



Designation: E 594 – 96 (Reapproved 2001)

Standard Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography¹

This standard is issued under the fixed designation E 594; 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 serves as a guide for the testing of the performance of a flame ionization detector (FID) used as the detection component of a gas or supercritical fluid (SF) chromatographic system.

1.2 This recommended practice is directly applicable to an FID that employs a hydrogen-air or hydrogen-oxygen flame burner and a d-c biased electrode system.

1.3 This recommended practice covers the performance of the detector itself, independently of the chromatographic column, the column-to-detector interface (if any), and other system components, in terms that the analyst can use to predict overall system performance when the detector is made part of a complete chromatographic system.

1.4 For general gas chromatographic procedures, Practice E 260 should be followed except where specific changes are recommended herein for the use of an FID. For definitions of gas chromatography and its various terms see Recommended Practice E 355.

1.5 For general information concerning the principles, construction, and operation of an FID, see Refs (1, 2, 3, 4).²

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific safety information, see Section 5.

2. Referenced Documents

2.1 ASTM Standards:

E 260 Practice for Packed Column Gas Chromatography³

E 355 Practice for Gas Chromatography Terms and Relationships³

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

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² The boldface numbers in parentheses refer to the list of references appended to this recommended practice.

³ *Annual Book of ASTM Standards*, Vol 3.06.

E 1449 Standard Guide for Supercritical Fluid Chromatography Terms and Relationships³

2.2 CGA Standards:

CGA P-1 Safe Handling of Compressed Gases in Containers⁴

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations⁴

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium⁴

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures⁴

CGA P-12 Safe Handling of Cryogenic Liquids⁴

HB-3 Handbook of Compressed Gases⁴

3. Terminology

3.1 Definitions:

3.1.1 *drift*—the average slope of the baseline envelope expressed in amperes per hour as measured over 1/2 h.

3.1.2 *noise (short-term)*—the amplitude expressed in amperes of the baseline envelope that includes all random variations of the detector signal of a frequency on the order of 1 or more cycles per minute (see Fig. 1).

3.1.2.1 *Discussion*—Short-term noise corresponds to the observed noise only. The actual noise of the system may be larger or smaller than the observed value, depending upon the method of data collection or signal monitoring from the detector, since observed noise is a function of the frequency, speed of response, and the bandwidth of the electronic circuit measuring the detector signal.

3.1.3 *other noise*—Fluctuations of the baseline envelope of a frequency less than 1 cycle per minute can occur in chromatographic systems.

3.1.4 *Discussion*—The amplitude of these fluctuations may actually exceed the short-term noise. Such fluctuations are difficult to characterize and are not typically to be expected. They are usually caused by other chromatographic components such as the column, system contaminants, and flow variations. These other noise contributions are not derived from the detector itself and are difficult to quantitate in a general

⁴ Available from Compressed Gas Association, Inc., 1725 Jefferson Davis Highway, Arlington, VA 22202-4100.

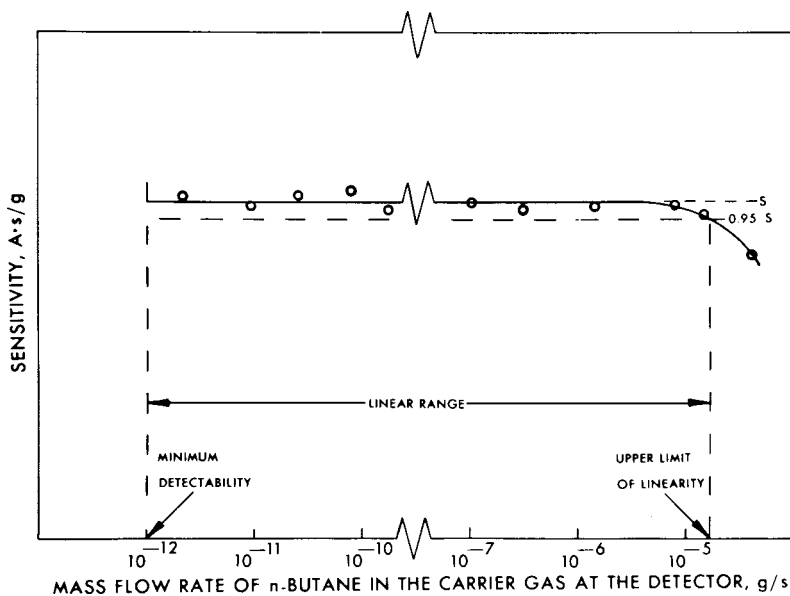


FIG. 1 Example of the FID Noise Level and Drift Measurement.

manner. It is, however, important for the practicing chromatographer to be aware of the occurrence of this type of noise contribution.

4. Significance and Use

4.1 Although it is possible to observe and measure each of the several characteristics of a detector under different and unique conditions, it is the intent of this recommended practice that a complete set of detector specifications should be obtained at the same operating conditions, including geometry, flow rates, and temperatures. It should be noted that to specify a detector's capability completely, its performance should be measured at several sets of conditions within the useful range of the detector. The terms and tests described in this recommended practice are sufficiently general so that they may be used at whatever conditions may be chosen for other reasons.

4.2 The FID is generally only used with non-ionizable supercritical fluids as the mobile phase. Therefore, this standard does not include the use of modifiers in the supercritical fluid.

4.3 Linearity and speed of response of the recording system or other data acquisition device used should be such that it does not distort or otherwise interfere with the performance of the detector. Effective recorder response, Refs. (5,6) in particular, should be sufficiently fast so that it can be neglected in sensitivity of measurements. If additional amplifiers are used between the detector and the final readout device, their characteristics should also first be established.

