



Designation: E840 – 95 (Reapproved 2021)^{ε1}

Standard Practice for Using Flame Photometric Detectors in Gas Chromatography¹

This standard is issued under the fixed designation E840; 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 reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Section references in 8.7.2 and 10.2.1.1 were corrected and editorial changes made throughout in May 2021.

1. Scope

1.1 This practice is intended as a guide for the use of a flame photometric detector (FPD) as the detection component of a gas chromatographic system.

1.2 This practice is directly applicable to an FPD that employs a hydrogen-air flame burner, an optical filter for selective spectral viewing of light emitted by the flame, and a photomultiplier tube for measuring the intensity of light emitted.

1.3 This practice describes the most frequent use of the FPD which is as an element-specific detector for compounds containing sulfur (S) or phosphorus (P) atoms. However, nomenclature described in this practice are also applicable to uses of the FPD other than sulfur or phosphorus specific detection.

1.4 This practice is intended to describe the operation and performance of the FPD itself independently of the chromatographic column. However, the performance of the detector is described in terms which the analyst can use to predict overall system performance when the detector is coupled to the column and other chromatographic system components.

1.5 For general gas chromatographic procedures, Practice E260 should be followed except where specific changes are recommended herein for use of an FPD.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific safety information, see Section 4, Hazards.

¹ This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.19 on Separation Science.

Current edition approved April 1, 2021. Published May 2021. Originally approved in 1981. Last previous edition approved in 2013 as E840 – 95 (2013). DOI: 10.1520/E0840-95R21E01.

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *CGA Standards:*³

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations

CGA P-1 Safe Handling of Compressed Gases in Containers

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium

CGA P-12 Safe Handling of Cryogenic Liquids

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures

HB-3 Handbook of Compressed Gases

3. Terminology

3.1 *Definitions*—For definitions relating to gas chromatography, refer to Practice E355.

3.2 *Descriptions of Terms*—Descriptions of terms used in this practice are included in Sections 7 – 17.

3.3 *Symbols*—A list of symbols and associated units of measurement is included in Annex A1.

4. Hazards

4.1 *Gas Handling Safety*—The safe handling of compressed gases and cryogenic liquids for use in chromatography is the responsibility of every laboratory. The Compressed Gas

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 Available from Compressed Gas Association (CGA), 8484 Westpark Drive, Suite 220 McLean, VA 22102, http://www.cganet.com.

Association, (CGA), a member group of specialty and bulk gas suppliers, publishes the following guidelines to assist the laboratory chemist to establish a safe work environment. Applicable CG publications include CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, and HB-3.

5. Principles of Flame Photometric Detectors

5.1 The FPD detects compounds by burning those compounds in a flame and sensing the increase of light emission from the flame during that combustion process. Therefore, the FPD is a flame optical emission detector comprised of a hydrogen-air flame, an optical window for viewing emissions generated in the flame, an optical filter for spectrally selecting the wavelengths of light detected, a photomultiplier tube for measuring the intensity of light emitted, and an electrometer for measuring the current output of the photomultiplier.

5.2 The intensity and wavelength of light emitted from the FPD flame depends on the geometric configuration of the flame burner and on the absolute and relative flow rates of gases supplied to the detector. By judicious selection of burner geometry and gas flow rates, the FPD flame is usually designed to selectively enhance optical emissions from certain types of molecules while suppressing emissions from other molecules.

5.3 Typical FPD flames are normally not hot enough to promote abundant optical emissions from atomic species in the flame. Instead, the optical emissions from an FPD flame usually are due to molecular band emissions or continuum emissions resulting from recombination of atomic or molecular species in the flame. For sulfur detection, light emanating from the S₂ molecule is generally detected. For phosphorus detection, light emanating from the HPO molecule is generally detected. Interfering light emissions from general hydrocarbon compounds are mainly comprised of CH and C₂ molecular band emissions, and CO + O → CO₂ + hν continuum radiation.

