



Designation: E 516 – 95a (Reapproved 2000)

## Standard Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation E 516; 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 to serve as a guide for the testing of the performance of a thermal conductivity detector (TCD) used as the detection component of a gas chromatographic system.

1.2 This practice is directly applicable to thermal conductivity detectors which employ filament (hot wire) or thermistor sensing elements.

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

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

1.5 For general information concerning the principles, construction, and operation of TCD see Refs. (1-4).<sup>2</sup>

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 4.<sup>3</sup>

### 2. Referenced Documents

#### 2.1 ASTM Standards:

E 260 Practice for Packed Column Gas Chromatography<sup>4</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>4</sup>

#### 2.2 CGA Standards:

CGA P-1 Safe Handling of Compressed Gases in Containers<sup>5</sup>

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations<sup>5</sup>

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium<sup>5</sup>

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures<sup>5</sup>

CGA P-12 Safe Handling of Cryogenic Liquids<sup>5</sup>

HB-3 Handbook of Compressed Gases<sup>5</sup>

### 3. Significance and Use

3.1 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 practice that a complete set of detector specifications should be obtained at the same operating conditions. It should be noted also 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 practice are sufficiently general so that they may be used at whatever conditions may be chosen for other reasons.

3.2 Linearity and speed of response of the recorder 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 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.

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

<sup>5</sup> Available from Compressed Gas Association, Inc., 1725 Jefferson Davis Highway, Arlington, VA 22202-4100.

<sup>1</sup> This 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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<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this practice.

<sup>3</sup> See Appendix X1.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.01

## 5. Sensitivity (Response)

### 5.1 Definition:

5.1.1 Sensitivity (response) of the TCD is the signal output per unit concentration of a test substance in the carrier gas, in accordance with the following relationship (7):

$$S = A F_c / W \quad (1)$$

where:

- $S$  = sensitivity (response), mV·mL/mg,
- $A$  = integrated peak area, mV·min,
- $F_c$  = carrier gas flow rate (corrected to detector temperature<sup>5</sup>), mL/min, and
- $W$  = mass of the test substance in the carrier gas, mg.

5.1.2 If the concentration of the test substance in the carrier gas, corresponding to a detector signal is known, the sensitivity is given by the following relationship:

$$S = E / C_d \quad (2)$$

where:

- $E$  = peak height, mV, and
- $C_d$  = concentration of the test substance in the carrier gas at the detector, mg/mL.

### 5.2 Test Conditions:

5.2.1 Normal butane is the preferred standard test substance.

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

5.2.3 The measurement must be made at a signal level at least 100 times greater than the minimum detectability (200 times greater than the noise level) at the same conditions.

5.2.4 The rate of drift of the detector at the same conditions must be stated.

5.2.5 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:

5.2.5.1 Type of detector (for example, platinum-tungsten filament type),

5.2.5.2 Detector geometry (for example, flow-type, diffusion-type),

5.2.5.3 Internal volume of the detector,

5.2.5.4 Carrier gas,

5.2.5.5 Carrier gas flow rate (corrected to detector temperature),

5.2.5.6 Detector temperature,

5.2.5.7 Detector current,

5.2.5.8 Method of measurement, and

5.2.5.9 Type of power supply (for example, constant voltage, constant current).

5.2.5.10 For capillary detectors, the make-up gas, carrier, and reference flows should be stated.

### 5.3 Methods of Measurement:

5.3.1 Sensitivity may be measured by any of three methods:

5.3.1.1 Experimental decay with exponential dilution flask (8, 9) (see 5.4),

5.3.1.2 Utilizing the permeation tube (10), under steady-state conditions (see 5.5),

5.3.1.3 Utilizing Young's apparatus (11), under dynamic conditions (see 5.6).

5.3.2 Calculation of TCD sensitivity by utilizing actual chromatograms is not recommended because in such a case the amount of test substance corresponding to the peak cannot be established with sufficient accuracy.

### 5.4 Exponential Decay Method:

5.4.1 A mixing vessel of known volume fitted with a magnetically driven stirrer is purged with the carrier gas at a known rate. The effluent from the flask is delivered directly to the detector. A measured quantity of the test substance is introduced into the flask, to give an initial concentration,  $C_o$ , of the test substance in the carrier gas, and a timer is started simultaneously.

