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Standard Practice for Using Flame Photometric Detectors in Gas Chromatography[1]

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.

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

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 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

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[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.

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[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), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, http://www.cganet.com.

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 S_2 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 C_2 molecular band emissions, and $CO + O \rightarrow CO_2 + h\gamma$ 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 S_2 molecular systems are highly favored in those regions of an FPD flame which are locally rich in H-atoms, while CH and C_2 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 S_2 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 S_2 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 S_2 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 S_2 and HPO molecules becomes sufficient to reabsorb light emitted from the radiating states of HPO and S_2.

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.

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,

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

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 S_2 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 (**5**) with a concomitant change in the flame gas flow rates to achieve maximum signal-to-noise response. Whereas interchanging the H_2 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 (**4**).

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, 5**)—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 S_2, HPO, OH, CH, and C_2 molecular systems (**1**). The principle objectives of the optical filters used in the FPD are to maximize the transmission ratios of HPO and S_2 light compared to the flame background and interfering hydrocarbon emissions. For phosphorus detection, a narrow-bandpass optical filter with peak transmission at 525 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 to 380 nm can also be employed. Typically, the filters used have an optical bandpass of approximately 10 nm.

6.3 *Photomultiplier Tube:*

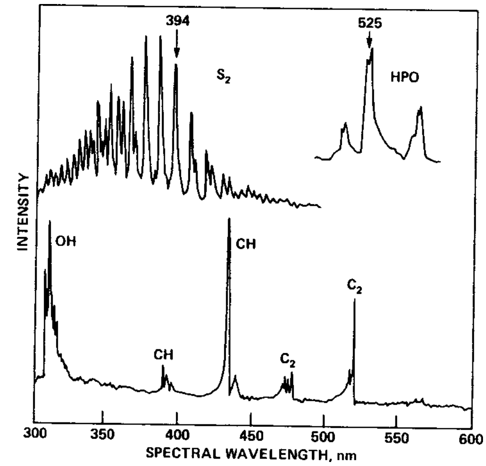

FIG. 1 Spectral Distribution of Molecular Emissions from an FPD Flame

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 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 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 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} to 10^{-10} A to maximum signal levels of 10^{-5} 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 given 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 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 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_o, 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/cm^3,
C_{oS} = initial concentration of S-atoms introduced into the flask, gS/cm^3,
F_f = carrier gas flow rate, corrected to flask temperature (see Annex A2), cm^3 /min,
t = time, min, and
V_f = volume of flask, cm^3.

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/cm^3, and
F_f = carrier gas flow rate, corrected to flask temperature (see Annex A2), cm^3 /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 and 500 cm^3 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, $A(s/gS)^n$,
A_i = integrated peak area, A·s,
m_S = mass of sulfur atoms injected, gS
t_S = peak width at $(½)^n$ 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 7.5.2 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 to 20 $A/(gS/s)^2$.

8.9.2 For phosphorus, 20 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} to 10^{-10} gS/s.

9.3.2 For phosphorus, 5×10^{-13} 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} 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 7.4.4. 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,

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

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 ½ 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 $(½)^n$ 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.

The value of the parameter n, therefore, defines the power law of sulfur response that the FPD obeys. For most sulfur compounds, n usually has a value in the range of 1.50 to 2.00. For those instances when $n = 2.00$, the FPD sulfur response is described as obeying a pure square law.

11.2 *Methods of Determination:*

11.2.1 Since the power law of sulfur response can vary with compound type as well as with the configuration and operating

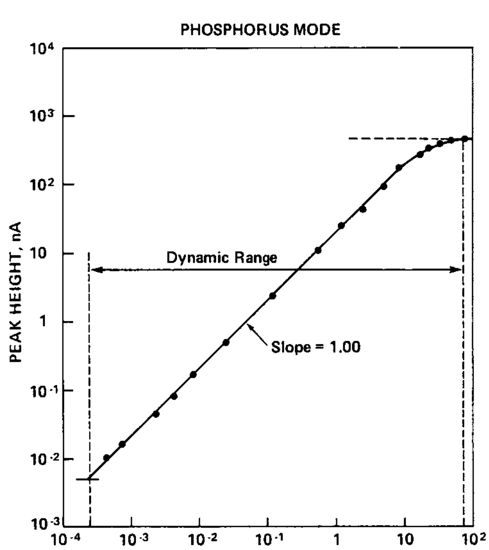

FIG. 2 Example of a Plot to Determine the Dynamic Range of an FPD in the Phosphorus Mode

