Designation: E594 – 96 (Reapproved 2011)

Standard Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography[1]

This standard is issued under the fixed designation E594; 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 covers 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 dc 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 E260 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 E355.

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

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 5.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *CGA Standards:*

CGA P-1 Safe Handling of Compressed Gases in Containers[4]

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations[4]

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium[4]

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures[4]

CGA P-12 Safe Handling of Cryogenic Liquids[4]

HB-3 Handbook of Compressed Gases[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *drift*—the average slope of the baseline envelope expressed in amperes per hour as measured over ½ 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

[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 Nov. 1, 2011. Published December 2011. Originally approved in 1977. The last previous edition approved in 2006 as E594 – 96 (2011). DOI: 10.1520/E0594-96R11.

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

[3] 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.

[4] Available from Compressed Gas Association (CGA), 4221 Walney Rd., 5th Floor, Chantilly, VA 20151-2923, http://www.cganet.com.

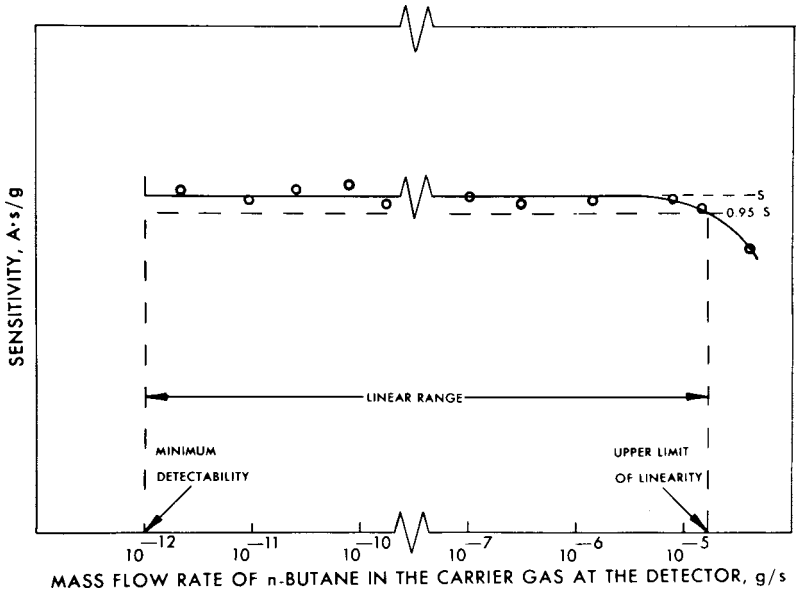

FIG. 1 Example of the FID Noise Level and Drift Measurement

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 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, Bonsall (**5**) and McWilliam (**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 chromtography is the responsibility of every laboratory. The 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:

$$S = \frac{A_i}{m} \tag{1}$$

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 presssure),

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 introducton 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 ⅓ % 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_t, the sensitivity of the detector can be obtained from the following equation:

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

where:

S = sensitivity, A·s/g,
E = detector signal, A, and
R_t = 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 7.2.3, 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-CO_2 would adversly affect the permeation tube by either

extracting the polymer or swelling the tube, resulting in a potential safety hazard.

7.6 *Dynamic Method:*

7.6.1 In this method, inject a known quantity of test substance into the flowing carrier gas stream. A length of empty tubing or an empty high-pressure cell between the sample injection point 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.

7.6.2 As an alternative to 7.6.1, an actual chromatogram may be generated by substituting a column for the length of empty tubing. This approach 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 overcome support adsorption effects. Likewise a nonpolar sample will minimize these adverse interactions. For example, a column prepared with OV101 on Chromosorb G[5] with a *n*-octane sample should best ensure that the entire sample introduced will reach the detector.

7.6.3 Calculate the sensitivity of the detector from the peak area and the mass injected in accordance with 7.1.

NOTE 9—Care should be taken that the peak obtained is sufficiently wide so the accuracy of the integration is not limited by the response time of the recording device.

NOTE 10—The approach given here should be used with caution as it has not been applied over a wide concentration range.

8. Minimum Detectability

8.1 Minimum detectability is the mass flow rate of the test substance in the carrier gas that gives a detector signal equal to twice the noise level and is calculated from the measured sensitivity and noise level values as follows:

$$D = 2N/S \tag{5}$$

where:

D = minimum detectability, g/s,
N = noise level, A, and
S = sensitivity of the detector, A·s/g.

8.2 *Test Conditions*—Measure sensitivity in accordance with the specifications given in Section 6. Measure noise level in accordance with the specifications given in Section 5. Both measurements must be carried out at the same conditions (for example, carrier gas flow rate and detector temperature) and preferably at the same time. When giving minimum detectability, state the noise level on which the calculation was based.