5.4.2 The concentration of the test substance in the carrier gas at the outlet of the flask, at any time is given as follows:

$$C_t = C_o \exp [- F_c t / V_f] \quad (3)$$

where:

- $C_t$  = concentration of the test substance at time  $t$  after introduction into the flask, mg/mL,
- $C_o$  = initial concentration of test compound introduced in the flask, mg/mL,
- $F_c$  = carrier gas flow rate, corrected to flask temperature 4 mL/min,
- $t$  = time, min, and
- $V_f$  = volume of flask, mL.

5.4.3 To determine the concentration of the test substance at the detector,  $C_d$ , it is necessary to apply the following temperature correction:

$$C_d = C_t (T_f / T_d) \quad (4)$$

where:

- $C_d$  = concentration of the test substance at the detector, mg/mL,
- $T_f$  = flask temperature, K, and
- $T_d$  = detector temperature, K.

5.4.4 The sensitivity of the detector at any concentration can be calculated by:

$$S = E / C_d \quad (5)$$

where:

- $S$  = sensitivity, mV·mL/mg,
- $E$  = detector, signal, mV, and
- $C_d$  = concentration of the test substance at the detector, mg/mL.

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 1/3 % 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 mL have been found the most convenient. Larger volumes should be avoided due to difficulties in obtaining efficient mixing and likelihood of temperature gradients.

### 5.5 Method Utilizing Permeation Tubes:

5.5.1 Permeation tubes consist of a volatile liquid enclosed in a section of plastic tubing. They provide low concentrations of vapor by diffusion of the vapor through the walls of the tubing. The rate of diffusion for a given permeation tube is dependent only on the temperature. As the weight loss over a period of time can be easily and accurately measured gravimetrically, the rate of diffusion can be accurately determined. Hence, these devices have been proposed as primary standards.

5.5.2 Accurately known concentrations can be prepared by passing a gas over the previously calibrated permeation tube at constant temperature. The concentration of the test substance in the gas can then be easily calculated according to the following relationship:

$$C = R_T/F_c \quad (6)$$

where:

- $C$  = concentration of the test substance in the gas, mg/mL,
- $R_T$  = permeation rate of the test substance at the temperature of the permeation tube, mg/min, and
- $F_c$  = flow rate of the gas over the tube at the temperature of the tube, mL/min.

NOTE 5—If the flow rate of the gas is measured at a temperature different from the tube temperature, correction must be made, as described in Appendix X1.

5.5.3 When using a permeation tube for the testing of a TCD, the carrier gas is passing over a previously calibrated permeation tube containing the test substance at constant temperature and introduced immediately into the detector, kept at the desired temperature. Knowing the concentration of the test substance in the carrier gas leaving the permeation tube at the temperature of the tube, the concentration at detector temperature can be calculated directly, by applying the correction specified in 5.4.2. Knowing this value and the detector signal, the sensitivity of the detector can be obtained according to the equation given in 5.4.4.

NOTE 6—Permeation tubes are suitable only for preparing relatively low concentrations in the part-per-million range. Hence for detectors of relatively low sensitivity or of higher noise levels, this method may not satisfy the criteria given in 5.2.3, which requires that the signal be at least 100 times greater than the noise level.

### 5.6 Dynamic Method:

5.6.1 In this method a known quantity of test substance is injected into the flowing carrier gas stream. A length of empty tubing between the sample injection point and the detector permits the band to spread and be detected as a Gaussian band. The detector signal is then integrated by any suitable method. This method has the advantage that no special equipment or devices are required other than conventional chromatographic hardware. For detectors optimized for capillary column flow rates, uncoated, deactivated, fused silica tubing should be used.

5.6.2 The sensitivity of the detector is calculated from the peak area according to 5.1.1.

NOTE 7—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 detector or of the recording device.

NOTE 8—Peak areas obtained by integration ( $A_i$ ) or by multiplying peak height by peak width at half height ( $A_c$ ) differ by 6 % for a Gaussian peak:

$$A_c = 0.94 A_i \quad (7)$$

## 6. Minimum Detectability

6.1 *Definition*—Minimum detectability is the concentration of the test substance in the carrier gas which gives a detector signal equal to twice the noise level and is calculated from the measured sensitivity and noise level values as follows:

$$D = 2N/S \quad (8)$$

where:

- $D$  = minimum detectability, mg/mL,
- $N$  = noise level, mV, and
- $S$  = sensitivity of the detector, mV·mL/mg.