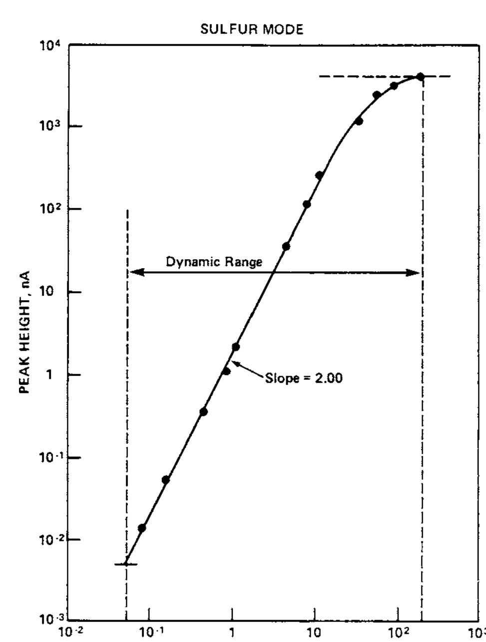

FIG. 3 Example of a Plot to Determine the Dynamic Range and Power Law of Response of an FPD in the Sulfur Mode

conditions of the FPD flame burner, the test substance should be selected according to the expected application and operating conditions of the detector. Where the FPD is to be used for quantitative analysis of many sulfur compounds, the power law of response should be determined for each compound in question.

11.2.2 Any of the methods of measurement cited in 8.3 can be used to determine the power law of sulfur response. The method used should be capable of generating mass flow rates of sulfur atoms ranging from the minimum detectability (that is, detector signal equal to twice noise level) to a S-atom mass flow rate at least 100 times the minimum detectability.

11.2.2.1 Using the exponential decay, permeation device, or diffusion dilution methods, measure the detector output signal E at various sulfur atom mass flow rates, $\dot{m}_S$, where $\dot{m}_S$ is determined as follows:

(a) For the exponential decay method:

$$\dot{m}_S = C_{fS} F_f/60 \text{ (see 7.4)} \quad (16)$$

(b) For the permeation device method:

$$\dot{m}_S = R_S/60 \text{ (see 7.5)} \quad (17)$$

(c) For the diffusion dilution method:

$$\dot{m}_S = R_S'/60 \text{ (see 7.7)} \quad (18)$$

Plot E versus $\dot{m}_S$ on log – log graph paper as in the dynamic range graphs in Fig. 2 and Fig. 3 and determine the slope of a straight line through the data using a linear regression analysis. The slope so determined is the sulfur power law parameter n.

11.2.2.2 Using the dynamic method or actual chromatograms, measure the integrated peak area A_i or peak height H of a series of Gaussian or chromatographic peaks obtained by injecting various concentrations of the test substance. On log – log graph paper, plot A_i or H versus the mass of sulfur atoms corresponding to each peak. Fit a straight line to the data and determine the slope by a linear regression analysis. The slope so determined is the sulfur power law parameter n.

11.2.2.3 In some instances, the data in 11.2.2.1 or 11.2.2.2 may exhibit more than one slope over the range of $\dot{m}_S$ or m_S. For example, there have been reports of some FPD sulfur responses which are linear ($n = 1.00$) at low sulfur amounts and follow a square law dependence ($n = 2.00$) at high sulfur amounts. In those cases, the different values of n and the range of $\dot{m}_S$ over which they apply should be stated.

11.2.2.4 To ensure accurate quantitation over a wide range of sulfur atom mass flow rates, the parameter n should be determined to three significant figures.

11.3 *Typical Values*—For sulfur compounds, typical values for n range from 1.50 to 2.00.

12. Linear Range—Phosphorus Mode

12.1 *Description of Term:*

12.1.1 The linear range of the FPD in the phosphorus mode is the range of phosphorus atom mass flow rates over which the phosphorus sensitivity of the detector is constant to within 5 % as determined from the linearity plot specified in 12.2.

12.1.2 The linear range may be expressed in three different ways:

12.1.2.1 As the ratio of the upper limit of linearity obtained from the linearity plot to the minimum detectability, both measured for the same test substance as follows:

$$LR = \dot{m}P_{max}/D_P \quad (19)$$

where:

LR = linear range of the detector,
$\dot{m}P_{max}$ = upper limit of linearity obtained from the linearity plot, gP/s, and
D_P = phosphorus minimum detectability, gP/s.

