



Standard Guide for Measurement of Gases Present or Generated During Fires¹

This standard is issued under the fixed designation E 800; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 Analytical methods for the measurement of carbon monoxide, carbon dioxide, oxygen, nitrogen oxides, sulfur oxides, carbonyl sulfide, hydrogen halides, hydrogen cyanide, aldehydes, and hydrocarbons are described, along with sampling considerations. Many of these gases may be present in any fire environment. Several analytical techniques are described for each gaseous species, together with advantages and disadvantages of each. The test environment, sampling constraints, analytical range, and accuracy often dictate use of one analytical method over another.

1.2 These techniques have been used to measure gases under fire test conditions (laboratory, small scale, or full scale). With proper sampling considerations, any of these methods could be used for measurement in most fire environments.

1.3 This document is intended to be a guide for investigators and for subcommittee use in developing standard test methods. A single analytical technique has not been recommended for any chemical species unless that technique is the only one available.

1.4 The techniques described herein determine the concentration of a specific gas in the total sample taken. These techniques do not determine the total amount of fire gases that would be generated by a specimen during conduct of a fire test.

1.5 *This standard is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.*

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 123 Terminology Relating to Textiles²

¹ This guide is under the jurisdiction of ASTM Committee E-5 E05 on Fire Standards and is the direct responsibility of Subcommittee E05.21 on Smoke and Combustion Products.

Current edition approved ~~March~~ October 10, 1999; ~~2001~~. Published ~~June 1999~~; November 2001. Originally published as E 800 – 81. Last previous edition E 800 – 958.

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres³

D 3162 Test Method for Carbon Monoxide in the Atmosphere (Continuous Measurement by Nondispersive Infrared Spectrometry)³

E 84 Test Method for Surface Burning Characteristics of Building Materials⁴

E 176 Terminology Relating to Fire Standards⁴

E 535 Practice for Preparation of Fire-Test-Response Standards⁴

E 603 Guide for Room Fire Experiments⁴

E 662 Test Method for Specific Optical Density of Smoke Generated by Solid Materials⁴

3. Terminology

3.1 *Definitions*—Definitions used in this guide are in accordance with Terminology D 123, Terminology D 1356, Terminology E 176, and Practice E 535 unless otherwise indicated.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *batch sampling*—sampling over some time period in such a way as to produce a single test sample for analysis.

3.2.2 *combustion products, n*—airborne effluent from a material undergoing combustion; this may also include pyrolysates.

3.2.2.1 *Discussion*—combustion products without mass, such as heat or other radiation, are not addressed in this guide.

3.2.3 *fire test, n*—a procedure, not necessarily a standard test method, in which the response of materials to heat or flame, or both, under controlled conditions is measured or otherwise described.

3.2.4 *sample integrity*—the unimpaired chemical composition of a test sample upon the extraction of said test sample for analysis.

3.2.5 *sampling*—a process whereby a test sample is extracted from a fire test environment.

3.2.6 *test sample*—a representative part of the experimental environment (gases, liquids, or solids), for purposes of analysis.

4. Significance and Use

4.1 Because of the loss of life in fires from inhalation of fire gases, much attention has been focused on the analyses of these species. Analysis has involved several new or modified methods, since common analytical techniques have often proven to be inappropriate for the combinations of various gases and low concentrations existing in fire gas mixtures.

4.2 In the measurement of fire gases, it is imperative to use procedures that are both reliable and appropriate to the unique atmosphere of a given fire environment. To maximize the reliability of test results, it is essential to establish the following:

4.2.1 That gaseous samples are representative of the compositions existing at the point of sampling,

4.2.2 That transfer and pretreatment of samples occur without loss, or with known efficiency, and

4.2.3 That data provided by the analytical instruments are accurate for the compositions and concentrations at the point of sampling.

4.3 This document includes a comprehensive survey that will permit an individual, technically skilled and practiced in the study of analytical chemistry, to select a suitable technique from among the alternatives. It will not provide enough information for the setup and use of a procedure (this information is available in the references).

4.4 Data generated by the use of techniques cited in this document should not be used to rank materials for regulatory purposes.

5. Sampling

5.1 More errors in analysis result from poor and incorrect sampling than from any other part of the measurement process (1, 2).⁵ It is therefore essential to devote special attention to sampling, sample transfer, and pretreatment aspects of the analysis procedures.

5.2 *Planning for Analysis*—Definitive answers should be sought and provided to the following questions during the planning stage: (1) *Why* is the sampling (analysis) being performed? (2) *What* needs to be measured? (3) *Where* will samples be taken? (4) *When* does one sample? (5) *How* are samples collected? (3).

5.2.1 All aspects of sampling and analysis relate to the fundamental reasons for performing the analysis. Analysis of combustion products is normally performed for one of the following reasons: for research on the composition of the gases; to relate directly to flammability, smoke generation, toxic or irritant effects; to study mechanisms of combustion; or for development of test equipment. The experimenter should decide exactly what type of information the analysis must provide. The necessary detection limits, acceptable errors, and possible or tolerable interferences must be determined.

5.2.2 A representative sample must be obtained; however, sampling must not interfere with the test (for example, sampling could alter the atmosphere in an animal toxicity experiment or in a smoke measurement device). The size and shape of the test chamber affects the possible location and number of sampling probes.

² Annual Book of ASTM Standards, Vol 07.01.

³ Annual Book of ASTM Standards, Vol 11.03.

⁴ Annual Book of ASTM Standards, Vol 04.07.

⁵ The boldface numbers in parentheses refer to the list of references appended to this standard.

5.2.3 Single or cumulative samples may be adequate for many requirements; however, a continuous monitor may be desirable for the determination of concentration-time dependence, or in the case of analysis of reactive species (for example, hydrochloric acid (HCl)).

5.2.4 Collection and transport of samples must be accomplished in such a way that the analyses properly reflect the nature and concentration of species in the combustion gas stream. Heated sampling lines made from an inert material are often required. Direct sampling and immediate analysis are preferable to retention of the sample for later analysis. Filtration of combustion gases prior to analysis may be necessary for some applications, but may be totally incorrect for other cases (see 5.9).

5.3 *Test Systems*—Many devices of various sizes can generate “fire gases” for analysis (**4, (5)**). These systems include large-scale facilities (fire situations simulated on a 1:1 scale (see Guide E 603 and Ref (**6**)); large laboratory-scale tests (for example, Test Method E 84); laboratory-scale chambers (for example, Test Method E 662 (**7, 8**)); and microcombustion furnace or tube furnace assemblies (**2, (9)**).

5.3.1 In general, the combustion devices (test chambers) fall into three categories:

- (1) closed chambers (for example, Test Method E 662);
- (2) open chambers (for example, a full-scale room burn);
- (3) flow-through systems (for example, Test Method E 84).

5.3.2 Different test chamber sizes and configurations require different methods of sampling and analysis. Appropriate analytical procedures and equipment must be selected. In a full-scale fire experiment the sampling frequency and detection level and accuracy may not need to be the same as in a small laboratory-scale experiment.

5.4 *Reactivity of Fire Gases:*

5.4.1 Fire gases to be analyzed range from relatively inert and volatile substances, such as carbon monoxide (CO) and carbon dioxide (CO₂), to reactive acid gases such as hydrogen fluoride (HF), HCl, and hydrogen bromide (HBr). Other species frequently determined are oxygen, the sulfur-oxide species sulfur dioxide (SO₂) and sulfur trioxide (SO₃); the nitrogen-containing species hydrogen cyanide (HCN), nitric oxide (NO), and nitrogen dioxide (NO₂); and hydrocarbons and partially oxidized hydrocarbons.