5.4 Hydrogen – air or hydrogen – oxygen diffusion flames are normally employed for the FPD. In such diffusion flames, the hydrogen and oxygen do not mix instantaneously, so that these flames are characterized by significant spatial variations in both temperature and chemical species. The important chemical species in a hydrogen – air flame are the H, O, and OH flame radicals. These highly reactive species play a major role in decomposing incoming samples and in the subsequent production of the desired optical emissions. Optical emissions from the HPO and S₂ molecular systems are highly favored in those regions of an FPD flame which are locally rich in H-atoms, while CH and C₂ light emissions from hydrocarbons originate mainly from those flame regions which are locally rich in O-atoms. The highest sensitivity and specificity for sulfur and phosphorus detection are achieved only when the FPD flame is operated with hydrogen in excess of that stoichiometric amount required for complete combustion of the oxygen supplied to the flame. This assures a large flame volume that is locally abundant in H-atoms, and a minimal flame volume that is locally abundant in O-atoms. The sensitivity and specificity of the FPD are strongly dependent on the absolute and relative flow rates of hydrogen and air. The

optimum hydrogen and air flow rates depend on the detailed configuration of the flame burner. For some FPD designs, the flows which are optimum for phosphorus detection are not the same as the flows which are optimum for sulfur detection. Also, the flows which are optimum for one sample compound may not necessarily be optimum for another sample compound.

5.5 Although the detailed chemistry occurring in the FPD flame has not been firmly established, it is known that the intense emissions from the HPO and S₂ molecules are the result of chemiluminescent reactions in the flame rather than thermal excitation of these molecules (1).⁴ The intensity of light radiated from the HPO molecule generally varies as a linear function of P-atom flow into the flame. In the case of the S₂ emission, the light intensity is generally a nonlinear function of S-atom flow into the flame, and most often is found to vary as the approximate square of the S-atom flow. Since the FPD response depends on the P-atom or S-atom mass flow per unit time into the detector, the FPD is a mass flow rate type of detector. The upper limit to the intensity of light emitted from both the HPO and S₂ molecules is generally determined by the onset of self-absorption effects in the emitting flame. At high concentrations of S and P atoms in the flame, the concentrations of ground state S₂ and HPO molecules becomes sufficient to reabsorb light emitted from the radiating states of HPO and S₂.

5.6 In the presence of a hydrocarbon background in the FPD flame, the light emissions from the phosphorus and sulfur compounds can be severely quenched (2). Such quenching can occur in the gas chromatographic analysis of samples so complex that the GC column does not completely separate the phosphorus or sulfur compounds from overlapping hydrocarbon compounds. Quenching can also occur as the result of an underlying tail of a hydrocarbon solvent peak preceding phosphorus or sulfur compounds in a chromatographic separation. The fact that the phosphorus or sulfur response is reduced by quenching is not always apparent from a chromatogram since the FPD generally gives little response to the hydrocarbon. The existence of quenching can often be revealed by a systematic investigation of the variation of the FPD response as a function of variations in sample volume while the analyte is held at a constant amount.

5.7 The chromatographic detection of trace level phosphorus or sulfur compounds can be complicated by the fact that such compounds often tend to be highly reactive and adsorptive. Therefore, care must be taken to ensure that the entire chromatographic system is properly free of active sites for adsorption of phosphorus or sulfur compounds. The use of silanized glass tubing as GC injector liners and GC column materials is a good general practice. At near ambient temperatures, GC packed columns made of FEP TFE-fluorocarbon, specially coated silica gel, or treated graphitized carbon are often used for the analysis of sulfur gases.

⁴ The boldface numbers in parentheses refer to a list of references at the end of this standard.

6. Detector Construction

6.1 Burner Design:

6.1.1 *Single Flame Burner (2, 3)*—The most popular FPD burner uses a single flame to decompose sample compounds and generate the optical emissions. In this burner, carrier gas and sample compounds in the effluent of a GC column are mixed with air and conveyed to an orifice in the center of a flame tip. Excess hydrogen is introduced from the outer perimeter of this flame tip so as to produce a relatively large, diffuse hydrogen-rich flame. With this burner and flow configuration, light emissions from hydrocarbon compounds occur primarily in the locally oxygen-rich core of the flame in close proximity to the flame tip orifice, while HPO and S₂ emissions occur primarily in the upper hydrogen-rich portions of the flame. Improved specificity is therefore obtained by the use of an optical shield at the base of the flame to prevent hydrocarbon emissions from being in the direct field of view. The light emissions generated in this flame are generally viewed from the side of the flame. Some of the known limitations of this burner are as follows:

6.1.1.1 Solvent peaks in the GC effluent can momentarily starve the flame of oxygen and cause a flameout. This effect can be avoided by interchanging the hydrogen and air inlets to the burner (4) with a concomitant change in the flame gas flow rates to achieve maximum signal-to-noise response. Whereas interchanging the H₂ and air inlets will eliminate flameout problems, this procedure will often yield a corresponding decrease in the signal-to-noise ratio and hence compromise the FPD detectability.