6.2 *Test Conditions*—Measure sensitivity in accordance with the specifications given in Section 5. Measure noise level in accordance with the specifications given in Section 9. Both measurements have to be carried out at the same conditions (for example, carrier gas identity and flow rate, detector temperature, and current) and preferably at the same time. When giving minimum detectability, state the noise level on which the calculation was based.

## 7. Linear Range

7.1 *Definition*—The linear range of a TCD is the range of concentrations 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 7.2.2.

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

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

$$\text{L.R.} = (C_d)_{\max}/D \quad (9)$$

where:

- L.R. = linear range of the detector,
- $(C_d)_{\max}$  = upper limit of linearity obtained from the linearity plot, mg/mL, and
- $D$  = minimum detectability, mg/mL.

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

7.1.1.2 By giving the minimum detectability and the upper limit of linearity (for example, from  $1 \times 10^{-6}$  mg/mL to  $2 \times 10^{-1}$  mg/mL).

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

### 7.2 Method of Measurement:

7.2.1 For the determination of the linear range of a TCD, either the exponential decay or the dynamic methods described in 5.4 and 5.6 respectively may be used. The permeation tube method (5.5) will not be suitable except for detectors of extremely unusual characteristics because of the limited range of concentrations obtainable with that method.

7.2.2 Measure the sensitivity at various concentrations of the test substance in the carrier gas in accordance with the methods described above. Plot the sensitivity versus log concentration on a semilog paper as shown in Fig. 1. Draw a smooth line through the data points. The upper limit of

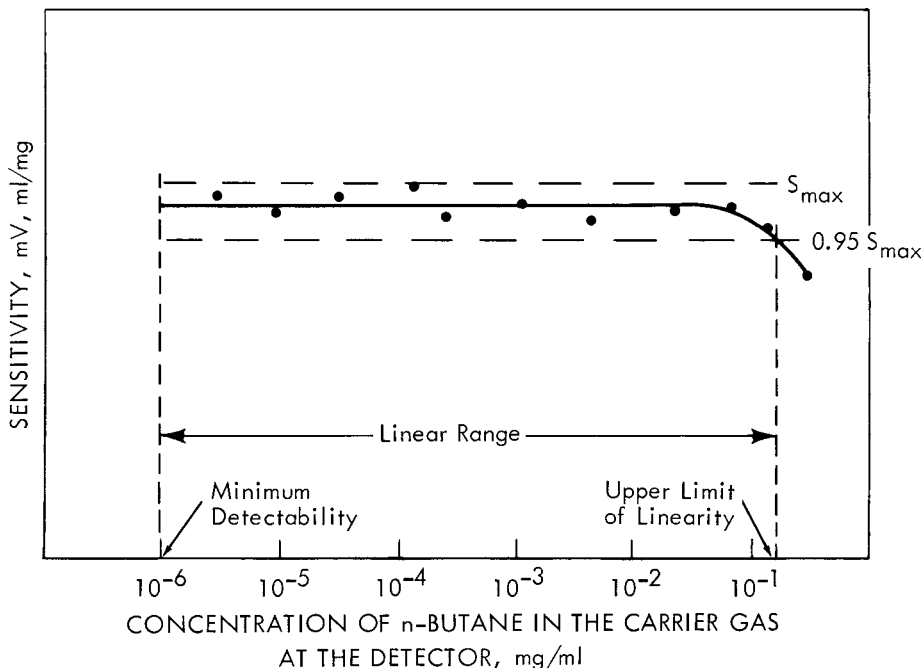


FIG. 1 Example for a Linearity Plot of a Thermal Conductivity Detector

linearity is given by the intersection of the line with a value  $0.95 \times S_{\max}$  where  $S_{\max}$  is the highest value of sensitivity on the fitted curve.

NOTE 9—The dynamic method will give somewhat larger values for the upper limit of linearity as compared to the exponential decay method, because the integrated signal will average increments of signal obtained over the linear range of the detector with those obtained in the nonlinear range.

7.2.3 Express the linear range in accordance with 7.1.1.

7.2.4 In giving the linear range of the linearity plot, specify the test conditions in accordance with 5.2.5.

## 8. Dynamic Range

8.1 *Definition*—The dynamic range of the detector is that range of concentrations of the test substance, over which a change in concentration produces a change in detector signal. The lower limit is given by the minimum detectability. The upper limit is the highest concentration at which a slight further increase in concentration will give an observable increase in detector signal, and the dynamic range is the ratio of the upper and lower limits. The dynamic range can be greater than the linear range, but obviously cannot be smaller.

