



Standard Guide for Measurement of Gases Present or Generated During Fires¹

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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.*

¹ 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.

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2. Referenced Documents

2.1 ASTM Standards:²

- D123 Terminology Relating to Textiles
- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D2036 Test Methods for Cyanides in Water
- D3612 Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography
- D6696 Guide for Understanding Cyanide Species
- D6888 Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
- D7295 Practice for Sampling and Determination of Hydrogen Cyanide (HCN) in Combustion Effluents and Other Stationary Sources
- E84 Test Method for Surface Burning Characteristics of Building Materials
- E176 Terminology of Fire Standards
- E535 Practice for Preparation of Fire-Test-Response Standards
- E603 Guide for Room Fire Experiments
- E662 Test Method for Specific Optical Density of Smoke Generated by Solid Materials

3. Terminology

3.1 *Definitions*—Definitions used in this guide are in accordance with Terminology D123, Terminology D1356, Terminology E176, and Practice E535 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.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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).³ 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.

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 E603 and Ref (6)); large laboratory-scale tests (for example, Test Method E84); laboratory-scale chambers (for example, Test Method E662 (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 E662);

(2) open chambers (for example, a full-scale room burn);

(3) flow-through systems (for example, Test Method E84).

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

³ The boldface numbers in parentheses refer to the list of references appended to this standard.

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 combus-

tion 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 oxide⁴ (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.

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.

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 heated 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:

⁴ Tenax, a trademark of Enka BV, Ressort Pantentwesen, Postfach 100149, D-5600, Wuppertal, Federal Republic of Germany, available through gas chromatography supply houses, has been found suitable for this purpose.

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:

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 D3612.)

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 detector 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 methods 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