6.1.1.2 Response to sulfur compounds often deviates from a pure square law dependence on sulfur-atom flow into the flame. Furthermore, the power law of sulfur response often depends on the molecular structure of the sample compound (5).

6.1.1.3 The phosphorus or sulfur sensitivity often depends on the molecular structure of the sample compound.

6.1.1.4 Hydrocarbon quenching greatly reduces the response to phosphorus and sulfur compounds (2).

6.1.2 *Dual Flame Burner (2, 4)*—A second FPD burner design uses two hydrogen-rich flames in series. The first flame is used to decompose samples from the GC and convert them into combustion products consisting of relatively simple molecules. The second flame reburns the products of the first flame in order to generate the light emissions that are detected. A principal advantage of the dual flame burner is that it greatly reduces the hydrocarbon quenching effect on the phosphorus and sulfur emissions (6). Other advantages of the dual flame burner compared to a single flame burner are that sulfur responses more uniformly obey a pure square law response, and more uniform responses to phosphorus and sulfur compounds are obtained irrespective of the molecular structure of the sample compound. A disadvantage of the dual flame burner is that it generally provides lower sensitivity to sulfur compounds than a single flame burner in those analyses where hydrocarbon quenching is not a problem.

6.2 *Optical Filter*—Fig. 1 illustrates the spectral distributions of emissions from the S₂, HPO, OH, CH, and C₂ molecular systems (1). The principle objectives of the optical filters used in the FPD are to maximize the transmission ratios

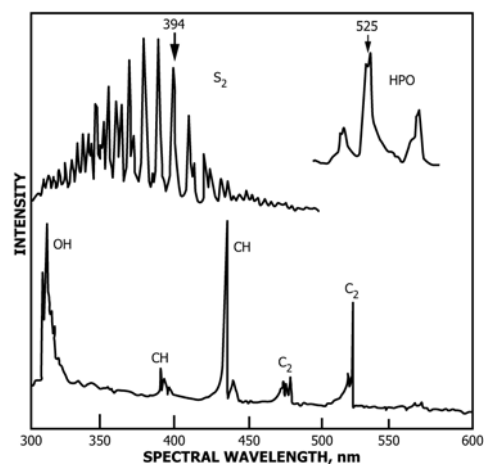


FIG. 1 Spectral Distribution of Molecular Emissions from an FPD Flame

of HPO and S₂ light compared to the flame background and interfering hydrocarbon emissions. For phosphorus detection, a narrow-bandpass optical filter with peak transmission at 525 nm to 530 nm is generally used. For sulfur detection, a filter with peak transmission at 394 nm is most often used although the optical region between 350 nm to 380 nm can also be employed. Typically, the filters used have an optical bandpass of approximately 10 nm.

6.3 Photomultiplier Tube:

6.3.1 The photomultiplier tube used in the FPD generally has a spectral response extending throughout the visible spectrum with maximum response at approximately 400 nm. Some specific tubes that are used are an end-viewing EMI 9524B, and side-viewing RCA 4552 or 1P21 tubes or their equivalents. For FPD applications, the photomultiplier tube should have a relatively low dark current characteristic (for example, 0.1 nA to 1.0 nA) so that the FPD background signal and noise levels are determined by the FPD flame rather than by the photomultiplier limitations. The photomultiplier dark current and its associated noise (see Section 15) depend strongly on the photomultiplier's operating voltage and its ambient temperature.

6.3.2 Operating voltages are typically in the range of 400 V to 900 V, depending on the tube type. Generally, it is unlikely that two photomultiplier tubes of the same type have exactly the same current amplification at a given voltage. Also, the current amplification of a given photomultiplier tube often decreases as the tube ages. Therefore, it is generally necessary to periodically adjust the tube operating voltage in order to maintain the same FPD sensitivity.

