



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.

1.8 *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

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), 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 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 $CO + O \rightarrow CO_2 + h\nu$ 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.

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

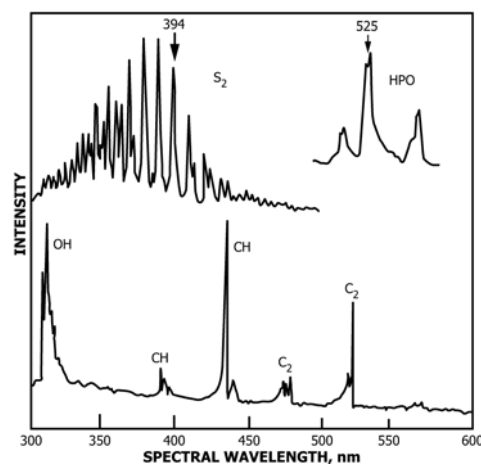


FIG. 1 Spectral Distribution of Molecular Emissions from an FPD Flame

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.