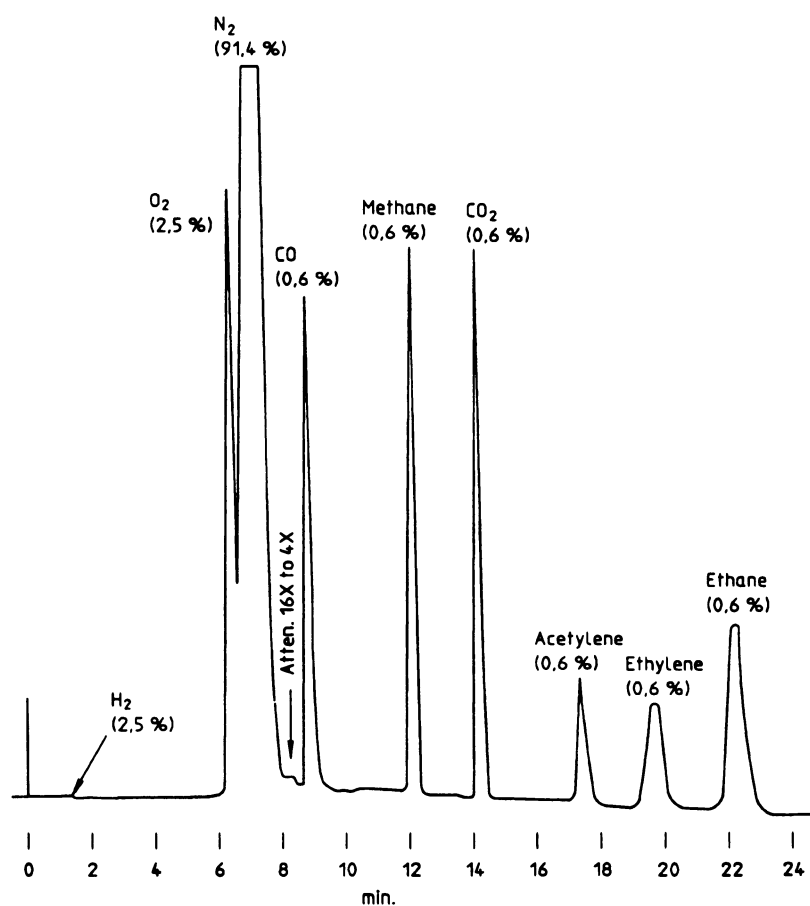
Figure A.1 — Permanent gases, methane and C2 hydrocarbons on Carbosieve S-II

60/80 Molecular Sieve 5A, 3′ × 1/4″ SS [figure a)] or 80/100 Chromosorb 102, 6′ × 1/4″ SS [figure b)], Col. temp.: 60 °C, Flow rate: 65 cc/min [figure a)] or 60 cc/min [figure b)], He, Det.: thermal conductivity, Sens: 250 mA, 4X, Instrument: Fisher 2 400, Sample: 0,5 cc, 1 % each other component in N_2.

Figure A.2 — Isothermal analyses of permanent gases require two columns

Annex B (informative)
Other gases of interest

Efficient methods exist for the sampling and analysis of many important fire gases. However, many other gases of interest can be present or generated in fire atmospheres, and an outline analysis method for each of these gases is given below. These include nitrogen, sulfur dioxide, carbonyl sulfide, ammonia, isocyanates, nitriles, organophosphorus compounds, styrene, aldehydes, polynuclear hydrocarbons, compounds of antimony and arsenic, total hydrocarbons and solid particles.

These species have been listed in this annex until further information about their analysis allows standard methods to be established. There is no reference method cited for any compound and only brief guidance is given in each case.

B.1 Nitrogen

Nitrogen is a major component of the air; its analysis in fire atmospheres seems to be unimportant.

The most common method for determining nitrogen is gas chromatography by use of a molecular sieve column which can separate oxygen from nitrogen[50]. The gas chromatograph has to be equipped with a thermal conductivity detector[51].

B.2 Sulfur dioxide

Many methods are used to analyse sulfur dioxide present in the atmosphere, especially in the field of air pollution.

Some of them can be used to measure sulfur dioxide in fire effluents such as non-dispersive infrared[52], gas chromatography with specific detectors[50 and 53], and colorimetry.

B.3 Carbonyl sulfide

The presence of this compound has been shown recently in the fire effluents of sulfur polymers. Infrared techniques can be used to measure carbonyl sulfide concentrations[54].