6.3.3 Since the FPD burner housing generally operates at elevated temperatures, a critical design constraint in the FPD is the coupling of the maximum amount of light from the flame to the photomultiplier with minimum thermal coupling. In some FPD designs, optical lenses or fiber optic light guides are used to allow the photomultiplier to be operated in as cool an environment as possible. Thermoelectric or cryogenic cooling are sometimes used to further reduce the photomultiplier dark current.

6.3.4 Although a photomultiplier tube is a device with a definite lifetime, this lifetime is normally in excess of 2 years to 3 years unless the tube is used at conditions of high current levels for extended time periods. FPD users are especially cautioned to avoid exposure of the photomultiplier tube to room light when the tube operating voltage is on.

6.4 Electronics:

6.4.1 *Electrometer*—The current output from the photomultiplier tube is generally measured using an electrometer. Typical currents detected range from noise levels of the order of 10^{-12} A to 10^{-10} A to maximum signal levels of 10^{-5} A to 10^{-4} A.

6.4.2 *Linearizer for Sulfur Responses (7)*—The nonlinear sulfur response is sometimes linearized by using an electronic circuit at the output of the electrometer. Usually this circuit is one which provides an output signal proportional to the square root of the electrometer output. When such a square root linearizer is used, the analyst should be aware of the following considerations:

6.4.2.1 The sulfur output signal will be exactly linear only if the sulfur emission from the flame obeys a pure square law dependence on S-atom flow into the flame.

6.4.2.2 The square root of the signal plus baseline offset does not equal the sum of the square root of the signal plus the square root of the baseline offset. Therefore, the flame background must be suppressed so that the baseline offset at the electrometer output is exactly zero in order to obtain output signals which vary linearly as a function of S-atom flow into the flame.

6.4.2.3 Square root circuits tend to be very noisy when the voltage input to the circuit approaches zero. Therefore, the output noise may not be an accurate representation of the flame noise.

6.4.2.4 Flame background levels which are drifting in a negative direction will give erroneous sample responses at the square root output since the square root of negative input voltages is not defined. (**Warning**—The FPD operates at high hydrogen flow rate. To avoid an accumulation of hydrogen gas and possible fire or explosion hazard, turn off hydrogen flow when removing column or when the FPD is not being used.)

7. Data Handling

7.1 All manufacturers supply an integral electrometer to allow the small electrical current changes to be coupled to recorder/integrators/computers. The preferred system will incorporate one of the newer integrators or computers that converts an electrical signal into clearly defined peak area counts in units such as microvolt-seconds. These data can then be readily used to calculate the linear range.

7.1.1 Another method uses peak height measurements. This method yields data that are very dependent on column performance and therefore not recommended.

7.1.2 Regardless of which method is used to calculate linear range, peak height is the only acceptable method for determining minimum detectability.

7.2 *Calibration*—It is essential to calibrate the measuring system to ensure that the nominal specifications are acceptable and particularly to verify the range over which the output of the

device, whether peak area or peak height, is linear with respect to input signal. Failure to perform this calibration may introduce substantial errors into the results. Methods for calibration will vary for different manufacturer's devices but may include accurate constant voltage supplies or pulse generating equipment. The instruction manual should be studied and thoroughly understood before attempting to use electronic integration for peak area or peak height measurements.

TERMS AND RELATIONSHIPS

8. Sensitivity (Response)

8.1 Description of Term:

8.1.1 In the phosphorus mode of operation, the FPD generally exhibits a response that is a linear function of mass flow rate of P-atoms into the flame. Therefore, the phosphorus sensitivity (response) of the FPD is the signal output per unit mass flow rate of P-atoms in a test substance in the carrier gas. A simplified relationship for the phosphorus sensitivity is:

$$S_P = A_I/m_P \quad (1)$$

where:

S_P = phosphorus sensitivity (response), A·s/gP;
 A_I = integrated peak area, A·s; and
 m_P = mass of P-atoms in the test substance, gP.

8.1.2 In the sulfur mode of operation, the FPD generally exhibits a response that is a nonlinear power law function of mass flow rate of S-atoms into the flame. Therefore, sulfur sensitivity requires first a determination of the power law of response in accordance with the specifications given in Section 11. In general, if the FPD sulfur response varies as the n th power of S-atom mass flow rate, then the sulfur sensitivity is determined as follows:

$$S_S = (A_I/m_S) \cdot (1/\dot{m}_S)^{n-1} \quad (2)$$

where:

S_S = sulfur sensitivity (response), A/(gS/s) ^{n} ;
 A_I = integrated peak area, A·s;
 m_S = mass of S-atoms in the test substance, gS; and
 \dot{m}_S = mass flow rate of S-atoms in the test substance, gS/s.

