



Designation: D 4599 – 9703

Standard Practice for Measuring the Concentration of Toxic Gases or Vapors Using Length-of-Stain Dosimeters¹

This standard is issued under the fixed designation D 4599; 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 describes the detection and measurement of time weighted average (TWA) concentrations of toxic gases or vapors using length-of-stain colorimetric dosimeter tubes. A list of some of the gases and vapors that can be detected by this practice is provided in Annex A1. This list is given as a guide and should be considered neither absolute nor complete.

1.2 Length-of-stain colorimetric dosimeters work by diffusional sampling. The results are immediately available by visual observation; thus no auxiliary sampling, test nor analysis equipment are needed. The dosimeters, therefore, are extremely simple to use and very cost effective.

1.3 *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.*

2. Referenced Documents

2.1 ASTM Standards:

¹ This practice is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

Current edition approved ~~March~~ April 10, 1997; 2003. Published ~~May~~ 1997; June 2003. Originally published as D 4599 – 86; approved in 1986. Last previous edition approved in 1997 as D 4599 – 907.

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres²

2.2 *Other Document:*

Federal Occupational Safety and Health Standard—Title 29 1910.1000 Subpart Z³

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology D 1356.

4. Summary of Practice

4.1 Length-of-stain colorimetric dosimeters consist of a sealed glass tube containing a detector inside the tube ~~(1-11)~~**(1-5)**.⁴ The detector is a length of granulated material impregnated with a reactive chemical that is sensitive to the particular gas for which the dosimeter is designed. To use the tube, one end is opened. The gas, if present, diffuses into the tube and reacts with the chemical reagent on the carrier material, causing the latter to change color. Each lot of dosimeters is individually calibrated so that by measuring the length of stain and the time of exposure, the TWA concentration to which the dosimeter has been exposed can be determined directly and immediately.

4.2 Information on the correct use of length of stain dosimeter tubes is presented.

5. Significance and Use

5.1 The Federal Occupational Safety and Health Administration in 29 CFR 1910.1000 Subpart Z designates that certain gases and vapors present in work place atmospheres must be controlled so that their concentrations do not exceed specified limits.

5.2 This practice will provide a means for the determination of airborne concentrations of certain gases and vapors listed in 29 CFR 1910.1000.

5.3 A partial list of chemicals for which this practice is applicable is presented in Annex A1 with current Threshold Limit Values (TLV) ~~(4)~~**(2)** and typical measurement ranges for the selected chemicals as obtained from various manufacturer's specifications.

5.4 This practice may be used for either personal or area monitoring.

6. Interferences

6.1 The instructions may provide correction factors to be applied when certain interferences are present. Some common interfering gases or vapors for each dosimeter are listed in the instruction sheets for the dosimeter provided by the manufacturers

7. Apparatus

7.1 *Dosimeter Tube:*

7.1.1 *General Description*—A length-of-stain dosimeter tube consists of a glass tube containing an inert granular material impregnated with a chemical system that reacts with the gas or vapor of interest. As a result of this reaction, the impregnated chemical changes color. The granular material is held in place within the glass tube by porous plugs of a suitable inert material. To protect the contents during storage, the ends of the glass tube are flame sealed. The calibration scale is printed on the tube to make it easy to read the length of stain of reacted chemical.

7.1.2 *Stability on Storage*—Stability on storage may vary depending on manufacturer and type of dosimeter, but most dosimeter tubes can be stored for at least 24 months with no deleterious effects.

7.2 *Tube Holders*— During use, the dosimeter tube is held in a lightweight, plastic holder. The tube holder protects the dosimeter during use and also helps to minimize effects of air currents on performance. The holder has a clip that allows it to be fastened to a collar or pocket during personal sampling or to some appropriate object during area sampling.