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

8.1.1.1 As the ratio of the upper limit of dynamic range and the minimum detectability by simultaneously stating the minimum detectability (for example,  $2 \times 10^6$  with a minimum detectability of  $1 \times 10^{-6}$  mg/mL).

8.1.1.2 By giving the minimum detectability and the upper limit of dynamic range (for example, from  $1 \times 10^{-6}$  mg/mL to 2 mg/mL).

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

8.2 *Methods of Measurement:*

8.2.1 Using the exponential decay method (see 5.4), measure the detector output signal ( $E$ ) at various concentrations ( $C_d$ ) of the test substance in the carrier gas. Plot  $E$  versus  $C_d$  on rectilinear 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 concentration at which the slope is zero.

8.2.2 Express the dynamic range according to 8.1.1.

8.2.3 In giving the dynamic range or the dynamic range plot, specify the test conditions in accordance with 5.2.5.

## 9. Noise and Drift

9.1 *Definitions:*

9.1.1 *noise*—the amplitude expressed in microvolts of the peak-to-peak envelope of the baseline which includes all observed random variations of the detector signal of a frequency on the order of one or more cycles per minute (see Fig. 3). This 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.

9.1.2 *drift*—the average slope of the noise envelope expressed in microvolts per hour as measured over  $\frac{1}{2}$  h.

9.2 *Methods of Measurement:*

9.2.1 With the attenuator set at maximum sensitivity (minimum attenuation) adjust the detector output with the “zero” control to read near mid-scale on the recorder. Allow at least  $\frac{1}{2}$  h of baseline to be recorded.

9.2.2 Draw two parallel lines to form an envelope which encloses the random excursions of a frequency of approximately 0.0167 Hz (1 cycle per minute) or more. Measure the



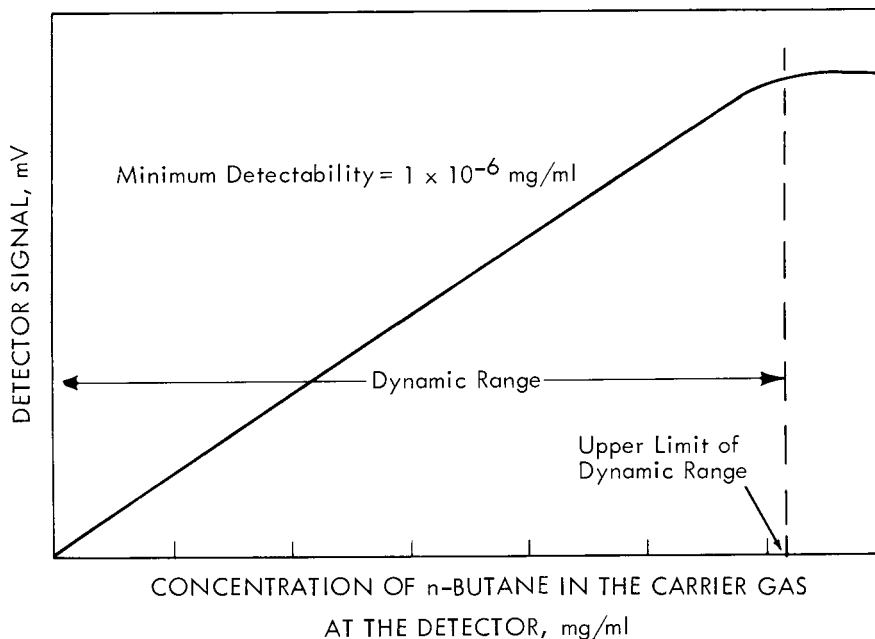


FIG. 2 Example for a Plot to Determine the Dynamic Range of a Thermal Conductivity Detector