Frequently, the sulfur response of an FPD obeys a pure square law, so that $n=2$ and the sensitivity, expressed in A/(gS/s)², is as follows:

$$S_S = (A_I/m_S) (1/\dot{m}_S) \quad (3)$$

8.2 Test Conditions:

8.2.1 Since the FPD response can depend on sample compound structure as well as sample matrix, the test substance for the determination of FPD sensitivity may be selected in accordance with the expected application of the detector. The test substance should always be well defined chemically. When specifying the sensitivity of the FPD, the test substance applied must be stated.

8.2.1.1 The recommended test substance is tributylphosphate for the phosphorus mode, and sulfur hexafluoride for the sulfur mode.

8.2.2 The measurement must be made at a signal level between 20-times and 200-times greater than the noise level.

8.2.3 For the phosphorus sensitivity, the measurement must be made within the linear range of response of the detector. For the sulfur sensitivity, the measurement must be made within the range of a uniform power law response of the detector versus S-atom flow.

8.2.4 The magnitude of the flame background current for the detector at the same conditions should be stated.

8.2.5 Since the output signal of a photomultiplier tube depends on its operating voltage, the FPD sensitivity is also a function of the photomultiplier voltage. Therefore, the type of photomultiplier tube used and its operating voltage should be stated.

8.2.6 The conditions under which the detector sensitivity is measured must be stated. This should include but not necessarily be limited to the following:

- 8.2.6.1 Mode of operation (S or P),
- 8.2.6.2 Detector burner geometry (single or dual flame),
- 8.2.6.3 Wavelength and bandpass of optical filter,
- 8.2.6.4 Hydrogen flow rate,
- 8.2.6.5 Air or oxygen flow rate,
- 8.2.6.6 Carrier gas,
- 8.2.6.7 Carrier gas flow rate (corrected to detector temperature),
- 8.2.6.8 Detector temperature,
- 8.2.6.9 Electrometer time constant, and
- 8.2.6.10 Method of measurement.

8.2.7 Linearity and speed of response of the recording system used should be such that it yields a true reading of the detector performance. The recorders should have a 0 mV to 1 mV range and a 1 s response time corresponding to 90 % of full scale deflection.

8.3 *Methods of Measurement:*

8.3.1 Sulfur sensitivity may be measured by any of five methods, while only two methods are applicable to the measurement of phosphorus sensitivity. Methods are as follows:

- 8.3.1.1 Experimental decay with exponential dilution flask (8) (see 8.4) for sulfur gas samples.
- 8.3.1.2 Permeation device (9) under steady-state conditions (see 8.5) for sulfur gas samples.
- 8.3.1.3 Dynamic method with Young's (10) apparatus for sulfur gas samples (see 8.6).
- 8.3.1.4 Diffusion dilution technique (11, 12) (see 8.7) for sulfur or phosphorus liquid samples.
- 8.3.1.5 Actual chromatograms (see 8.8) for sulfur or phosphorus liquid samples.

8.4 *Exponential Dilution Method:*

8.4.1 Purge a mixing vessel of known volume fitted with a magnetically driven stirrer with the carrier gas at a known rate. The effluent from the flask is delivered directly to the detector. Introduce a measured quantity of the test substance into the flask to give an initial concentration, C_{oS} , of the test substance in the carrier gas, and simultaneously start a timer.

8.4.2 Calculate the initial sulfur concentration using the equation $C_{oS} = Y_S C_o/100$, where Y_S is the mass percent of sulfur atoms in the test substance.

8.4.3 Calculate the concentration of S-atoms in the carrier gas at the outlet of the flask at any time as follows:

$$C_{fS} = C_{oS} \exp(-F_f t/V_f) \quad (4)$$

where:

- C_{fS} = concentration of S-atoms in the carrier gas at time t after introduction into the flask, gS/cm³;
- C_{oS} = initial concentration of S-atoms introduced into the flask, gS/cm³;
- F_f = carrier gas flow rate, corrected to flask temperature (see Annex A2), cm³/min;
- t = time, min; and
- V_f = volume of flask, cm³.