If the linear range is expressed by this ratio, the minimum detectability must also be stated.

12.1.2.2 By giving the minimum detectability and the upper limit of linearity (for example, from 5×10^{-13} to 1×10^{-8} gP/s).

12.1.2.3 By giving the linearity plot itself, with the minimum detectability indicated on the plot.

12.2 *Method of Measurement:*

12.2.1 For the determination of the linear range of the FPD in the phosphorus mode, use actual chromatograms as described in 8.8.

12.2.2 Measure the phosphorus sensitivity at various phosphorus atom mass flow rates $\dot{m}_P$ where $\dot{m}_P$ is defined in accordance with 10.2.1.2. Plot the phosphorus sensitivity versus log $\dot{m}_P$ on a semilog graph as shown in Fig. 4. Draw a smooth line through the data points. The upper limit of linearity is given by the intersection of this line with a value $0.95 \times S_P$, where S_P is the constant value of sensitivity as determined by a least squares fit of the lower three decades of phosphorus atom mass flow rate.

12.2.3 In giving the linear range or the linearity plot, specify the test condition in accordance with 5.2.

12.3 Values—For phosphorus, typical values range from 10^3 to 10^5.

13. Range of Unipower Response—Sulfur Mode

13.1 *Description of Term:*

13.1.1 The range of unipower response of the FPD in the sulfur mode is the range of sulfur atom mass flow rates over which the sulfur sensitivity of the detector is constant to within 10 % as determined from the plot specified in 13.2.

13.1.2 The range of unipower response may be expressed in three different ways:

13.1.2.1 As the ratio of the upper limit of unipower response as obtained from the plot described in 12.2 to the minimum detectability, both measured for the same test substance as follows:

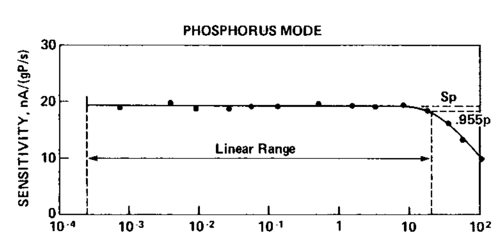

FIG. 4 Example of an FPD Linearity Plot for the Phosphorus Mode

$$UR = \dot{m}S_{max}/D_S \quad (20)$$

where:

UR = range of unipower response for the FPD in the sulfur mode,
$\dot{m}S_{max}$ = upper limit of unipower response, gS/s, and
D_S = sulfur minimum detectability, gS/s.

If the range of unipower response is expressed by this ratio, the minimum detectability must also be stated.

13.1.2.2 By giving the minimum detectability and the upper limit of unipower response (for example, from 5×10^{-11} gS/s to 2.5×10^{-8} gS/s).

13.1.2.3 By giving the plot of unipower response itself, with the minimum detectability indicated on the plot.

13.2 *Method of Measurement:*

13.2.1 For the determination of the range of unipower response for the FPD in the sulfur mode, use the exponential decay method (8.4) or the dynamic method (8.6) for sulfur gases, and actual chromatograms (8.8) for sulfur liquid samples.

13.2.2 Measure the sulfur sensitivity at various sulfur atom mass flow rates $\dot{m}_S$ where $\dot{m}_S$ is terminal in accordance with 10.2.1.1 or 10.2.1.2 depending on the method used. Plot the sulfur sensitivity versus log $\dot{m}_S$ on a semilog graph as shown in Fig. 5. Draw a smooth line through the data points. The upper limit of the unipower response is given by the intersection of this line with a value $0.90 \times S_S$, where S_S is the constant value of sensitivity as determined by a least squares fit of the lower two decades of sulfur atom mass flow rate.

13.2.3 In giving the rang
e of unipower response or the corresponding plot, specify the test conditions in accordance with 8.2.

13.3 *Typical Values*—For sulfur, typical values range from 10^2 to 10^3.

14. Noise and Drift

14.1 *Description of Terms:*

14.1.1 *Noise*—Noise is the amplitude expressed in amperes or Hertz of the baseline envelope which includes all random variations of the detector signal of the frequency on the order of 1 cycle/min or greater (see Fig. 6). This noise corresponds to the observed noise only. The actual amount of noise is a function of the whole system including the detector, signal cables, and the instrument monitoring the signal (recorder, integrator, or computer). Modern integrators and computers may contain electronic filters that selectively remove some types of noise and reduce the apparent amount of detector noise. To effectively use the filtering capacity, the user must have a basic understanding of how the electronic device monitors the detector output. A lack of understanding of the device's operation may lead to poor analytical results. Both noise measurements and sensitivity measurements should be made under the same conditions.