5.4.2 The following potential problems must be avoided or minimized by proper design of the sampling system and choice of materials of construction:

- (1) Reaction of the gaseous products with materials used in sampling lines and test equipment that could lead to loss of sample and potential equipment failure;
- (2) Adsorption, absorption, or condensation of gaseous products in the sampling system or on particles trapped in the filtration system;
- (3) Reaction among species present in the gaseous sample;
- (4) Interferences caused by species in the sample, other than the product being analyzed, that respond to the analytical method.

5.5 *Sampling Frequency*—The frequency of sampling is based primarily on the information sought. Most requirements will be met by one of the following three sampling modes:

- (1) The quantity formed during the experiment is determined by collecting one time-integrated sample (**2**);
- (2) The concentration is determined at a limited number of time points during the experiment (**10**);
- (3) The concentration is determined either continuously or with sufficient frequency to represent it as a function of time (**6, 8, 10, 11**).

5.5.1 The two techniques used most commonly in the past have been the single, integrated sample and sampling at fixed time intervals. However, techniques for continuous analysis of certain species are now readily available (CO, CO₂, and oxygen (O₂)); while continuous analysis of other compounds of interest have been reported (**12**).

5.5.2 The integrated sampling technique entails collection of all the products (or a continuous sample from the gas stream) into an unreactive sampling bag such as polytetrafluoroethylene (PTFE) or absorption of the species of interest in an appropriate solvent in an impinger for the duration of the experiment. Analyses are then performed on the contents of the bag or trapping medium (**9**). Water-soluble species such as HCl or HBr have been collected in solution impingers over the duration of the experiment, enabling analysis of the “integrated” sample. The gas flow rate through the impinger and the liquid volume determine the buildup of acid gas in the solution (the solubility of the species at the given gas flow rate should be verified). The integrated sampling techniques provide either the “average” concentration of the particular species over the duration of the test or, for certain flow-through test procedures, a measure of the total amount of that species produced in the experiment. In this latter case, a total gas flow measurement is required.

5.5.3 Continuous or frequent, periodic sampling is often desirable. This limits further reaction of reactive species (such as HCl, HBr, and HCN), and is useful for studies of time-dependent, cumulative effects of toxic gases (such as CO) on animals.

5.5.4 Samples of combustion gas can be collected sequentially for subsequent instrumental analysis. An electrically activated multiport stream selection valve or a manifold of solenoid valves can be used to sequentially divert the combustion gas into a series of gas collection devices. This collection procedure can be automated by using a valve sequence timer or a multipole relay timer (**13, 14**).

5.5.5 For noncontinuous sampling of combustion gases, the frequency of sampling is often determined by the instrumentation. For example, using gas chromatography, sampling will be dependent on the residence time of species in the instrument. Sampling

of species at time intervals using gas syringes, plastic sampling bags, sorption tubes, or the like, with analyses to be performed later, is not dependent on analysis time.

5.5.6 The volume of frequent or continuous gas samples removed must not significantly affect the concentration of remaining species. In small test chambers and some flowthrough systems, the volume of gas available for sampling is limited.

5.6 *Sampling Sites:*

5.6.1 The number and the locations of sampling sites are determined by the extent of analytical information sought and by the configuration of the test chamber (**15, 16**). To obtain representative samples from an NBS smoke density chamber, intake ports in one study (**11**) were located at three heights inside the chamber. The sample streams were then combined before being introduced into the analyzers. Previous experiments had demonstrated that significant stratification occurred in the chamber during part of the test. In a full-scale bedroom fire test (**6**), four gas sampling probes were used.

5.6.2 Guidelines developed for the monitoring of the emission of pollutants (**1, 17, 18**) can be utilized for the demonstration of the mass flow rates of combustion products through ducts. Traverses across the ducts (in a steady-state experiment) with a CO or CO₂-probe can be useful for determining whether a need exists for multiple sampling sites.

5.7 *Sampling Probes:*

5.7.1 Sampling probes must withstand exposure to the test environment and must not affect the integrity of the sample with respect to the substances being analyzed. Care should be exercised in heating probes of PTFE; temperatures above 250°C may affect their physical properties.

5.7.2 Probes fabricated from PTFE, PTFE-lined stainless-steel, glass-lined stainless-steel, unlined stainless-steel, borosilicate glass, or quartz tubing are frequently used for sample extraction from combustion or pyrolysis systems. Stainless steel should not be used with combustion products containing hydrogen halides since it reacts with these compounds. Glass and quartz react with fluorides; the latter substance can be extracted with PTFE probes if the atmospheric temperature is low enough. If the temperature is high, an alternative sampling technique would be placing absorption tubes at the sampling point, housing the tubes in an ice-water bath, and trapping HF upstream of all sampling lines and pumps (**13, 14**).

5.7.3 Probe and transfer lines should be heated to prevent losses of some combustion products such as total hydrocarbons due to condensation and HBr, HCl, nitrogen oxide (NO_x), and SO₂ due to solubility in condensed moisture (see Sections 7 and 9).

5.7.4 Commercially available gas syringes, evacuable glass or metal containers, plastic sample bags, and sorption tubes are often used for intermittent grab sampling (**19, 20, 21**).

5.7.4.1 The sorption tube should be appropriate for the gasses to be analyzed. Glass-lined stainless-steel sorption tubes filled with glass beads coated with a strong base solution give excellent collection efficiency for the hydrogen halides (**13, 14**). Glass-lined stainless-steel tubes packed with p-2,6-diphenylphenylene oxide⁶ (a porous polymer that withstands high temperatures) are effective in the collection of hydrogen cyanide, organic nitriles, and other organics generated in fires.

5.8 *Sample Volume, Sampling Rate:*

5.8.1 In any sampling technique, the same volume is determined by the sensitivity of the method used for analysis, the detection level sought, the concentration of the species to be analyzed, and the precision required for the determination.

5.8.2 In continuous sampling, the sampling rate is partially determined by the desired response time. To minimize the response time, small-diameter transfer lines are used and all in-line devices (for example, filters and scrubbers) are kept to minimum volumes. A pressure drop may result from use of small diameter sampling lines.

5.8.3 Response time cannot be calculated exactly from sample line volume and gas flow rate because of the viscous nature of gas flow in the transfer lines and the continuous mixing of gas in sensor compartments. Response times can be determined experimentally by making a rapid change in gas concentrations at the sampling probe inlet and determining the time to a given response (usually 90 % or greater). Furthermore, all instruments have an intrinsic response time independent of sampling procedure.

5.8.4 Information pertaining to sampling rate and sampling volume is contained in Refs (**21**) and (**22**).

5.9 *Sample Pretreatment:*

5.9.1 Pretreatment of the sample must not affect sample integrity with respect to the species being analyzed. Pretreatment is used for the following purposes:

(1) The removal of species that would interfere with the performance of the detectors or would react with the species being analyzed, and

(2) Chemical conversion of the species present in the sample to those that are detected by the sensors.

5.9.2 Removal of particulate matter may be required for certain analyses. Particulates interfere with optical measurements; they can deposit in transfer lines and valves, possibly causing malfunctioning; and they can adsorb gases of interest or chemically react with sample gases.

5.9.2.1 Loosely compacted PTFE-fiber filters have been found to be useful for the removal of particulate matter. Fiber filter thimbles of PTFE have been used in sampling probes (**11**). In that system, filter medium was also contained in a chamber where several sample streams were combined prior to analysis.

⁶ Tenax, a trademark of Enka BV, Ressort Pantentwesen, Postfach 100149, D-5600, Wupertal, Federal Republic of Germany, available through gas chromatography supply houses, has been found suitable for this purpose.

5.9.2.2 Glass-fiber filters can be used with many types of gaseous samples; however, they cannot be used for samples containing HF. Cellulosic filters should be used with caution because of their reactivity toward a variety of substances.