B.4 Ammonia

There are few references available on the analysis of ammonia in fire atmospheres. A colorimetric method can be suitable after collection of ammonia in an aqueous solution[55].

B.5 Isocyanates

Isocyanates are very reactive materials and analysis should be based on derivitization and high performance liquid chromatography[50 and 51]. Care should be taken to keep the sampling train prior to the derivitization trap very short to avoid losses on the surfaces. Some commercial detection systems based on sensitized paper tape can be useful for quick readings but these systems can suffer from lack of specificity or differential response to different isocyanate species when used to analyse fire effluents.

B.6 Nitriles

These compounds can be analysed by gas chromatography[50] and mass spectrometry[56].

B.7 Organophosphorus compounds

Organophosphorus compounds are a family of chemical species, some of which have been identified in fire effluents of materials containing phosphorus additives.

B.8 Styrene

Styrene is a hydrocarbon which can be analysed by gas chromatography[50] and mass spectrometry[57].

B.9 Aldehydes

Methods for acrolein are detailed in clause **11**. Formaldehyde is also important; but its analysis is more difficult due to reactivity of the mixture being analysed. Gas chromatography and high performance liquid chromatography can be suitable[58 and 59].

B.10 Polynuclear hydrocarbons

These compounds, many of which are carcinogenic, can be analysed by sophisticated methods, e.g. high performance liquid chromatography or gas chromatography/mass spectrometry[50 and 56].

B.11 Compounds of antimony and arsenic

Antimony and arsenic compounds are emitted by combustion of materials containing additives (flame retardants or others) containing antimony or arsenic.

B.12 Total hydrocarbons

The term "total hydrocarbons" is very misleading because it is defined only by the response of detectors, e.g. flame ionization or catalytic detectors, which is an indication of the concentration of combustible gases or vapours in an atmosphere[50]. These detectors can also react to oxygenated species (alcohols, aldehydes, ketones), nitriles, and amines which are present in fire effluents[60 to 62].

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 possible to obtain a true measurement of "total hydrocarbons".

B.13 Solid particles

Apart from noxious gases, solid particles can contribute to the overall toxicity of fire effluents.

Aerosols of particles are characterized by the concentration (mass or number of particles) and by the particle size distribution.

The following parameters have to be measured:

— concentration, as expressed by the total mass of particles per volume or by the number of particles per volume;

— particle size distribution, as the function between frequency and particle diameter in an aerosol.

Because of the reactivity and the nature of the mixture of fire effluents, it is difficult to measure these two parameters precisely.

Annex C (informative)
New methods

C.1 Introduction

It is to be anticipated that new methods for the analysis of any of the compounds discussed in this part of ISO/TR 9122 will become available, but without a full published protocol for use in fire effluent analysis. One such method is noted below.

C.2 Continuous on-line analysis using a Fourier transform infrared (FTIR) spectrometer

Almost all gases of interest in combustion toxicity show molecular absorption in the infrared spectrum. The only exceptions are symmetrical molecules (oxygen, nitrogen) and nearly symmetrical ones (hydrogen sulfide). Nevertheless, for many gases of possible toxic interest, suitable commercial infrared analysers are not available. It is possible, however, to quantify the concentrations of a large number of gases simultaneously by using a Fourier transform infrared (FTIR) spectrometer.

Commercial FTIR spectrometers are available with computers which are capable of solving the necessary equations every 60 s, or more frequently. To implement such an analysis method, a flow-through sampling system has to be set up. The flow rates in such a system will be very high, typically in the vicinity of 40 l/min. This is because the measuring cell to be used will normally be a folded-path 10 m or 20 m cell, which has a volume of 5 l to 7 l. If one sampling point per 30 s is desired, the sampling flow must exchange 3 cell volumes per 30 s. (The factor of 3 arises because measuring cells normally available are not streamlined and do not maintain plug flow.) The measuring cell and the sampling lines must be heated to about 150 °C to minimize losses and condensation. The sampling line must be preceded by a heated filter to remove particulates from the stream. The basic principles have been described by Nyden and Babrauskas[63]; the mathematical analysis needed to obtain concentration data from spectral measurements was given by Nyden, Forney and Chittur[64].

Practical use of FTIR for effluent analysis in a small-scale rate of heat release apparatus (the "cone calorimeter") has been reported by Kallonen[65].

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