8. Reagents

8.1 The reagents used to impregnate the granular material in the dosimeters are specific for each tube, and, to detect a specific gas or vapor, may vary from manufacturer to manufacturer. The instruction sheets supplied by the manufacturers usually give the principal chemical reaction(s) that occur(s) in the tube.

9. Diffusional Sampling Theory

9.1 Fick's First Law of Diffusion states that the mass (m) of material that diffuses is directly proportional to the diffusion coefficient (D) of the material, the diffusional cross sectional area (A), the concentration gradient (Δc) and the time (t), and inversely proportional to the length of the diffusion path (l). These parameters are linked by Fick's First Law of Diffusion as follows:

$$\frac{dm}{dt} = \frac{DA\Delta c}{l} \quad (1)$$

² *Annual Book of ASTM Standards*, Vol 11.03.

³ Code of Federal Regulations, available from U.S. Government Printing Office, Washington, DC 20402.

⁴ The boldface numbers in parentheses refer to the list of references appended to this practice.

The molecules of the contaminant reach the granular reagent layer. At this point the chemical conversion to a colored reaction product takes place. The increase in length of the color zone dl is proportional to the converted mass of contaminant dm (Eq 1).

$$dl = \frac{dm}{kA} \tag{2}$$

where:

k = absorption capacity of a layer element, ng/cm^3 , and

A = cross-sectional area of the reagent layer, cm^2 assumed constant.

This process, called chemisorption, has the following effects on the remaining measuring process:

9.1.1 Since the gas molecules to be measured are bound chemically, they are practically no longer present in the atmosphere directly above the granular carrier material. Thus, additional sample molecules are able to flow into the detector tube according to Fick's First Law of Diffusion, since the concentration gradient Δc is maintained.

9.1.2 The effect of the color zone formed in the process is that the subsequent contaminant molecules must cover a longer diffusion path, l , until they reach the unused reagent layer. This means that the diffusion path, l , as defined in the diffusion law, is not constant, but becomes greater with progressive exposure. The transport rate dm/dt of the sample molecules decreases in the process. The slowdown in mass transport has a direct effect on the shape of the calibration curves of the indicating tubes. The mathematical correlation can be traced to Formulas 1 and 2. Eliminating the contaminant mass, dm , from Eq 1 and 2 and integrating yields:

$$c_{TWA} \equiv \frac{1}{t} \int_0^t \Delta c \, dt = \left(\frac{k}{2Dt} \right) \times l^2 \tag{3}$$

where c_{TWA} is the time-weighted average of the time-dependent concentration, Δc . Calibration curves described by this equation are not linear, but have the shape of a parabola when c_{TWA} is plotted versus l . Accounting for an air gap between tube entrance and sorbent, and also transverse analyte flow (if present), modifies Eq 3 through an additive constant and also a term proportional to the stain length, l **(H)(5)**.

9.1.3 The correlation of Eq 3 is confirmed by actual calibration curves of diffusion tubes. The influence of the product resulting from the concentration c and the measuring duration t on the detector tube indication l is shown in Fig. 1. A linear correlation is obtained between the square of the detector tube indication and the product resulting from the concentration and increasing time as shown by Fig. 2.

9.2 **Measurement Range(7-10)**—The measurement range of the various length-of-stain dosimeters is shown in Annex A1.

9.3 **Air Velocity**—The sampling rate of the dosimeter tubes is very slow (of the order of $0.1 \text{ cm}^3/\text{min}$); thus the “starving” effect in static air is not significant for these devices, so that air velocity is not critical. However, a stream of high velocity air should not be permitted to flow directly into the open end of the tube (parallel to the axis of the tube). The tube holder provides additional protection from turbulence within the dosimeter.