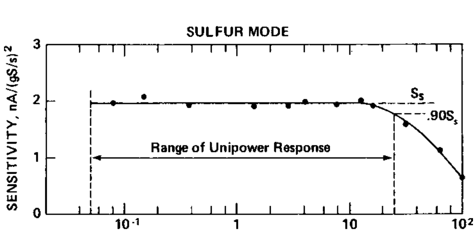

FIG. 5 Example of a Plot to Determine the Range of Unipower Response for an FPD in the Sulfur Mode

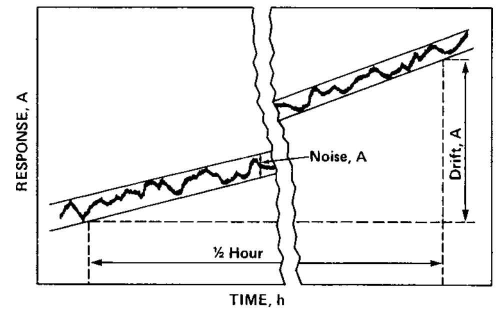

FIG. 6 Example of the FPD Noise Level and Drift Measurement

14.1.2 *Drift*—Drift is the average slope of the noise envelope expressed in amperes per hour as measured over a period of ½ h (see Fig. 6).

14.2 *Methods of Measurement:*

14.2.1 With the detector output set at maximum sensitivity and adjusted with the zero-control to read well above zero, allow at least ½ h of baseline to be recorded.

14.2.2 Draw two parallel lines to form an envelope that encloses the random excursions of a frequency of approximately 1 cycle/min and greater. Measure the distance perpendicular to the time axis between the parallel lines and express the value as amperes of noise.

14.2.3 Measure the net change in amperes of the envelope over ½ h and multiply by two. Express the value as amperes per hour of drift.

14.2.4 In specifications giving the measured noise and drift of the FPD, the conditions stated in 7.2 must be given.

14.3 *Typical Values*—For noise, depending on the photomultiplier voltage, typical values range from 5×10^{-12} to 5×10^{-10} A.

15. Specificity

15.1 *Description of Term:*

15.1.1 The specificity ratio of the FPD for phosphorus with respect to carbon is the weight of carbon atoms in the FPD flame that is required to generate the same detector output signal as a unit weight of phosphorus atoms. The specificity ratio is determined by measuring the phosphorus sensitivity (8.1.1) and carbon sensitivity (see 15.2.1) with the phosphorus filter in the FPD, and then applying the following equation:

$$X_{PC} = S_P / S_C \quad (21)$$

where:

X_{PC} = phosphorus to carbon specificity ratio, gC/gP,
S_P = phosphorus sensitivity, A·s/gP, and
S_C = carbon sensitivity with the phosphorus filter as described in 15.2.1, A·s/gC.

15.1.1.1 Typical values for X_{PC} range from 10^4 to 5×10^5 gC/gP.

15.1.2 The specificity ratio of the FPD for phosphorus with respect to sulfur is the weight of sulfur atoms in the FPD flame that is required to generate the same detector output signal as a unit weight of phosphorus atoms. The specificity ratio is determined by measuring the phosphorus sensitivity and the sulfur sensitivity (8.1.2) with the phosphorus filter in the FPD, and then applying the following equation:

$$X_{PS} = (S_P/S_S)(1/\dot{m}_s)^{n-1} \quad (22)$$

where:

X_{PS} = phosphorus to sulfur specificity ratio, gS/gP,
S_P = phosphorus sensitivity, A s/gP,
S_S = sulfur sensitivity with the phosphorus filter, A/(gS/s)^n,
$\dot{m}_S$ = mass flow rate of S-atoms, gS/s, and
n = power law of sulfur response.

Note that the phosphorus to sulfur specificity ratio decreases with increasing mass flow rate of S-atoms because the output signal of the FPD varies as the *n*th power of S-atom flow but only linearly with P-atom flow.

15.1.2.1 Typical values for X_{PS} range from 10^4 to 10^5 gS/gP at low sulfur amounts; and from 5 to 5 gS/gP at high sulfur amounts.