5. Hazards

5.1 *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 CGA publications include CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, and HB-3.

6. Noise and Drift

6.1 Methods of Measurement:

6.1.1 With the attenuator set at maximum sensitivity (minimum attenuation), adjust the detector output with the "zero" control to near mid-scale on the recorder. Allow at least ½ h of baseline to be recorded. Draw two parallel lines to form an envelope that encloses the random excursions of a frequency of approximately 1 cycle per minute or more. Measure the distance between the parallel lines at any particular time. Express the value as amperes of noise.

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

NOTE 1—This method covers most cases of baseline drift. Occasionally, with sinusoidal baseline oscillations of lower frequency, a longer measurement time should be used. This time must then be stated and the drift value normalized to 1 h.

6.1.3 In specifications giving the measured noise and drift of the FID, specify the test conditions in accordance with 7.2.4.

7. Sensitivity (Response)

7.1 Sensitivity (response) of the FID is the signal output per unit mass of a test substance in the carrier gas, in accordance with the following relationship:

$$S = \frac{A_i}{m} \quad (1)$$

where:

S = sensitivity (response), A·s/g,

A_i = integrated peak area, A·s, and

m = mass of the test substance in the carrier gas, g.

7.2 Test Conditions:

7.2.1 Normal butane is the preferred standard test substance.

7.2.2 The measurement must be made within the linear range of the detector.

7.2.3 The measurement must be made at a signal level at least 200 times greater than the noise level.

7.2.4 The test substance and the conditions under which the detector sensitivity is measured must be stated. This will include, but not necessarily be limited to, the following:

7.2.4.1 Type of detector,

7.2.4.2 Detector geometry (for example, electrode to which bias is applied),

7.2.4.3 Carrier gas,

7.2.4.4 Carrier gas flow rate (corrected to detector temperature and fluid pressure),

7.2.4.5 Make-up gas,

7.2.4.6 Make-up gas flow rate,

7.2.4.7 Detector temperature,

7.2.4.8 Detector polarizing voltage,

7.2.4.9 Hydrogen flow rate,

7.2.4.10 Air or oxygen flow rate,

7.2.4.11 Method of measurement, and

7.2.4.12 Electrometer range setting.

7.3 *Methods of Measurement:*

7.3.1 Sensitivity may be measured by any of three methods:

7.3.1.1 Experimental decay with exponential dilution flask (7) (see 7.4).

7.3.1.2 Utilizing the permeation device (8) under steady-state conditions (see 7.5).

7.3.1.3 Utilizing Young's apparatus (9) under dynamic conditions (see 7.6).

7.3.2 Calculation of FID sensitivity by utilizing actual chromatograms is not preferred because in such a case the amount of test substance at the detector may not be the same as that introduced.

7.4 *Exponential Dilution Method:*

7.4.1 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.

7.4.2 Calculate the concentration of the test substance in the carrier gas at the outlet of the flask at any time as follows (see Annex A1):

$$C_f = C_o \exp [-F_f t/V_f] \quad (2)$$

where:

C_f = concentration of the test substance at time t after introduction into the flask, g/mL,

C_o = initial concentration of the test compound introduced into the flask, g/mL,

F_f = carrier gas flow rate, corrected to flask temperature (see Annex A1), mL/min,

t = time, min, and

V_f = volume of flask, mL.

7.4.3 Calculate the sensitivity of the detector at any concentration as follows:

$$S = \frac{60E}{C_f F_f} \quad (3)$$

where:

S = sensitivity, A·s/g,

E = detector signal, A,

C_f = concentration of the test substance at time, t , after introduction into the flask, g/mL, and

F_f = carrier gas flow rate, corrected to flask temperature (see Annex A1), mL/min.

NOTE 2—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 3—A temperature difference of 1 C between flask and flow-measuring apparatus will, if uncompensated, introduce an error of 1/3 % into the flow rate.

NOTE 4—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 5—Flask volumes between 100 and 500 mL have been found the most convenient. Larger volumes should be avoided due to difficulties in obtaining efficient mixing and likelihood of temperature gradients.

NOTE 6—This method may not be used with supercritical-fluid mobile phases unless the flask is specifically designed and rated for the pressure in use.

7.5 *Method Utilizing Permeation Devices:*

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

7.5.2 Accurately known permeation rates can be prepared by passing a gas over the previously calibrated permeation device at constant temperature. Knowing this permeation rate, R_p , the sensitivity of the detector can be obtained from the following equation:

$$S = \frac{60E}{R_p} \quad (4)$$

where:

S = sensitivity, A·s/g,

E = detector signal, A, and

R_p = permeation rate of a test substance from the permeation device, g/min.

NOTE 7—Permeation devices are suitable only for preparing relatively low concentrations in the part-per-million range. In addition, only a limited range of linearity can be explored because it is experimentally difficult to vary the permeation rate over an extended range. Thus, for detectors of relatively low sensitivity or of higher noise levels, this method may not satisfy the criteria given in 4.2.3, which requires that the signal be at least 200 times greater than the noise level. A further limitation in the use of permeation devices is the relatively slow equilibration of the permeation rate, coupled with the life expectancy of a typical device which is on the order of a few months.

NOTE 8—This method may not be used with supercritical-fluid mobile phase. SC-CO₂ would adversely affect the permeation tube by either extracting the polymer or swelling the tube, resulting in a potential safety hazard.