5.9.2.3 Filters must be heated to the same temperature as the sampling probe and sample transfer lines to minimize adsorption and condensation in the filtration media.

5.9.2.4 In some circumstances, filtering material should *not* be present before the analysis point. An example is the measurement of acid gases using a liquid impinger as the trapping and analysis medium. A filter before the impinger would remove acid gases by adsorption onto liquids and particulates on the filter. Care must be taken that the impinger does not clog with particulates, and that oils or particles in the impinger liquid do not interfere with analysis.

5.9.3 Some analyzers require the removal of water vapor from the sampling line for proper operation or for valid data analysis purposes. Water vapor can be removed by a cold trap, by absorbent media, or by selective permeability media.⁷

5.9.3.1 A cold trap will remove any gases, such as the acid gases, that are soluble in water. The vapor pressure at the temperature of the cold trap of any gas to be measured must also be considered. Due to these factors, this technique is generally limited to use in O₂, CO, and CO₂ analysis systems.

5.9.3.2 The low capacity of most absorbent media generally limits the application of this technique to second stage desiccation, following a cold trap. Water vapor as well as other gases, especially water soluble ones can also be removed. Conversion of NO₂ to NO has been observed (22). Due to these considerations, the absorbent media technique is generally limited to use in O₂, CO, and CO₂ analysis systems.

5.9.3.3 The performance of selective permeability driers in removing or not removing classes of compounds present in the sample stream has been studied (23, 24). Water and, in general, water soluble hydrocarbons are removed. Many inorganic gases, CO, CO₂, and others, are not removed.

5.9.4 Some analyses require chemical conversion of species to that detected by the analytical sensors (for example, reduction of chlorine to chloride). Most chemical conversions are performed within the detector (for example, reduction of NO₂ to NO (see Section 9)).

5.10 *Sample Transfer:*

5.10.1 Sample transfer is usually effected by pumping devices. Sample integrity must be retained during transfer. Materials suitable for sample probes and pretreatment devices are usable for transfer lines. For certain applications, stainless steel (no exposure to acid gases) and glass (no exposure to HF) can be used.

5.10.2 The internal surfaces of the pumps must be inert to the substances being transferred. Interior parts coated with PTFE are commonly used. In the transfer of acid gases, the impingers or scrubbers used for the adsorption of these species should precede the pumps in the sample transfer system.

5.10.3 To retain sample integrity, transfer lines leading to analyzers for nitrogen oxides, hydrogen halides, sulfur dioxide, and hydrocarbons should be heated⁸ to prevent condensation and reduce adsorption.

5.10.4 Quantitative sample transfer requires flow rate determination. Rotameters and orifice-type meters are generally useful in combustion gas analysis.

5.11 *System Maintenance:*

5.11.1 Preventive maintenance is essential for analysis systems in which the gas streams contain reactive and condensable components.

5.11.2 In addition to normal instrument maintenance, the following preventive steps are recommended:

5.11.2.1 Filters should be examined and replaced before they become heavily loaded with particulate matter. Some filters should be replaced after each experiment.

5.11.2.2 The inside surfaces of gas transfer lines, valves, and pumping devices should be examined and cleaned periodically. Deposits should be removed with appropriate solvents.

5.11.2.3 Rotameters should be examined to ascertain that the floats are moving freely. The rotameter tubes and the floats should be periodically cleaned with appropriate solvents.

6. Analytical Methods for Carbon Monoxide, Carbon Dioxide, Oxygen, and Nitrogen

6.1 The gases carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), and nitrogen (N₂) will be considered as a group, since several of the analytical methods to be discussed can be applied to more than one of them, sometimes simultaneously. The techniques to be described are gas chromatography, infrared spectrophotometry, and “other methods” including electrochemistry.

6.2 *Gas Chromatography:*

6.2.1 *General Description*—Gas chromatography is an ideal batch method for analyzing nonreactive gases in combustion products (25). These gases can be separated on columns with solid stationary phases operated isothermally and detected using thermal conductivity (TC) detectors. Some of the column configurations and alternative detectors are described below.

6.2.2 *Apparatus and Procedures:*

⁷ Selective permeability driers available from Perma Pure Products, Inc., Monmouth Airport, Farmingdale, NJ 07727, have been found satisfactory for this purpose.

⁸ Technical Heaters Inc., 708-710 Jessie St., San Fernando, CA 91340, and Conrad Co., 120-B Outerbelt St., Columbus, OH 43213, are possible sources of complete heated sampling-line assemblies.

6.2.2.1 Apparatus requirements are modest. A basic gas chromatograph with standard temperature controls and thermal conductivity detector can be used. A gas sampling valve is a very useful accessory. Temperature programming, automated valve operation, electronic integration, etc., are convenient but not necessary.

6.2.2.2 Complete separation of all of these gases normally requires the use of two columns—a molecular sieve, which separates O₂, N₂, and CO but irreversibly absorbs CO₂ at normal operating temperatures; and a porous polymer column which readily separates CO and CO₂ from air but does not resolve O₂ and N₂. The two columns have been used together, in various configurations and with column-switching valves, to achieve complete separation of the gases (26).

6.2.2.3 An arrangement, using dual columns and a column-switching valve, has been successfully used to analyze O₂, N₂, CO, and CO₂ gases (27). Total analysis time was approximately 15 min.

6.2.2.4 Concentric single columns, consisting of an inner and an outer column of different packing, are also available (28). These will separate O₂, N₂, CO, and CO₂ in a single pass. The use of such columns eliminates the column-switching valve required in the dual-column arrangement; however, their use to date has been limited.

6.2.2.5 The sensitivity of the gas chromatographic method depends on sample size, the type of detector, and temperature and filament current for TC detectors. Thermal conductivity detector filaments will deteriorate if large air samples are repeatedly measured at high current. These gases can be measured at concentrations as low as 0.05 %.

6.2.2.6 Lower concentrations of CO can be detected by converting CO to methane (CH₄) by catalytic hydrogenation (29). The CH₄ is then detected, using a flame ionization detector (FID).

6.2.3 *Advantages and Disadvantages:*

6.2.3.1 The major limitation of gas chromatography for monitoring combustion products is its inherent restriction to batch sampling, since each analysis requires several minutes to complete. Therefore, only a limited number of points can be obtained during a test. However, samples can be collected, intermittently during a run, in suitable gas-tight containers (for example, syringes with close-off valves or gas sampling bags) and the contents analyzed at a later time. The relative nonreactivity of these gases allows them to be stored for extended periods of time before analysis.

6.2.3.2 The gradual build-up of organic pyrolysis and combustion products in the analytical columns may result in eventual degradation of performance. When this occurs, columns can be purged overnight at elevated temperatures or back-flushed; however, after a long period of use, it may be necessary to replace the column.

6.3 *Infrared Analysis:*

6.3.1 *General Description:*

6.3.1.1 Infrared (IR) methods are useful for continuously monitoring the concentration of CO or CO₂ in fire gases. Symmetric diatomic molecules, such as oxygen and nitrogen, cannot be detected because they are infrared inactive.

6.3.1.2 Infrared analysis is based on absorption of radiation at specific wavelengths when the species of interest is present. By varying the length of the sample cell, gas concentrations from a few parts per million up to 100 % can be analyzed.

6.3.2 *Apparatus and Procedures:*

6.3.2.1 A standard (dispersive) infrared spectrophotometer can be used to measure CO or CO₂ by operating with the monochromator fixed at a particular wavelength; or a conventional infrared spectrum of the gas mixture can be obtained.

6.3.2.2 A nondispersive infrared (NDIR) analyzer continuously monitors a single wavelength or wavelength band (30, 31). Such instruments are often less expensive than dispersive instruments; however, they are restricted to a particular wavelength or chemical species. (See Test Method D 3162.)