15.1.3 The specificity ratio of the FPD for sulfur with respect to carbon is the weight of carbon atoms in the FPD flame that is required to generate the same detector output signal as a unit weight of sulfur atoms. The specificity ratio is determined by measuring the sulfur sensitivity and the carbon sensitivity with the sulfur filter in the FPD, and then applying the following equation:

$$X_{SC} = (S_S/S_C)(\dot{m}_S)^{n-1} \quad (23)$$

where:

X_{SC} = sulfur to carbon specificity ratio, gC/gS,
S_S = sulfur sensitivity, A/(gS/s)^n,
S_C = carbon sensitivity with the sulfur filter, A s/gC,
$\dot{m}_S$ = mass flow rate of S-atoms, gS/s, and
n = power law of sulfur response.

Note that the sulfur to carbon specificity ratio increases with increasing mass flow rate of S-atoms because the output signal of the FPD varies as the *n*th power of S-atom flow but only linearly with C-atom flow.

15.1.3.1 Typical values for X_{SC} are 10^3 gC/gS at low sulfur amounts and 10^6 gC/gS at high sulfur amounts.

15.1.4 The specificity ratio of the FPD for sulfur with respect to phosphorus is the weight of phosphorus atoms in the flame that is required to generate the same detector output signal as a unit weight of sulfur atoms. The specificity ratio is determined by measuring the sulfur sensitivity and the phosphorus sensitivity with the sulfur filter in the FPD, and then applying the following equation:

$$X_{SP} = (S_S/S_P)(\dot{m}_S)^{n-1} \quad (24)$$

where:

X_{SP} = sulfur to phosphorus specificity ratio, gP/gS,
S_S = sulfur sensitivity, A/(gS/s)^n,
S_P = phosphorus sensitivity with the sulfur filter, A s/gP,
$\dot{m}_S$ = mass flow rate of S-atoms, gS/s, and
n = power law of sulfur response.

Note that the sulfur to phosphorus specificity ratio increases with increasing mass flow rate of S-atoms because the output signal of the FPD varies as the *n*th power of S-atom flow but only linearly with P-atom flow.

15.1.4.1 Typical values for X_{SP} are 10 gP/gS at low sulfur amounts and 10^4 gP/gS at high sulfur amounts.

15.2 *Method of Measurement:*

15.2.1 The carbon sensitivity of the FPD is determined using a relationship analogous to that given in 7.1.1 for the phosphorus sensitivity.

15.2.1.1 Normal-butane is the recommended test substance for determining carbon sensitivity.

15.2.1.2 The exponential dilution method (8.4) is the recommended procedure for determining carbon sensitivity although any of the other methods described in 8.3 may also be used.

15.2.1.3 Using the exponential dilution method, calculate the carbon sensitivity of the FPD in a manner analogous to 8.4 using the following relationship:

$$S_C = E(60/C_{fC}F_f) \quad (25)$$

where:

S_C = carbon sensitivity, A·s/gC,
E = detector signal, A,
C_{fC} = concentration of C-atoms in the carrier gas at time t after introduction into the flask, gC/cm^3, and
F_f = carrier gas flow rate corrected to flask temperature, cm^3 /min.

15.2.2 Determine the phosphorus and sulfur sensitivities in accordance with Section 7, and the mass flow rate of sulfur atoms in accordance with 9.1.2.

15.2.3 Using values of S_P, S_S, and S_C measured with the same optical filter in the FPD, calculate the specificity ratios X_{PC}, X_{PS}, X_{SC}, or X_{SP} in accordance with the equations given in 15.1.

16. Photomultiplier Dark Current and Noise

16.1 The photomultiplier dark current is the magnitude of the FPD output signal measured with the FPD flame off.

16.2 The photomultiplier dark noise is the noise (see 13.1.1) associated with the photomultiplier dark current.

16.3 Both photomultiplier dark current and noise generally increase with increasing photomultiplier voltage and temperature.

17. Flame Background Current

17.1 Flame background current is the difference in FPD output signal with the flame on and with the flame off in the absence of phosphorus or sulfur compounds in the flame.

