



Designation: E516 – 95a (Reapproved 2005)

Standard Practice for Testing Thermal Conductivity Detectors Used in Gas Chromatography¹

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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 E260 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 E355.

1.5 For general information concerning the principles, construction, and operation of TCD see Refs. (1-4).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 4.³

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 The boldface numbers in parentheses refer to the list of references at the end of this practice.

³ See Appendix X1.

2. Referenced Documents

2.1 ASTM Standards:⁴

E260 Practice for Packed Column Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

2.2 CGA Standards:⁵

CGA P-1 Safe Handling of Compressed Gases in Containers
CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations

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

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

CGA P-12 Safe Handling of Cryogenic Liquids

HB-3 Handbook of Compressed Gases

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

⁴ 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.

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

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.

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 temperature⁵), 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 temperature⁴ 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 $\frac{1}{3}$ % 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:

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

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 1×10^{-6} mg/mL to 2×10^{-1} mg/mL).