6.3.3 *Advantages and Disadvantages:*

6.3.3.1 Interferences can occur in infrared analyses when absorption bands of other components in the sample overlap the absorption band of the compound being analyzed. The magnitude of the interference is highly dependent on the specific instrument and on the relative concentrations of the gases.

6.3.3.2 The major interferences found are of CO for CO₂ and vice versa. For most applications, CO interference with CO₂ analysis is minor. The interference of CO₂ with a CO measurement can be reduced (if necessary) by incorporating a trap (for example, soda-lime or granular lithium hydroxide (LiOH)) to remove CO₂ from the sample stream before reaching the analyzer.

6.3.3.3 Water vapor can interfere with CO₂ analysis; however, this is not usually a problem. If necessary, a moisture trap in-line can reduce this interference (see 5.9.3). Smoke particulates must be filtered out (see 5.9.2).

6.3.3.4 The instrument readings will be affected by the total gas pressure in the measuring cell. This arrangement is usually adequate if the measuring cell is vented to ambient conditions.

6.4 *Other Methods:*

6.4.1 *General Description*—Electrochemical techniques are available for measuring CO and O₂ (32), but not for CO₂. Such devices are usually designed for air pollution or stack gas monitoring. A standard technique for CO involves oxidation in an electrolytic cell. Techniques for measuring oxygen include galvanic cells, polarographic analyzers, and paramagnetic analyzers.

6.4.2 *Advantages and Disadvantages*—All of these methods can be accurate and specific, but have slower response than the IR methods previously described. Accurate measurement of oxygen concentration with a paramagnetic analyzer requires compensation for the effects of measuring cell pressure.

7. Analytical Methods for Hydrogen Halides

7.1 *General Comments:*

7.1.1 The analysis of the hydrogen halide gases (hydrogen fluoride (HF), hydrogen chloride (HCl), and hydrogen bromide (HBr)) in combustion atmospheres has always been considered difficult, due primarily to the highly reactive nature of these species. The gases must be analyzed immediately or converted to a stable form to be analyzed at a later time (for example, dissolved aqueous solution in an impinger). The reactivity of these gases has led most workers to limit the length of sampling lines and to ensure that these lines are both heated and prepared from an inert material such as PTFE or glass (**33, 34**), as described in 5.7. Instead of in-line pumps, gas samples are generally pulled into the analytical device using a vacuum source (**33, 35**).

7.1.2 The techniques used for the quantitative detection of hydrogen halides (HX) can be classified into three broad categories: (1) “proton-detection devices,” in which the HX is dissociated in solution and the activity of the hydrated proton is analyzed (for example, pH, conductometric); (2) “anion detector devices,” in which the HX is dissociated in solution and the anion is analyzed (for example, ion-selective electrode, titrimetry, and ion chromatography); and (3) “hydrogen halide detection devices,” in which the intact molecule is analyzed (for example, infrared and gas chromatography). These will be discussed in the following sections.

7.2 Proton Detection Devices:

7.2.1 *General Description*—One of the simplest ways to measure the concentration of acid gases in a combustion environment is to draw a portion of the gases into an aqueous solvent and measure the pH of the resulting solution, using a conventional pH electrode. This technique is not specific to any particular species (see below). Another approach involves the measurement in the change of conductance of a solution in which sample gases have been dissolved.

7.2.2 Apparatus and Procedures:

7.2.2.1 Two approaches have been described (**12, 35**) which use a microelectrolytic conductivity detector⁹ originally developed for use in gas chromatography (**36**). In the approach described by Herrington (**12**), filtered gases were continually pumped into the conductance cell and continuously monitored. Hileman (**35**) sampled gases through an 8-port gas-sampling valve, followed by discrete analysis using the conductance cell. The analysis time for a given sample was approximately 30 s.

7.2.2.2 For pH measurement, a research-quality pH meter should be employed.

7.2.3 Advantages and Disadvantages:

7.2.3.1 Simple pH measurement is prone to interferences from any other gases that can generate or remove protons on dissolving in water (that is, CO₂, SO₂, SO₃, HCN, NO₂). Thus, the pH electrode is best used to obtain a value of total acid gas concentration.

7.2.3.2 Many of the interference problems encountered in using pH electrodes are eliminated by using a nonaqueous electrolyte in the conductometric procedures. The conductometric apparatus can be used as a continuous monitor of the hydrogen halide gas; however, frequent calibration is recommended.

7.3 Anion Detection Devices:

7.3.1 *General Description*—The use of ion-selective electrodes (for fluoride, chloride, or bromide) has become increasingly popular for the analysis of hydrogen halides. These types of analyses can be conducted in either a continuous mode (**33, 35, 37**) or a batch mode (**38, 39**). Ion chromatography and titration procedures are also available for halide ion analysis.

7.3.2 Apparatus and Procedures:

7.3.2.1 Combustion gases may be continuously bubbled into a solution containing an ion-selective electrode and the anion concentration measured while it is constantly increasing (**33**). The rate of production of hydrogen halide is determined by differentiating the concentration-versus-time curve. A batch analysis may involve obtaining a gas sample in a syringe containing the dissolving solution (**38, 39**) or a single time-integrated sample in an impinger solution.

7.3.2.2 Recent advances in ion chromatographic methods¹⁰ have permitted separation of anions (**40, 41**) with subsequent conductivity measurement of the eluted species. The carbonate anion and various organic acids are interferences for chloride with the conductivity detector if they are not well separated chromatographically. The silver/silver chloride (Ag/AgCl) detector is specific for chloride and bromide with a very low sensitivity for carbonate and other anions. The fluoride detector is a specific detector for fluoride in combustion gas samples (**42, 43**). The ultraviolet (UV) detector for ion chromatography is sensitive to all anions. With indirect photometric chromatography light-absorbing eluent anions enable the sample anions to appear as negative peaks in the absorbance record (**44**).

7.3.2.3 A variety of methods involving titration of the hydrogen halides in municipal drinking water (**43, 45**) have been developed but have not been extensively applied to the analysis of combustion gases (**46**).

7.3.2.4 Collection tubes containing dry soda lime have proven to be useful for sampling HCl from combustion atmospheres (**10**). The test atmosphere is sampled over a time period, such as 3 or 5 min, but the interval can be shortened if the concentration of HCl is high. Consecutive samples can be obtained in order to provide a concentration/time plot. The chloride is extracted from the soda lime by water and is analyzed by titration.

7.3.2.5 A continuous analyzer for HCl has been described (**47**). It employs readily available commercial “stat” titration equipment. The method monitors HCl concentration by continuously titrating chloride ion in an impinger with silver nitrate (AgNO₃).

⁹ The model 700 Hall Conductivity Detector, available from Tracor Instruments, 6500 Tracor Lane, Austin, TX 78725-2000, or its equivalent, has been found satisfactory for this purpose.

¹⁰ Ion chromatography units from the Dionex Corp., 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088 or their equivalent, have been found satisfactory for this purpose.

7.3.3 *Advantages and Disadvantages:*

7.3.3.1 Ion selective electrodes avoid many of the problems encountered in other HX analyses, since they are ion specific. Anion interferences such as cyanide and sulfide can be minimized with proper consideration of the interfering species. Cyanide and sulfide degrade the electrode membrane, slowing the response and reducing the accuracy. Slight corrosion effects on the electrode can be removed by repolishing. Bromide interferes with the chloride ion electrode; however, chloride does not interfere with the bromide ion electrode, except at very high concentrations of chloride.

7.3.3.2 Ion chromatography may be particularly useful when strong interference from anions causes other techniques to fail. However, this technique has the disadvantage of being noncontinuous.

7.3.3.3 Collection tubes containing dry soda lime can often be used to sample from locations which would be difficult to sample from using solution absorbers or other techniques. They are compact and easy to handle and have high absorption efficiency. Care must be taken to avoid breakthrough due to too high gas-flow rate or high HCl concentration or the tendency to plug up in extremely smokey atmospheres.