17.2 The magnitude of flame background current will generally depend on which optical filter is used.

18. Chromatographic Test Sample

18.1 The performance of the FPD can be periodically monitored by using a chromatographic test sample which allows both sensitivity and specificity to be determined from a single chromatogram. Such a test sample should include compounds containing the heteroatoms in question (phosphorus or sulfur) as well as a hydrocarbon compound, with the concentration of the hydrocarbon being several orders of magnitude greater than the heteroatom compounds. The specific test substances used should be well resolved by the gas chromatographic column that is used. One example is a test sample consisting of 20 ng of *n*-dodecanethiol, 20 ng of tributylphosphate, and 4000 ng of *n*-pentadecane in an isooctane solvent. These compounds are generally easily resolved on an OV-101 column.

18.2 The FPD sensitivity is determined from the absolute detector response to the heteroatom compounds, while the FPD specificity is determined from the ratio of responses of the heteroatom compounds relative to each other or relative to the hydrocarbon compound.

19. Keywords

19.1 flame ionization detector (FID); flame photometric detectors (FPD); gas chromatography (GC); packed columns; supercritical fluid chromatography (SFC)

ANNEXES

(Mandatory Information)

A1. LIST OF UNITS AND SYMBOLS

A	=	amperes of current
V	=	volts
nm	=	nanometres of optical wavelength
s	=	seconds of time
cm^3	=	cubic centimetre of volume
g	=	grams of a test substance
gP	=	grams of phosphorus atoms
gS	=	grams of sulfur atoms
gC	=	grams of carbon atoms
A_i	=	integrated peak area, A·s
$m_{P,S}$	=	mass of P-atoms or S-atoms, gP or gS
$\dot{m}_{P,S}$	=	mass flow rate of P-atoms or S-atoms, gP/s or gS/s
$S_{P,S,C}$	=	detector sensitivity to phosphorus, sulfur, or carbon, A·s/gP, A/(gS/s) ^{n}, or A·s/gC
n	=	power law of sulfur response
C_{tS}	=	concentration of S-atoms in the carrier gas at time *t* after introduction into a dilution flask, gS/cm^3
C_o	=	initial concentration of a test substance introduced into a dilution flask, g/cm^3
Y_S	=	mass percent of sulfur atoms in a test substance
C_{oS}	=	initial concentration of S-atoms introduced into a dilution flask, gS/cm^3
V_f	=	volume of a dilution flask, cm^3
F_f	=	carrier gas flow rate corrected to temperature of the dilution flask, cm^3 /min
E	=	detector signal, A
R_S	=	permeation rate of S-atoms from a permeation device, gS/min
t_S	=	peak width at (½)^n of the maximum peak height of sulfur compound chromatographic peak, s
$R'_{P,S}$	=	diffusion rate of P-atoms or S-atoms from a diffusion bulb apparatus, gP/min or gS/min
$D_{P,S}$	=	minimum detectability for phosphorus or sulfur, gP/s or gS/s
$N_{P,S}$	=	peak-to-peak noise level in phosphorus or sulfur modes, A
H	=	peak height of a chromatographic peak, A
t_P	=	peak width at one half of the maximum peak height of a phosphorus compound chromatographic peak, s
LR	=	linear range of the detector in the phosphorus mode
$\dot{m}_{Pmax}$	=	mass flow rate of P-atoms at the upper limit of linearity, gP/s
UR	=	range of unipower response of the detector in the sulfur mode
$\dot{m}_{Smax}$	=	mass flow rate of S-atoms at the upper limit of unipower response, gS/s
X_{PC}	=	phosphorus to carbon specificity ratio with the phosphorus optical filter, gC/gP
X_{PS}	=	phosphorus to sulfur specificity ratio with the phosphorus optical filter, gS/gP
X_{SC}	=	sulfur to carbon specificity ratio with the sulfur optical filter, gC/gS
X_{SP}	=	sulfur to phosphorus specificity ratio with the sulfur optical filter, gP/gS

A2. CORRECTION OF FLOW RATE TO DETECTOR TEMPERATURE

A2.1 Since carrier gas flow rate is usually measured at ambient (room) temperature, it has to be corrected to express conditions at the temperature of the detector.

A2.2 The correction is made according to the following equation:

$$F_f = F_o \, T_d/T_a \, (1 - p_w/p_a) \tag{A2.1}$$

where:

F_f = corrected flow rate, mL/min,
F_o = flow rate measured at column or detector outlet and ambient temperature, mL/min,
T_d = detector temperature, K,
T_a = ambient temperature, K,
p_w = partial pressure of water at ambient temperature, torr, and
p_a = ambient pressure, torr.

A2.3 The factor $(1 - p_w / p_a)$ is to be applied only if a wet (for example, soap bubble) flow meter is used for the measurement.

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