8.4.4 Calculate the sulfur sensitivity of the detector at any concentration as follows:

$$S_S = E(60/C_{fS} F_f)^n \quad (5)$$

where:

- S_S = sulfur sensitivity, A/(gS/s) ^{n} ;
- E = detector signal, A;
- C_{fS} = concentration of S-atoms in the carrier gas at time t after introduction into the flask, gS/cm³; and
- F_f = carrier gas flow rate, corrected to flask temperature (see Annex A2), cm³/min.

NOTE 1—This method is subject to errors due to inaccuracies in measuring the flow rate and flask volume. An error of 1 % in the measurement of either variable will propagate to 2 % over two decades in concentration and to 6 % over six decades. Therefore, this method should not be used for concentration ranges of more than two decades over a single run.

NOTE 2—A temperature difference of 1 °C between flask and flow measuring apparatus will, if uncompensated, introduce an error of 0.33 % into the flow rate.

NOTE 3—Extreme care should be taken to avoid unswept volumes between the flask and the detector, as these will introduce additional errors into the calculations.

NOTE 4—Flask volumes between 100 cm³ and 500 cm³ have been found to be the most convenient. Larger volumes should be avoided due to difficulties in obtaining efficient mixing and the likelihood of temperature gradients.

8.5 *Method Utilizing Permeation Devices:*

8.5.1 Permeation devices consist of a volatile liquid enclosed in a container with a permeable wall. These devices provide low concentrations of vapor by diffusion of the vapor through the permeable surface. The rate of permeation for a given device is dependent only on the temperature. The weight loss over a period of time is carefully and accurately determined and these devices have been proposed as primary standards.

8.5.2 Accurately known permeation rates can be prepared by passing a gas over the previously calibrated permeation device at constant temperature. Knowing the permeation rate of S-atoms in the test substance, the sulfur sensitivity can be obtained from the following equation:

$$S_S = E(60/R_S)^n \quad (6)$$

where:

- S_S = sulfur sensitivity, A/(s/gS) ^{n} ;
- E = detector signal, A;
- R_S = permeation rate of S-atoms in a test substance from the permeation device, gS/min; and
- n = power law of sulfur response (see Section 11).

8.6 Dynamic Method:

8.6.1 In this method, inject a known weight of S-atoms in a test substance into the flowing carrier gas stream. A length of empty tubing between the sample injection port and the detector permits the band to spread and be detected as a Gaussian band. Then integrate the detector signal by any suitable method. This method has the advantage that no special equipment or devices are required other than conventional chromatographic hardware.

8.6.2 Calculate the sulfur sensitivity as follows:

$$S_S = (A_i/m_S)(t_S/m_S)^n \quad (7)$$

where:

- S_S = sulfur sensitivity, A/(gS)ⁿ;
- A_i = integrated peak area, A·s;
- m_S = mass of sulfur atoms injected, gS;
- t_S = peak width at (1/2)ⁿ of the maximum peak height, s; and
- n = power law of sulfur response (see Section 10).

8.7 Diffusion Dilution Method:

8.7.1 This method is analogous to the permeation device method and may be used for sulfur and phosphorus-bearing test substances that are not volatile enough to pass through a permeation tube. In this method, the test substance is contained in a diffusion bulb apparatus. The diffusion bulb and a corresponding capillary outlet tube are maintained in a constant-temperature oven. The oven temperature is sufficiently high to liquify the test substance and the liquid phase slowly evaporates and diffuses through the capillary tube due to the driving force of the concentration gradient. Carrier gas flows into a mixing chamber attached to the outlet port of the capillary tube. Since the diffusion rate is constant for a constant temperature and a known cross-sectional area of capillary tube, various vapor concentrations of the test substance are obtained by varying the diluent flow of carrier gas through the mixing chamber. The diffusion rates can be calculated from the diffusion equation, or measured experimentally from the changes in weight of the diffusion bulb as a function of time.

8.7.2 The sulfur sensitivity is calculated using the equations in 8.5.2 by replacing the permeation rate R_S by the diffusion rate R_S' of S-atoms in the test substance in gS/min.

8.7.3 The phosphorus sensitivity is calculated as follows:

$$S_P = 60E/R_P' \quad (8)$$

where:

- S_P = phosphorus sensitivity, A s/gP;
- E = detector signal, A; and
- R_P' = diffusion rate of P-atoms in the test substance, gP/min.