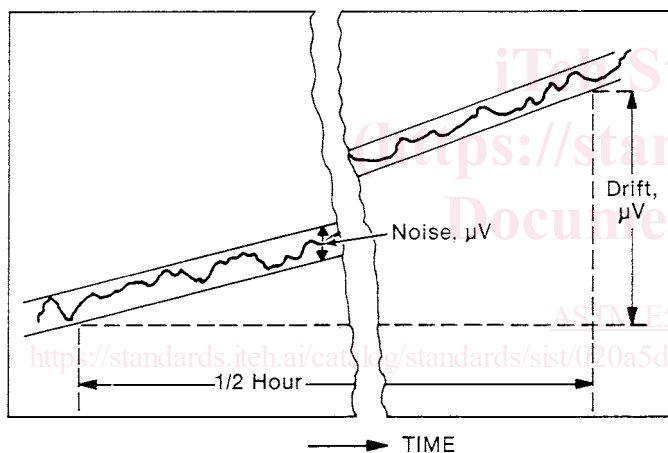


FIG. 3 Example for the Measurement of the Noise Level and Drift of a Thermal Conductivity Detector

distance between the parallel lines at right angles to the edge of the chart paper. Express the value as microvolts of noise.

9.2.3 Measure the net change in microvolts of the lower line of the envelope over 1/2 h and multiply by two. Express as microvolts per hour drift.

9.2.4 In specifications giving the measured noise and drift of the TCD, specify the test conditions in accordance with 5.2.5.

## 10. Response Time

10.1 *Definition*—The response time (speed of response) of the detector at a given flow rate is the time required for the output signal to reach 63 % of the new equilibrium value when the composition of the gas entering the detector is changed in a stepwise manner, within the linear range of the detector. Internal volume and geometry of the detector must also be stated as part of this specification. Response time may be determined and specified at various flow rates.

10.1.1 The response time of the detector is determined by a combination of effective volume and time constant of the sensing elements. Effective volume determines the time required to introduce a compositional change into the measuring region. Time constant is the time required for the elements to respond to concentration changes. Effective volume and time constant may also be separately specified in addition to the response time.

NOTE 10—For diffusion geometry detectors, the time required for the composition to come to equilibrium in the measuring region depends primarily on the volume, length, and diameter of the measuring region and diffusion channels, and of the diffusion constant of the carrier gas-test substance pair. For flow-geometry detectors, the response time is dependent primarily on the volume of the measuring region and the carrier gas flow rate. Hence a statement of the internal volume and geometry of the detector and of the flow rate is necessary for the specification to be complete.

### 10.2 Method of Measurement:

10.2.1 The composition of the gas entering the detector is changed in a stepwise manner and the output signal recorded. The time required for the signal to reach 63.2 % of the new equilibrium value is determined from the recorder chart (see Fig. 4). The test may be repeated at various flow rates.

10.2.2 Flow rates for the measurement should be chosen with due regard for the types (diameter) of columns for which the detector is designed. Table 1 lists typical flow rates used with various column types. The flow rates should be corrected to detector temperatures.<sup>6</sup>

10.2.3 A stepwise change in composition may be obtained by means of high-speed valves which rapidly substitute carrier gas with added test substance for pure carrier gas or for gas containing a different amount. The test substance may be added

<sup>6</sup> For correlation, see Appendix X1.

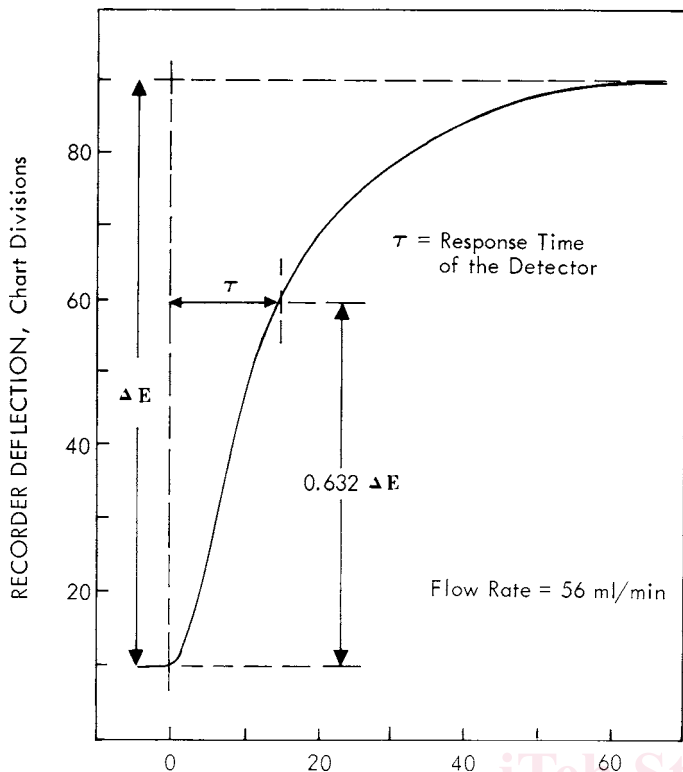


FIG. 4 Example for the Measurement of Response Time of a Thermal Conductivity Detector (12)

