TECHNICAL REPORT

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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

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Foreword

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

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 Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.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)*

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— *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

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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

a) 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);

b) 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.

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Toxicity testing of fire effluents —

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

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.

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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 subdivided 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

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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

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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, ⌀ 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 inert 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.

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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, ⌀ 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

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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 prechromatographic 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.

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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

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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.

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