8.8 Actual Chromatograms:

8.8.1 This method consists of generating an actual chromatogram of a phosphorus or sulfur-bearing test substance. Generally, this method is not preferred because it is common for the sample to have adverse interaction with the column. These problems can be minimized by using an inert stable liquid phase loaded sufficiently to limit support adsorption effects.

8.8.2 Calculate the phosphorus sensitivity of the detector in accordance with 8.1.1.

8.8.3 Calculate the sulfur sensitivity of the detector in accordance with 8.6.2.

8.9 Typical Values of Sensitivity:

NOTE 5—These values will depend on photomultiplier voltage.

8.9.1 For sulfur, 2 A/(gS/s)² to 20 A/(gS/s)².

8.9.2 For phosphorus, 20 A·s/gP to 200 A·s/gP.

9. Minimum Detectability

9.1 Description of Term:

9.1.1 Minimum detectability for phosphorus is the mass flow rate of phosphorus atoms in the carrier gas that gives a detector signal equal to twice the peak-to-peak noise level and is calculated from the measured sensitivity and noise level values as follows:

$$D_P = 2N_P/S_P \quad (9)$$

where:

- D_P = minimum detectability for phosphorus, gP/s;
- N_P = noise level in phosphorus mode, A; and
- S_P = phosphorus sensitivity of the FPD, A·s/gP.

9.1.2 Minimum detectability for sulfur is the mass flow rate of sulfur atoms that gives a detector signal equal to twice the noise level and is calculated from the measured sensitivity and noise level values as follows:

$$D_S = (2N_S/S_S)^{1/n} \quad (10)$$

where:

- D_S = minimum detectability for sulfur, gS/s;
- N_S = noise level in sulfur mode, A;
- S_S = sulfur sensitivity of the FPD, A/(gS/s)ⁿ; and
- n = power law of sulfur response (see Section 10).

Frequently, the sulfur response of an FPD obeys a pure square law, so that $n = 2$ and the minimum detectability is as follows:

$$D_S = \sqrt{2N_S/S_S} \quad (11)$$

9.2 Test Conditions—Measure sensitivity in accordance with Section 8. Measure noise level in accordance with Section 14. Both measurements must be carried out at the same conditions (see 8.2.6) and, preferably at the same time. When giving minimum detectability, state the noise level on which the calculation was based.

9.3 Typical Values:

9.3.1 For sulfur, 10⁻¹¹ gS/s to 10⁻¹⁰ gS/s.

9.3.2 For phosphorus, 5 × 10⁻¹³ gP/s to 5 × 10⁻¹² gP/s.

10. Dynamic Range

10.1 Description of Term:

10.1.1 The dynamic range of the FPD is that range of mass flow rates of phosphorus or sulfur atoms over which a change in mass flow rate produces a change in detector output signal. The lower limit of the dynamic range is the mass flow rate which produces a detector signal that is twice the noise level in accordance with Section 8 for minimum detectability. The upper limit is the highest mass flow rate at which a slight further increase in mass flow rate will give an observable

increase in detector signal. The dynamic range is the ratio of the upper and lower limits.

10.1.2 The dynamic range may be expressed in three different ways:

10.1.2.1 As the ratio of the upper limit of dynamic range to the minimum detectability. The minimum detectability must also be stated.

10.1.2.2 By giving the minimum detectability and the upper limit of dynamic range (for example, from 5×10^{-13} gP/s to 1×10^{-7} gP/s).

10.1.2.3 By giving the dynamic range plot itself with the minimum detectability indicated on the plot.

10.2 Method of Measurement:

10.2.1 For the determination of the dynamic range of the FPD, use the exponential decay method (8.4) or the dynamic method (8.6) for sulfur gases, and actual chromatograms (8.8) for sulfur or phosphorus liquid samples. The permeation device method (8.5) or the diffusion dilution method (8.7) are usually not adequate for generating a wide enough range of sample concentrations.

10.2.1.1 Using the exponential decay method, measure the detector output signal E at various sulfur atom mass flow rates \dot{m}_S , where \dot{m}_S is determined as follows:

$$\dot{m}_S = C_{FS} F_f / 60 \tag{12}$$

where C_{FS} and F_f are determined as in 8.4.4. Plot E versus \dot{m}_S on log – log graph paper, and draw a smooth curve through the data points as shown in Fig. 2. The upper limit of the dynamic range is the mass flow rate at which the slope is zero.