7.3.3.4 There are insufficient data yet to accurately describe the advantages and disadvantages of the “stat” titration method; however, it has the potential to be a versatile continuous method for HCl with few problems from smoke particulates or liquids and requiring no calibration gases. Its disadvantages include interferences from other halide and cyanide gases and efficiency of absorption of the HCl.

7.4 *Hydrogen Halide Detection Devices:*

7.4.1 Hydrogen halides can be analyzed with gas chromatography, however, this is not commonly used because of difficulties with corrosion and poor analysis caused by problems with poorly formed peaks (48).

7.4.2 The gas filter-correlation analysis technique has been developed for a number of gases (49-52). Commercial instruments for HCl are available.¹¹ The technique also lends itself to in situ measurements, specifically, a beam passed across an exhaust stack section (53, 54). A commercial instrument suitable for full-scale stack measurements is available.¹² Gas-filter correlation analyzers can be designed to minimize the problem of instrument drift. Care must be taken to avoid precipitating the HCl as an aerosol; limited measurements indicate that this is unlikely if the relative humidity in the measuring system is kept below 70 to 80 % (55).

8. Analytical Methods for Hydrogen Cyanide

8.1 Several analytical approaches have been used to measure hydrogen cyanide (HCN). These may be generally categorized as electrochemical, spectroscopic (infrared), colorimetric, and gas chromatographic. A review of many of these methods was recently published (56).

8.2 *Electrochemical Methods:*

8.2.1 *General Description*—Electrochemical techniques that have been used to measure HCN in fire gases include an amperometric method, two potentiometric techniques (including ion-selective electrodes), and differential pulse polarography. All of these techniques entail measurement of cyanide ion in solution.

8.2.2 *Apparatus and Procedures:*

8.2.2.1 In the amperometric method for HCN (12), the current flow between two electrodes is measured while HCN is being absorbed into the electrolyte solution.

8.2.2.2 The cyanide-ion selective electrode has been used widely for HCN measurement (12, 57-60). A silver/sulfide electrode,¹³ which measures cyanide ion indirectly, can be used. A “specific-ion meter” or expanded-scale pH meter is necessary for these electrodes.

8.2.2.3 Ion-selective electrodes have generally been used for intermittent analysis, where sample gas is bubbled into the impinger for a specified time (for example, 5 min). However, continuous analysis setups have been explored.

8.2.2.4 Standard titrimetric techniques (61, 62) can also be used for determination of hydrogen cyanide. In the absence of halide ions, cyanide can be titrated potentiometrically using (AgNO₃).

8.2.2.5 Differential pulse polarography (63) can be used for time-integrated or grab sampling of cyanide.¹⁴

8.2.3 *Advantages and Disadvantages:*

8.2.3.1 The amperometric technique permits continuous determination of gaseous HCN in the range from 0.1 ppm to greater than 100 ppm. Only H₂S exhibits a major interference using this technique; however, this can be eliminated by using a solid lead carbonate scrubber.

8.2.3.2 The ion selective electrode methods are very sensitive; however, response is slow at low solution concentrations. Sulfide, iodide, bromide, and chloride interfere with the measurement of cyanide, when using the cyanide ion electrode (64). Certain interferences can often be eliminated by a change of the type of electrode used or by the addition of a masking agent to the solution.

¹¹ This guide is under the jurisdiction of ASTM Committee E05 on Fire Standards and is the direct responsibility of Subcommittee E05.21 on Smoke and Combustion Products.

Current edition approved October 10, 2001. Published November 2001. Originally published as E 800 – 81. Last previous edition E 800 – 98.

¹² An instrument available from Bodenseewerk Geosystem GmbH, Postfach 1120, D-7770 Ueberlingen, West Germany, has been found satisfactory for this purpose.

¹³ The Orion Model 94-16 Silver/Sulfide electrode, available from Orion Research Inc., 529 Main St., Boston, MA 02129, or equivalent, has been found satisfactory for this purpose.

¹⁴ Model 174 Polarograph with necessary electrochemical accessories available from Princeton Gamma-Tech, Inc., 1200 State Rd., Princeton, NJ 08540, has been found satisfactory for this purpose.

8.2.3.3 Titrimetric procedures remain among the simplest techniques for a time-integrated analysis of cyanide in the absence of interfering ions. Interferences in differential pulse polarography include oxygen and compounds containing carbonyl groups.

8.3 *Infrared and Colorimetric Methods:*

8.3.1 *Apparatus and Procedure:*

8.3.1.1 Dispersive and Fourier transform (65) infrared spectroscopy have been used to measure HCN gas directly. Standard gas cells have been used; however, longer path length, nondispersive infrared instruments are better suited for low concentrations. Gas filter correlation techniques have also been proven useful for HCN analysis (see 7.4.2). A commercial analyzer is available.¹⁵

8.3.1.2 Colorimetry has been successfully used in measuring low concentrations of HCN. The standard colorimetric procedures for cyanide are the picrate procedure (66), and the pyridine-pyrazolone method (58). A simple spectrophotometer is suitable for the colorimetric methods. Instruments have been modified to accommodate flow-through cells for continuous analysis (66).

8.3.2 *Advantages and Disadvantages:*

8.3.2.1 Potential interferences to infrared determination of HCN are acetylene, propane, and water vapor. This technique offers a means for continuous analysis of HCN in the gas phase, if interferences can be accounted for or eliminated.

8.3.2.2 Colorimetry is limited to low concentrations and therefore may require dilution of sample solutions. Colorimetric methods are generally time-consuming. Acetaldehyde, acrolein, acetone, and sulfur dioxide have exhibited interferences in the picrate procedure.

8.4 *Gas Chromatographic Methods:*

8.4.1 *General Description*—Gas chromatography can be used effectively to measure HCN in combustion products. Several different columns and types of detectors have been used to give the desired specificity and sensitivity.

8.4.2 *Apparatus and Procedures:*

8.4.2.1 A gas chromatographic method using a thermal conductivity detector (67) was developed for measuring high concentrations of HCN. However, this method had a lower limit of detectability of 0.3 volume %, which would require concentrating HCN for most fire test studies. A concentrator with a thermistor detector has been used (68, 69) to lower the detectable limit of HCN to 10 to 15 ppm per 2-mL injection volume.

8.4.2.2 A flame ionization detector (FID) is more sensitive and specific than either the thermal conductivity (TC) or thermistor type and has been used to measure HCN in a simulated hydrocarbon combustion atmosphere from 10 ppm to several hundred parts per million (70). Hydrogen cyanide in the pyrolysis products of nitrogen-containing fibers has also been measured (71).

8.4.2.3 A nitrogen-specific modification to an alkali-flame (or thermionic) detector gives greatly enhanced sensitivity for nitrogen-containing compounds. It has been used to monitor HCN in an animal exposure chamber containing CO and air (72). It was also used successfully for measurement of HCN during thermal degradation of nitrogen-containing polymeric materials (73). This detector has also been used to measure HCN trapped from combustion products using glass-lined stainless-steel tubes packed with p-2,6-diphenylphenylene oxide⁶, a porous polymer that withstands high temperatures. For the analysis, the HCN is thermally released from the porous polymer (42).

8.4.2.4 In other studies on the analysis of HCN in the decomposition products of rigid polyurethane (35), the alkali flame detector was tuned with a sample containing normal hydrocarbons (methane through n-pentane up to 20 000 ppm) in order to achieve minimal interference from these species.

8.4.2.5 Another gas-chromatographic approach to HCN analysis has been to chemically react the HCN (74, 75) and then measure the resultant product with an electron-capture detector (76).