TABLE 1 Typical Carrier Gas Flow Rates for Various Column Types

Column Outside Diameter, in. (mm)	Column Inside Diameter, <sup>A</sup> in. (mm)	Flow Rate, mL/min
0.02 (0.5)	0.01 (0.25–0.32)	1 to 3
0.03 (0.75)	0.2 (0.53)	5 to 25
1/16 (1.6)	0.01 to 0.04 (0.25–1.02)	1 to 10
1/8 (3.2)	0.085 (2.16)	10 to 30
1/4 (6.4)	0.180 (4.57)	50 to 100

<sup>A</sup> Typical values.

TABLE 2 Typical Values for Thermal Conductivity Detector Performance Characteristics

Performance Characteristics	Unit	Range of Typical Values
Sensitivity	mV·mL/mg	5000 to 15 000
Minimum detectability	mg/mL	$3 \times 10^{-7}$ to $1 \times 10^{-5}$
Linear range (upper limit)	mg/mL	0.2 to 2.0
Dynamic range (upper limit)	mg/mL	2.1 to 2.4
Noise	$\mu$ V	5 to 50
Drift	$\mu$ V/h	20 to 250
Response time	s	0.5 to 5
Effective volume	$\mu$ L	5 to 500
Time constant	s	0.05 to 0.5

by means of a saturator which saturates the carrier gas with the vapor of a volatile liquid in the manner of Schmauch (12).

NOTE 11—Design of the apparatus should be such as to prevent backmixing of the two gases ahead of the detector, which would result in

a diffuse composition change.

10.2.4 Alternatively, a mixture of the carrier gas containing a known amount of the test substance may be used.

10.2.5 The concentration of the test substance must be within the linear range of the detector.

NOTE 12—Extreme care must be exercised to adjust the flow rates so that a change in flow rate does not occur when compositions are switched; otherwise errors due to flow sensitivity of the detector are introduced.

10.3 Calculation:

10.3.1 The response time of TCD may be expressed in two ways:

10.3.1.1 As the time, in seconds, obtained from a plot similar to Fig. 4 and the flow rate in millilitres per minute at which the test was made.

10.3.1.2 As a rectilinear plot of response time, in seconds, versus carrier gas flow rate, in millilitres per minute (see Fig. 5).

NOTE 13—Use of the plot of response time versus carrier gas flow rate is strongly recommended because it provides a better picture of the contributions of effective volume and sensing element time constant.

10.3.1.3 In either case, the internal geometry (for example, diffusion- or flow-through type) and the internal volume (in microlitres) of the detector must be stated.

10.3.2 The effective volume of the detector and the time constant of the sensing element may be established from the same data in the following way:

10.3.2.1 Plot the response time in seconds versus the reciprocal of the flow rate (that is, seconds per millilitre), draw a straight line through the data points, and extrapolate back to zero reciprocal flow rate (for example, infinite flow rate), as shown in Fig. 6.

10.3.2.2 The effective volume of the TCD is given by the slope of the straight line:

$$V_e = [\Delta\tau/\Delta(1/F_c)60]10^3 \quad (10)$$

where:

$V_e$  = effective volume of the detector,  $\mu$ L,

$\tau$  = response time of the detector, s, and

$F_c$  = carrier gas flow rate corrected to detector temperature,<sup>4</sup> mL/min.

10.3.2.3 The time constant of the sensing element is equal to the value of the ordinate at the intersection of the straight line at zero reciprocal flow rate.

10.3.3 The effective volume of the detector and the time constant of the sensing element may also be determined by the method of Kieselbach (13), in the following way:

10.3.3.1 Use a high-speed sampling valve to inject a plug sample of air into the detector. Determine the response time at various flow rates from the shape of the recorded peak, by drawing tangents through the inflection points. The response time is equal to the time interval from the intersection of the tangents to the point at which the signal has returned to 37 % of the value of the height of the intersection of the tangents (see Fig. 7).

10.3.3.2 Plot the data as described in 10.3.2.1 and calculate effective volume and time constant as described in 10.3.2.2 and 10.3.2.3.