10.2.1.2 In using the dynamic method or actual chromatograms, prepare a set of test samples covering a wide range of concentrations of the test substance. Inject a fixed volume of each concentration of the test substance and measure the height H of the resultant Gaussian or chromatographic peaks. For each peak, also determine the mass flow rate of sulfur or phosphorus atoms as follows:

For the phosphorus mode,

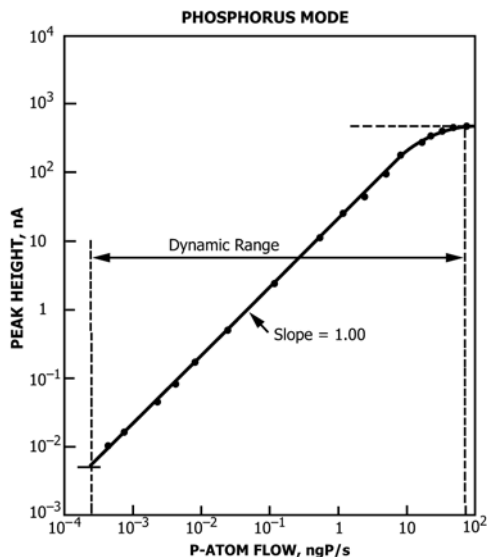


FIG. 2 Example of a Plot to Determine the Dynamic Range of an FPD in the Phosphorus Mode

$$\dot{m}_P = m_P / t_P \tag{13}$$

where:

- \dot{m}_P = mass flow rate of P-atoms in test substance, gP/s;
- m_P = mass of P-atoms in the test substance, gP; and
- t_P = peak width at $1/2$ of the maximum peak height, s.

For the sulfur mode,

$$\dot{m}_S = m_S / t_S \tag{14}$$

where:

- \dot{m}_S = mass flow rate of S-atoms in test substance, gS/s;
- m_S = mass of S-atoms in the test substance, gS;
- t_S = peak width at $(1/2)^n$ of the maximum peak height, s; and
- n = power law of sulfur response (see Section 10).

Plot the peak height H versus m_S or m_P on log – log graph paper, and draw a smooth curve through the data points as shown in Fig. 2 and Fig. 3. The upper limit of the dynamic range is the mass flow rate at which the slope is zero.

10.2.2 When giving the dynamic range or the dynamic range plot, specify the test conditions in accordance with 8.2.

11. Power Law of Sulfur Response

11.1 Description of Term—In the sulfur mode of operation the output signal of the FPD generally varies as a nonlinear function of the mass flow rate of sulfur atoms into the flame. This relationship is expressed by the following equation:

$$E = S_S (\dot{m}_S)^n \tag{15}$$

where:

- E = detector signal, A;
- S_S = sulfur sensitivity, A/(gS/s)ⁿ; and
- \dot{m}_S = mass flow rate of S-atoms, gS/s.

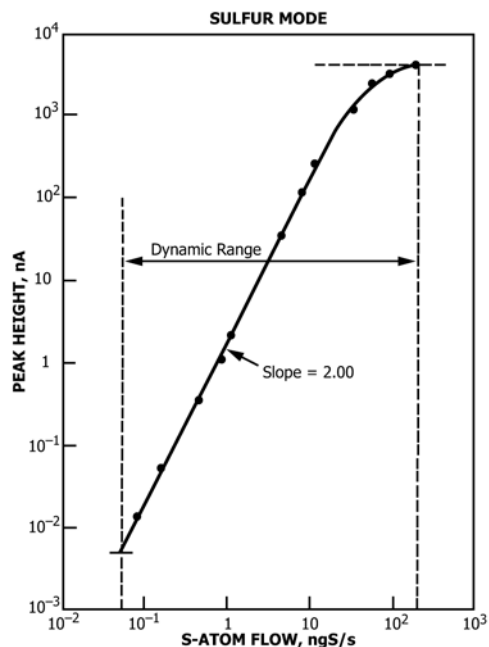


FIG. 3 Example of a Plot to Determine the Dynamic Range and Power Law of Response of an FPD in the Sulfur Mode