8.4.3 *Advantages and Disadvantages:*

8.4.3.1 An advantage of gas chromatography, for most combustion gas studies, is that it requires a small gas sample size. However, analyses are intermittent, rather than continuous, and sample elution times are often several minutes.

8.4.3.2 The flame ionization detector suffers from interference from low molecular weight organic species; and its response is affected by small changes in detector geometry, gas flow rates, etc. The thermionic detector minimizes the hydrocarbon and water interference problems. With a thermal-conductivity detector, water, CO, and CO₂ can interfere with analysis of HCN (depending on the column used).

8.4.3.3 Hydrogen cyanide must be trapped in an impinger, for analysis by the electron-capture detector. Total treatment and analysis time is about 30 min.

9. Analytical Methods for Nitrogen Oxides, Sulfur Oxides, and Carbonyl Sulfide

9.1 Oxides of nitrogen include nitric oxide (NO) and nitrogen dioxide (NO₂). Fire gases contain mostly NO; NO₂ formation is usually a secondary oxidation process. Sulfur oxides include sulfur dioxide (SO₂) and sulfur trioxide (SO₃), the former being the more prevalent in fire gases generated from sulfur-containing materials.

9.2 *Nitrogen Oxides:*

9.2.1 *Chemiluminescence:*

9.2.1.1 *General Description*—Chemiluminescence is the principle of operation of several process analyzers for nitrogen

¹⁵ A commercial analyzer available from Thermo Environmental Instruments, has been found satisfactory for this purpose.

oxides.¹⁶ Either NO or total nitrogen oxide content (NO_x) can be measured. The amount of NO₂ is calculated from the difference between NO and NO_x.

9.2.1.2 Sampling is continuous in either the NO or NO_x mode; however, sampling volumes are large. Samples of NO cannot be stored for later analysis. Both NO and NO₂ measurements can be obtained simultaneously in an electrochemical-type analyzer equipped with two cells.¹⁷

9.2.1.3 *Interferences*—Significant interference from other nitrogen-containing compounds such as HCN, can occur if high temperature (760°C) thermal converters are utilized for the NO_x determination (77). This has been eliminated, in most of the instruments, by using a catalyst at lower temperatures. The sensitivity to non-NO_x nitrogen-containing species potentially present in the samples of interest should be established before the unit is used for making measurements. It appears that water and CO₂ may act as third-body quenchers (78) and H₂ can be a source of interference in the stainless-steel converter (79). Interference from halogen containing compounds can also occur (80).

9.2.1.4 *Advantages and Disadvantages*—Many instruments for analysis of nitrogen oxides were designed for ambient-air monitoring. Therefore their analysis range can be too low for direct fire gas determinations. Instruments for high concentration NO_x are available.¹⁸

9.2.2 Ion Chromatography:

9.2.2.1 Ion chromatography has been used to determine nitrogen dioxide (40, 41). If NO is first converted to NO₂ by reaction with oxygen, total nitrogen oxide (NO_x = NO + NO₂) is measured (81).

9.2.2.2 Sample gas is collected in a polyethylene bag or impingers for a specified time period. A determination of the concentration-time history requires a series of samples taken at intervals.

9.2.2.3 A conductivity detector is used to detect and measure NO₂- and NO₃ which are formed when the NO₂ is dissolved in water. If a conventional suppressor column is used, the response of the conductivity detector will change greatly as the suppressor is expended. Greater sensitivity and constant response is obtained with fiber suppressor columns (82).

9.2.2.4 *Advantages and Disadvantages*—The holding time while NO reacts with oxygen is long. The concentration range over which the methods are useful has not been established. The efficiency of collection of NO₂ has not been established.

9.3 Sulfur Oxides:

9.3.1 General Description:

9.3.1.1 Nondispersive infrared (NDIR) spectrometry is often used to monitor oxides of sulfur. These instruments permit continuous sampling and analysis of gases.

9.3.1.2 Water-vapor interference occurs in the SO₂ spectral region. Water removal, without appreciable loss of sulfur oxides, can be accomplished with a permeation distillation dryer (see 5.9.3.3). Condensation of moisture (and adsorption of sulfur oxides) should be avoided by using heated sample transfer lines.

9.3.1.3 Sulfur oxides can also be determined with either of two sulfur-specific gas chromatography detectors. These are the flame photometric (83) and Hall electrolytic conductivity detectors. Parts per billion concentrations can be measured with these detectors.

9.3.2 *Advantages and Disadvantages*—The advantages and disadvantages of methods for sulfur oxides are not apparent at this time, since these techniques are relatively new.

9.4 *Carbonyl Sulfide*—Generation of carbonyl sulfide (COS), which is highly toxic, during the pyrolysis of sulfur-containing polymers was recently reported (84). A gas chromatograph-mass spectrometer was used for the determination.

10. Analytical Methods for Total Hydrocarbons and Aldehydes

10.1 General Comments:

10.1.1 Numerous organic compounds may be generated during pyrolysis and combustion of materials. Identification and quantification of each individual compound in such a mixture is difficult, and beyond the scope of “total hydrocarbons” analysis as described below. However, analytical studies have been reported (85, 86, 87) on the use of gas chromatography and mass spectrometry for the identification of complex mixtures obtained by thermal degradation of polymers.

10.1.2 Determination of “total hydrocarbons” and analysis of certain compounds of interest have become commonplace. “Total hydrocarbons” includes many compounds containing oxygen, nitrogen, sulfur, or halogen, in addition to those comprised solely of carbon and hydrogen. Methods for total hydrocarbon analysis, including gas chromatography and infrared, will be presented. Then, the specific techniques used to measure aldehydes will be described.

10.2 Measurement of Total Hydrocarbons:

10.2.1 *General Description*—The most widely used methods for measuring total hydrocarbons are those relying on a flame ionization response. Such methods use either a flame ionization detector (FID) alone or in combination with a catalytic converter or gas chromatograph (25). Another method for analyzing total hydrocarbons is based on nondispersive infrared (NDIR).

¹⁶ Process analyzers for nitrogen oxides produced by Thermo Environmental Instruments; Beckman Instruments, 2500 Harbor Blvd., P.O. Box 3100, Fullerton, CA 92634-3100; and Monitor Labs., Inc., 10180 Scripps Ranch Blvd., San Diego, CA 92131, have been found satisfactory for this purpose.

¹⁷ The Ecolyzer Model 7000, a dual-range instrument for a 0 to 100 and 0 to 500 ppm of either NO or NO₂ available from National Draeger, Inc., 101 Technology Dr., P.O. Box 120, Pittsburgh, PA 15230, has been found satisfactory for this purpose.

¹⁸ Instruments for high concentrations of NO_x produced by Beckman Instruments, Monitor Lab. Inc., and Environmental Instruments have been found satisfactory for this purpose.

10.2.2 *Apparatus and Procedure:*

10.2.2.1 In the flame ionization approach, the organic sample is ionized in a hydrogen flame. The FID analyzers are usually calibrated in terms of a gas, such as methane or hexane, and the output read in parts per million of carbon. Sampling is continuous in some commercial analyzers. Sample pretreatment recommendations and cautions (5.9) should be followed, and proper maintenance to the system (5.11) is important.

10.2.2.2 In order to detect the non-methane portion of total hydrocarbons, two methods based on a selective catalytic combustor were reported by King (88). A dual FID analyzer has also been reported (89) to continuously monitor the methane and non-methane components in ambient air.

10.2.2.3 In the gas chromatographic approach to total hydrocarbon analysis, a predetermined volume of sample is introduced. As the various components emerge from the column, they are detected by an FID.

10.2.2.4 The nondispersive infrared (NDIR) technique is based on the absorption characteristics of the gases to be analyzed. If methane or ethane is used as the detector gas, unsaturated compounds will not be adequately measured. Mixtures of hydrocarbon gases for the detector have not been commonly employed.