9. Linear Range

9.1 The linear range of an FID is the range of mass flow rates of the test substance in the carrier gas, over which the sensitivity of the detector is constant to within 5 % as determined from the linearity plot specified in 9.2.2.

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

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

$$LR = \dot{m}_{max}/D \tag{6}$$

where:

LR = linear range of the detector,
$\dot{m}_{max}$ = upper limit of linearity obtained from the linearity plot, g/s, and
D = minimum detectability, g/s.

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

9.1.1.2 By giving the minimum detectability and the upper limit of linearity (for example, from 1×10^{-12} g/s to 1×10^{-5}g/s).

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

9.2 *Method of Measurement:*

9.2.1 For the determination of the linear range of an FID, use either the exponential decay or the dynamic methods described in 7.4 and 7.6 respectively. The permeation device method (7.5) will not be suitable because of the limited range of concentrations obtainable with that method.

9.2.2 Measure the sensitivity at various mass flow rates of the test substance in the carrier gas in accordance with the methods described above. Plot the sensitivity versus log mass flow rate on a semilog paper as shown in Fig. 2. Draw a smooth line through the data points. The upper limit of linearity is given by the intersection of this line with a value $0.95 \times S$, where S is the constant value of sensitivity as determined by a least squares fit of the lower four decades of sample mass flow rate.

9.2.3 In giving the linear range or the linearity plot, specify the test condition in accordance with 7.2.4.

10. Dynamic Range

10.1 The dynamic range of the detector is that range of mass flow rates of the test substance, over which an incremental change in mass flow rate produces an incremental change in detector signal. The lower limit is given by the 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, and the dynamic range is the ratio of these upper and lower limits. The dynamic range is larger than or equal to the linear range, but obviously cannot be smaller.

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

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

10.1.1.2 By giving the minimum detectability and the upper limit of dynamic range (for example, from 1×10^{-12} g/s to 1×10^{-3} g/s).

[5] Chromasorb G is a registered trademark of Johns-Manville Products Corp. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

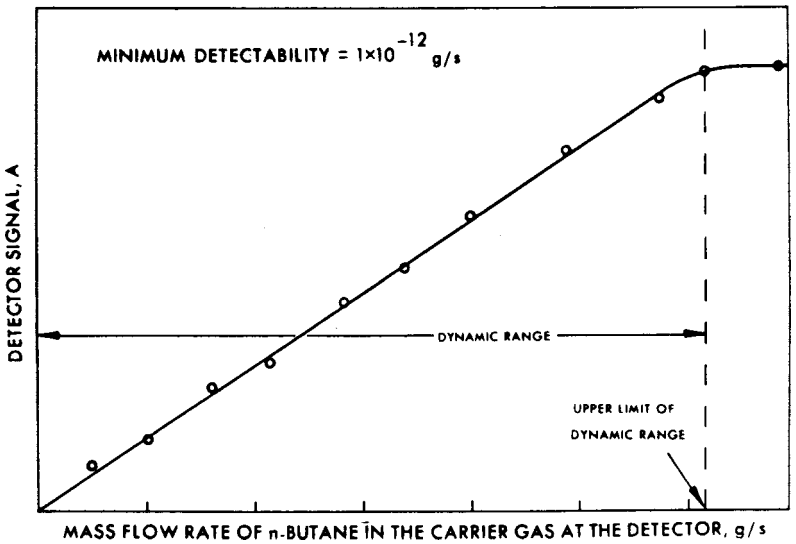

FIG. 2 Example of an FID Linearity Plot

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

10.2 *Methods of Measurement:*

10.2.1 Using the exponential decay method (see section 7.4), measure the detector output signal (E) at various mass flow rates ($\dot{m}$) of the test substance in the carrier gas. Plot E versus $\dot{m}$ on rectilinear graph paper, and draw a smooth curve through the data points as shown in Fig. 3. The upper limit of the dynamic range is the concentration 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 7.2.4.

11. Response Time

11.1 For an FID, response time is not an important parameter. The FID is a mass-sensitive detector and does not directly depend on flow rate or concentration. The time constant for ionization is negligible (sub-second). Because the detector is not diffusion based, the transit time of the sample through the detector has little influence. Provided that measurements are made within the linear range of operation, the response time should not have an appreciable effect. In actuality, in a typical FID system, the electrometer/amplifier is the limiting factor and imposes a time constant of a few hundred milliseconds.

12. Standard Values

12.1 Detector characteristics measured at optimum conditions recommended by the manufacturer may be expected to fall within the typical range of values listed in Table 1, which also indicates the way these values should be expressed. All data refer to *n*-butane as the test substance.