10. Sampling with Length-Of-Stain Dosimeter Tubes

10.1 **General**—Since these dosimeters work by diffusion, the procedure for using them is very simple. All that is necessary is

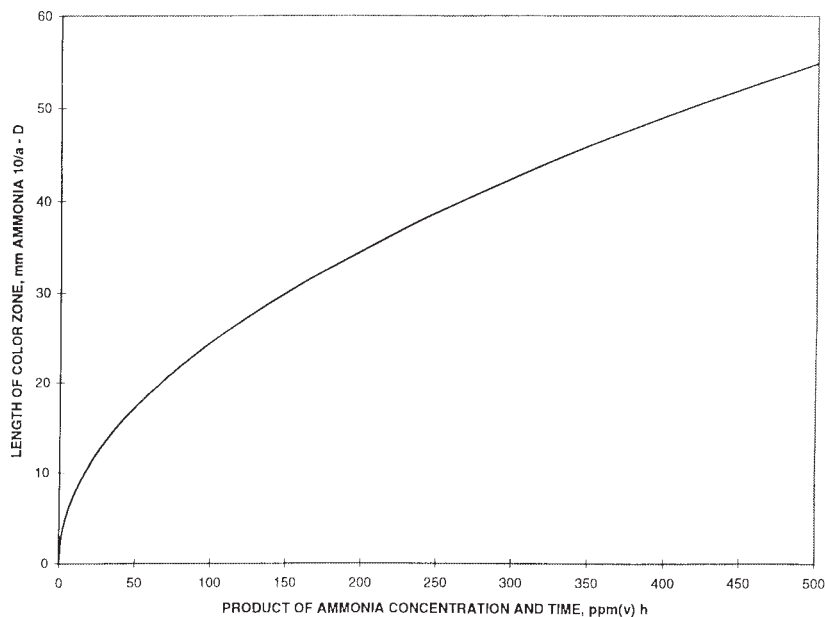


FIG. 1 Dosimeter Calibration Curve Relating Length of Color Zone to Concentration × Time

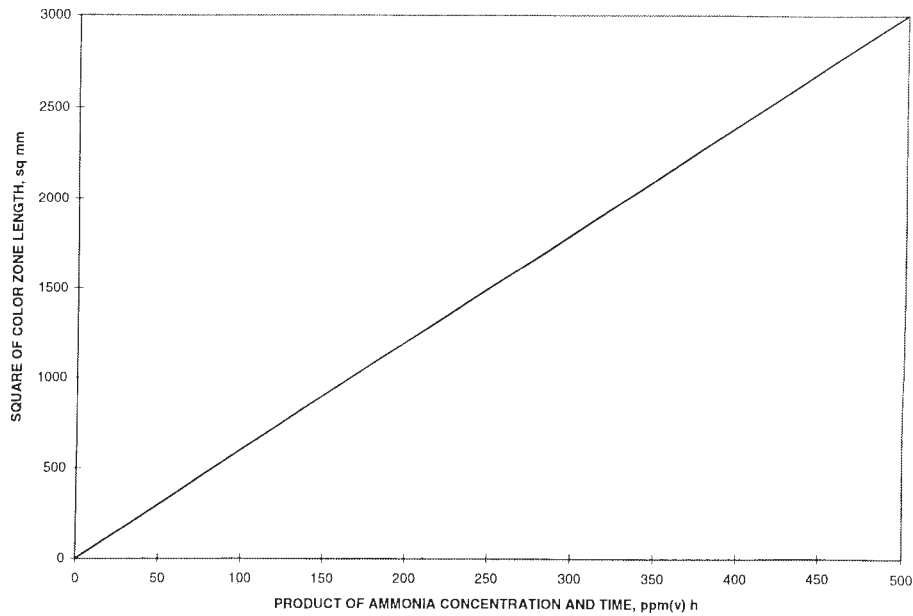


FIG. 2 Dosimeter Calibration Curve Relating Square of Color Zone Length to Concentration × Time

to open one end of the dosimeter properly, place the opened tube into its holder, and fasten the holder to an object at a point where the sampling is to be done. Follow the instruction sheet of the manufacturer for the proper use of each dosimeter tube. The sampling starting time and ending time must be recorded so that the sampling time is known. This is needed to estimate the average concentration (TWA) over the sampling time.