10.2.3 *Advantages and Limitations:*

10.2.3.1 Most of the readily available commercial instruments for measuring total hydrocarbons are based on an FID detector. Separation of methane and non-methane portions, while important for air pollution studies, is usually unnecessary for fire-safety studies. The response of the FID detector constitutes an approximate counting of carbon atoms. This relation, however, fails to hold for oxygenated molecules and certain aromatic and unsaturated hydrocarbons (104). The latter may be a limitation since it has been found (105) that even for fires of non-oxygenated fuels $\frac{1}{4}$ to $\frac{1}{2}$ of the unburned total hydrocarbons can comprise oxygenated species and a significant further fraction can comprise unsaturated hydrocarbons.

10.2.3.2 For NDIR, removal of water will avoid its interferences during analysis of combustion gases. The infrared spectral properties of hydrocarbons vary considerably so that an NDIR signal roughly proportional to hydrocarbon concentration can be obtained if the combustion-product sample stream contains hydrocarbons of only a single class. Quantitative results cannot be expected for a mixture of hydrocarbons of unspecified structure.

10.3 *Measurement of Aldehydes:*

10.3.1 *General Description*—Various materials produce aldehydes when involved in fires. Morikawa (90) studied evolution of formaldehyde and acrolein from wood, polyethylene, polypropylene, cellulose, glucose, and eight other materials. He used a colorimetric method for the determination of formaldehyde and gas chromatography for acrolein. These are the most common techniques.

10.3.2 *Apparatus and Procedures:*

10.3.2.1 The gas chromatographic approach utilizes packed columns and either a flame ionization detector (FID), a thermal conductivity detector, or mass spectrometer. There are a number of columns suitable for formaldehyde and acrolein. A number of these have been recently reported (90, 91). Sixteen liquid phases, used before 1967, are listed in an ASTM publication (92).

10.3.2.2 The FID is not sensitive to formaldehyde. When the concentration is high enough, a thermal conductivity detector can be used. However, water interference could be a problem in this case. Formaldehyde can be converted to another organic compound that is sensitive to FID (93, 94). For the purpose of increasing the concentration of aldehydes in sample gas, or to stabilize labile compounds, a short precolumn was used in cigarette smoke analysis (95, 96). Aldehydes were trapped and released by changing the temperature of the precolumn.

10.3.2.3 A colorimetric method specific for acrolein has been reported (97). It is based on a chemical reaction to produce a blue-colored product. Other aldehydes do not react to form products absorbing significantly in the same spectral region.

10.3.2.4 Instruments have also been developed for analysis of formaldehyde by gas filter correlation (see 7.4.2).

10.3.3 *Advantages and Disadvantages*—Analysis of aldehydes is, in general, difficult and must be performed with great care. Standardization is a major problem due to instability of the pure aldehydes.

11. Analytical Methods for Water Vapor Analysis

11.1 *General Comments:*

11.1.1 Water vapor is often desirable to measure in combustion systems when it is necessary to make chemical stoichiometry calculations, compute elemental compositions to be ascribed to pyrolysates, or to correct readings from other gas analyzers where water vapor had to be removed.

11.1.2 The highest fraction of water vapor present can often be computed from reaction stoichiometry; readings of 10 % or greater can be expected. The sample lines must be heated and the measuring instrument so designed that water is not condensed in the lines nor inside the instrument.

11.2 *Apparatus and Procedures:*

11.2.1 *Infrared Techniques*—Water vapor is a very strong absorber in the infrared and has numerous spectral lines and bands. It can be readily measured by conventional nondispersive infrared techniques, or monitored as part of spectral scanning. The requirement that condensation must not occur limits the use of those instrument designs where sufficiently high case-heater

temperatures are not available.¹⁹ Due to the strong-absorber nature of water vapor and the fact that much higher concentrations of water vapor are encountered than of most other species, the discrimination against interfering species tends to be good for even simple optics designs.

11.2.2 *Other Techniques*—Commercial instruments are available for water-vapor measurements which are based on numerous other principles including semiconductor surface effects, chilled-mirror dew point, hygroscopic length change, and others. These are generally designed for the measurement of water-vapor levels in relatively clean environments and are normally not appropriate for use in fire-gas environments due to the highly corrosive and reactive nature of most combustion streams.

12. Analytical Methods Capable of Simultaneous Determination of a Wide Range of Gases

12.1 *General Comments*—With a steady increase in the number of gases deemed important to track for characterizing combustion gas toxicity, techniques geared towards analyzing each gas separately can become unwieldy or impractical. Simultaneous determination of concentrations of a large number of gases can be done by molecular spectroscopy, specifically, by infrared or mass spectrometric techniques. Development efforts in recent years have generally focused on infrared, specifically Fourier-Transform InfraRed (FTIR), techniques. The general principles of this application have been described by Nyden and Babrauskas (98). Experimental techniques and results have been reported by Kallonen (99). A NORDTEST standard has been published which gives the details of conducting such FTIR analyses (100). The FTIR method is suitable for monitoring most unsymmetric molecules that have a reasonably large infrared molecular absorbance. In practice, this means that the technique is suitable for most gas species of interest in combustion studies with the exception of O₂ and H₂S.

¹⁹ Commercial instruments are available from Beckman Instruments; Inficon Leybold-Heraeus, 6500 Fly Rd., East Syracuse, NY 13057; and MSA, MSA Building, P.O. Box 426, Pittsburgh, PA 15230.

ANNEXES

(Mandatory Information)

A1. CALIBRATION

A1.1 Introduction

A1.1.1 All analytical instruments require calibration by internal electronic means and also by using a carefully prepared standard material or mixture to set the range. For the latter, it is preferable that the calibrant be in the same physical form as the test sample. Thus, for calibration of instruments to measure fire gases, it is usually best to use “calibration gases” as described below. It is advisable to employ several different concentration mixtures to cover the entire range of the instrument, rather than relying on one calibration point.

A1.2 Calibration Gases

A1.2.1 Calibration gas mixtures can be obtained for almost all of the species discussed herein. Such mixtures can be obtained from manufacturers of high quality compressed gases. The gas should be analyzed by the manufacturer and certified as to the accuracy of the analysis. Some of the gas mixtures are quite stable (for example, CO or CO₂ in air), while others are not (for example, the halogen acids in air). Storage of the less-stable mixtures demands frequent checks of the actual gas content by the user.

A1.2.2 Gaseous standards can be freshly prepared in the laboratory by metering a specific amount of pure gas into a diluent stream of air (35) or injecting a known amount of pure gas into a specially treated glass bulb (101). One of the best, and more widely used, techniques for laboratory preparation of accurate standard gases is the use of permeation devices (33). The pure gas of interest penetrates a semipermeable membrane at a known rate and mixes with the flow of diluent gas. Varying either the permeation rate (by changing either temperature or pressure) or the flow of diluent gas allows a wide range of concentrations to be obtained.²⁰

A1.2.3 For gas chromatography experiments, only a small volume of calibration gas is necessary. It is possible to prepare a large number of gas dilutions by using gas-tight syringes with shut-off valves. However, it is still good practice to have one or more analyzed compressed gas standards for accurate calibration points.

A1.2.4 Absorbance in infrared spectroscopy is not directly proportional to gas concentrations; however, over two decades of concentrations, the curvature is not excessive. Manufacturers of NDIR equipment furnish calibration curves for their instruments. Recalibration then involves merely adjusting the span control using one or more standard gas mixtures. Linearizer accessories are available which will convert a nonlinear calibration curve into a linear curve.

²⁰ Gas permeation devices for halogen acids and hydrogen cyanide available from Kin-Tek Laboratories, P.O. Box Drawer J, Texas City, TX 77590, have been found satisfactory for this purpose. Tubes are also available for CO, CO₂, O₂, low molecular weight hydrocarbons, and SO₂.