13. Keywords

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

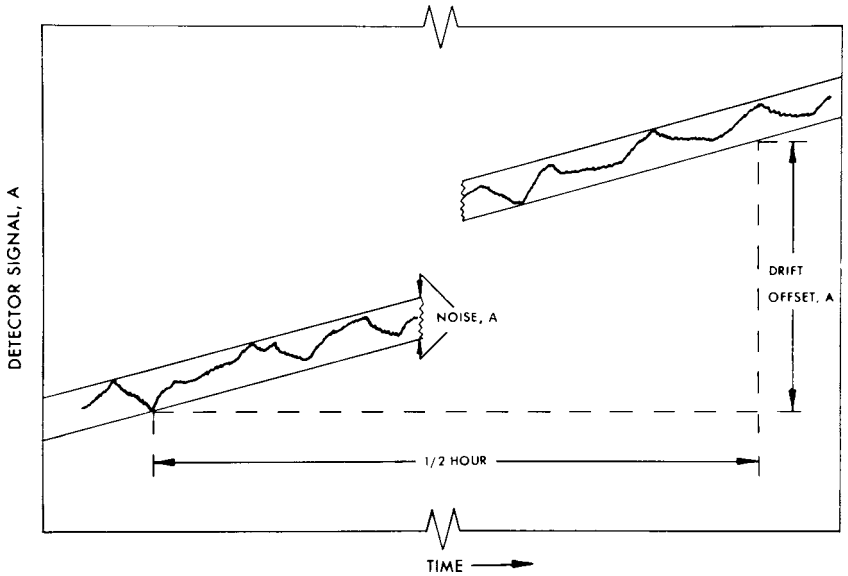

FIG. 3 Example of a Plot to Determine the Dynamic Range of an FID

TABLE 1 Typical Values for Flame Ionization Detector Performance Characteristics

Performance Characteristics	Unit	Typical Values
Sensitivity	A·s	0.005 to 0.02
Minimum detectability	g/s	10^{-12} to 10^{-11}
Linear range	...	10^{6} to 10^{7}
Dynamic range	...	10^{8} to 10^{9}
Noise	A	10^{-14} to 10^{-13}
Drift	A/h	10^{-13} to 10^{-12}

ANNEXES

A1. CORRECTION OF FLOW RATE TO DETECTOR TEMPERATURE

A1.1 Since the carrier gas flow rate is usually measured at ambient (room) temperature, it has to be corrected to the conditions at the detector.

A1.2 The correction is made using the following equation:

$$F_f = F_o\,(T_f/T_a)\,(p_f/p_a)\,[1 - (p_w/p_a)] \qquad \text{(A1.1)}$$

where:

F_f = corrected flow rate, mL/min,
F_o = flow rate measured at column or detector outlet and ambient temperature, mL/min,
T_f = flask temperature, **K**,
T_a = ambient temperature, **K**,
p_w = partial pressure of water at ambient temperature, torr (**9**)
p_a = ambient pressure, torr, and
p_f = flask pressure, torr.

A1.3 Soap bubble flow meters may only be used with gases such as helium, hydrogen and nitrogen with low permeation rates through soap bubble films. Soap bubble meters are usually not suitable to measure CO_2 flows. Since CO_2 is soluble in water and will dissolve in the soap solution, it is not possible to accurately measure slow CO_2 flow rates with conventional soap-bubble procedures. Several possible ways to compensate for the dissolution of CO_2 in the soap solution are: (*1*) Acidify the soap bubble solution (that is, with acetic acid) to reduce CO_2 solubility, (*2*) substitute glycerine for water, or (*3*) use a standard flow meter calibrated for CO_2 .

A2. LIST OF SYMBOLS AND ABBREVIATIONS

A_i = peak area obtained by integration, A·s
C_f = concentration of a test substance in the carrier gas at time t (minutes) after introduction into the dilution flask, g/mL
C_o = initial concentration of a test substance in the dilution flask, g/mL
D = detectability, g/s
E = detector signal, A
F_t = carrier gas flow rate corrected to the temperature of flask, mL/min
F_o = carrier gas flow rate measured at the outlet of the column or detector, at ambient temperature, mL/min
FID = flame ionization detector
LR = linear range
m = mass of test substance, g
$\dot{m}$ = mass flow rate, g/s
$\dot{m}_{max}$ = mass flow rate at upper limit of linearity, g/s
N = noise level, A
p_a = ambient pressure, torr
p_w = partial pressure of water at ambient temperature, torr
p_f = carrier gas pressure in the flask, torr
R_T = permeation rate of a test substance from the permeation tube, g/min
S = detector sensitivity, A· s/g
T_a = ambient temperature, K
T_d = temperature of the detector, K
t = time from sample introduction into the dilution flask, min
V_f = volume of the dilution flask, mL

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