A1.3 Liquid Standards

A1.3.1 Techniques using liquid impingers to trap gases permit the use of solutions of the particular species (for example, HCl) for calibration. However, it is still preferable to check the procedure, using gaseous calibration standards (37). Absorption efficiencies may be very different for different experimental setups, and can be influenced by particulates or condensables in the sample stream.

A1.3.2 When solutions are used to absorb gaseous components, care must be taken in converting solution concentrations, which are weight/volume ratios, to gas concentrations, which are volume/volume.

A1.3.3 Standards for acetaldehyde and acrolein are prepared by using either freshly distilled material in carbon disulfide or by using a compressed-gas standard of butane in air (for FID response). The acetaldehyde and acrolein standards must be freshly prepared daily, since their useful storage life is only several hours. The butane standard must be calibrated every 2 weeks against liquid standards of freshly distilled aldehydes.

A1.4 Cautions During Calibration

A1.4.1 All aspects of “sampling” test gases, as discussed in Section 5, must be considered during calibration. If possible, the calibration gas mixture should be introduced into the analyzer in the same manner as the test sample (that is, a flow-through sample or a gas-tight syringe). In flow-through systems, the pressure of the gas affects the concentrations; thus, the calibration gas and test sample should both be either “pushed” or “pulled” through the analysis unit in the same manner.

A1.4.2 Pretreatment aspects of sample gases and calibration mixtures are important. Effects of filtration or pretreatment can be measured by running a calibration gas through the system, both before and after the test run. In cases where this seems to make a difference, calibration checks ought to be made with and without the filtration or pretreatment device. The running of a calibration gas through the sampling system prior to an experiment may serve to saturate many of the active (adsorptive) sites for certain reactive species.

A1.4.3 Calibration of the analytical device is necessary, even if a calibration curve is supplied with the instrument.

A1.5 Instrument Response Time

A1.5.1 Instrument response time depends on three factors, as follows:

A1.5.1.1 *Analyzer Detection Lag*—This is usually small. Most instruments will give a 90 % response to a change in analyzer cell contents in less than 10 s.

A1.5.1.2 *Line Purge Lag*—The interval between introduction of a sample gas at the probe inlet and its arrival at the analysis cell depends upon the volume of the transfer system and the pumping rate. Delays of 5 to 45 s are common.

A1.5.1.3 *Cell Purging Lag*—The time for the sample cell (for example, infrared) concentration to reach 90 % of the gas concentration at the cell inlet depends on the cell volume, its flow geometry, and the flow rate. Usually from four to six cell volumes must be pumped through to accomplish this. Maximum gas flow rates are obviously desirable. However, they must not be high enough to induce pressure effects in the analytical cell.

A1.5.2 Mathematical techniques have been developed to correct observed concentration/time curves for the effects of line transfer lags and instrument response delays (102). This permits calculation of “real-time” concentration data. Experimental step-changes in concentration must be used to define the necessary parameters. Such methods are especially useful when computer data handling techniques are being employed.

A1.5.3 Sensitivity in infrared cells depends on the optical path length of the radiation in the sample cell. The cell length should be selected to match the anticipated range of concentrations. Path lengths of 100 to 200 mm are useful for moderate concentrations and can detect CO and CO₂ down to 50 to 100 ppm. Multiple-path cells increase the sensitivity limits by more than an order of magnitude; however, they lose the ability to discriminate at concentrations in the percent range.

A2. GAS DETECTOR TUBES

A2.1 Gas detector tubes (often called “pull tubes”) change color when a specific gas reacts with the solid inside the tube. The length of the coloration or “stain” is proportional to the concentration of the gas when a fixed volume of sample gas is drawn through the tube.

A2.1.1 Gas detector tubes are available for CO, CO₂, and O₂ with little or no interference from other gases. Detector tubes of HCl will not detect HCl/water vapor mist (103). Detector tubes for HCN are useable at low concentrations (they can be “extended” to 150 ppm). Some “high-range” gas detector tubes for HCN are not appropriate for fire gas studies due to carbon monoxide interference.

A2.2 Gas detector tubes are not good quantitative tools for analysis of fire gases; their stated accuracies (under ideal conditions) are only 10 to 15 % (103). They are relied on more for a semiquantitative indication of the presence of the particular species. Sampling time is relatively long (one to several minutes). However, these devices are handy and easy to use. Most interfering species have been eliminated in each type of tube. Temperature of the gas being sampled has an influence on the reading.

Additional factors such as aging and batch-to-batch variability may affect the accuracy of the tubes.

A3. SUMMARY TABLE

A3.1 Table A3.1 is a listing of analytical techniques described in the text. For each technique, there is a brief statement as to the type of procedure and its limitations, and a reference to the text.

TABLE A3.1 Summary of Analytical Methods for Fire Gases^A

| Method | Species ^B | Sampling Mode ^C | Interferences/Limitations | Text Reference |
|-----------------------------------|---|--------------------------------|--|--|
| Gas chromatography | CO, CO ₂ , O ₂ , N ₂ | batch | no single column will resolve all four species | 6.2 |
| | HX | batch | not commonly used | 7.4 |
| | HCN | batch | see text | 8.4 |
| | hydrocarbons | batch | suitability to mixtures of hydrocarbons depends on calibration | 10.2 |
| Ion chromatography | aldehydes | batch | see text | 10.3 |
| | X ⁻ | batch, solution | specific detector and conditions required | 7.3 |
| | NO ₂ , NO ₃ | batch, solution | specific detector and conditions required | 9.2 |
| Infrared | CO, CO ₂ | continuous or batch | continuous mode (NDIR) usually limited to analysis of one species; batch mode not limited | 6.3 |
| | HX | continuous | technique under development | 7.4 |
| | HCN | continuous | technique under development | 8.3 |
| | SO _x | continuous | | 9.3 |
| | hydrocarbons | continuous | not very accurate for mixtures of hydrocarbons | 10.2 |
| | Ion-selective electrodes | X ⁻ | batch or continuous, solution | cyanide, sulfide, and other halides can interfere. Each electrode specific to that species |
| CN ⁻ | | batch or continuous, solution | (same as above) | 8.2 |
| Electrochemical methods: | | | | |
| Oxidation | CO | continuous | relatively slow | 6.4 |
| Conductometric | HX | continuous, solution | nonspecific | 7.2 |
| Amperometric | HCN | continuous, solution | interference from H ₂ S | 8.2 |
| Chemiluminescent | NO _x | continuous | large sampling volumes | 9.2 |
| Colorimetry | HCN | batch, solution | limited to low concentrations | 8.3 |
| | acrolein | batch, solution | (same as above) | 10.3 |
| pH Measurement | HX, HCN, CO ₂ , SO ₂ , etc. | batch, solution | determines total acid gas component (that is, anything that will remove or pick up proton in solution) | 7.2 |
| Titrimetric procedures | HX | batch, or continuous, solution | not commonly used | 7.3 |
| | HCN | batch, solution | interference from halide ions | 8.2 |
| Gas analysis tubes ("pull tubes") | CO, CO ₂ , O ₂ , HCl, HCN | batch | only semiquantitative. HCl tube very limited | A2 |

^AA summary listing of manufacturers of instrumentation for each method type is being prepared.

^BX = halide (F, Cl, Br, I)

SO_x = sulfur oxides (SO₂, SO₃)

NO_x = nitrogen oxides (NO, NO₂)

^C"Batch" refers to a sample obtained over some period (whether it be 30 s or the entire run). "Continuous" refers to a continuous measure of the species' concentration for the duration of the experiment. "Solution" means that the species must be absorbed into solution in order to be measured.

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