10.2 *Determining the Concentration from the Dosimeter Tube*—The dosimeter tubes are calibrated in units of concentration × time, typically [ppm(v) × hours]. The average gas concentration can be determined by the following formula:

$$\begin{aligned} & \text{average concentration [ppm(v)]} && (4) \\ & = \frac{\text{dosimeter tube reading [ppm(v) hours]}}{\text{actual sampling time [hours]}} \end{aligned}$$

11. Accuracy of Dosimeter Tubes ~~(2,3,6,11)~~ (4-5)

11.1 The accuracy of dosimeter tubes is generally within ±25 %; however, some tube types may vary from this, and specific tube accuracy may vary from lot to lot and manufacturer to manufacturer. Therefore, if users want to know the accuracy of a certain tube, they should check with the manufacturer for an accuracy statement or run their own tests to determine accuracy under their particular conditions of use.

12. Keywords

12.1 air monitoring; colorimetric dosimeter tubes; diffusional sampling; dosimeter tubes; sampling and analysis; toxic gases and vapors; workplace atmospheres

ANNEX

(Mandatory Information)

A1. SOME GASES AND VAPORS THAT CAN BE MEASURED BY LENGTH-OF-STAIN DOSIMETER TUBES

TABLE A1.1 Threshold Limit Values (4)
TABLE A1.1 Threshold Limit Values (2)

NOTE 1—The measurement ranges given in the table are not for a single tube. They are the lowest and highest concentrations (over 8 h exposure) listed in the various manufacturer's brochures.

Substance	TLV ^R TWA Values ^A		Measurement Range (ppm(v))
	ppm(v)	mg/m ³	
Acetic acid	10	25	0.63–25
Acetone	500	1187	6.3–187.5
Ammonia	25	17	2.5–187.5
Butadiene	2	4.4	1.3–37.5
Carbon dioxide	5000	9000	62.5–37 500
Carbon monoxide	25	29	1.3–125
Chlorine	0.5	1.5	0.3–6.3
Ethanol	1000	1881	12.5–3125
Ethyl acetate	400	1440	62.5–1250
Formaldehyde	C0.3 ^B	C0.37 ^B	0.13–2.5
Hydrogen chloride	C5 ^B	C7.5 ^B	1.3–25
Hydrogen cyanide	C4.7 ^B	C5 ^B	1.3–25
Hydrogen peroxide	1	1.4	0.63–5
Hydrogen sulfide	10	14	1.3–37.5
Methyl ethyl ketone	200	590	2.5–75
Nitrogen dioxide	3	5.6	0.1–25
Olefin	12.5–250
Perchloroethylene	25	170	3.1–187.5
Sulfur dioxide	2	5.2	0.6–18.8
Toluene	50	188	12.5–250
Trichloroethylene	50	269	3.1–125
Water vapor	0.63–12.5 mg/l

^A Values for ppm(v) and mg/m³ are Time-Weighted Average (TWA).

^B C = Ceiling limit.

NOTE 1—The measurement ranges given in the table are not for a single tube. They are the lowest and highest concentrations (over 8 h exposure) listed in the various manufacturer's brochures.

Substance	TLV ^R TWA Values ^A		Measurement Range (ppm(v))
	ppm(v)	mg/m ³	
Acetic acid	10	25	0.63–25
Acetone	500	1180	6.3–187.5
Ammonia	25	17	2.5–187.5
Butadiene	2	4.4	1.3–37.5
Carbon dioxide	5000	9000	62.5–37 500
Carbon monoxide	25	29	1.3–125
Chlorine	0.5	1.5	0.3–6.3
Ethanol	1000	1881	12.5–3125
Ethyl acetate	400	1440	62.5–1250
Formaldehyde	C0.3 ^B	C0.37 ^B	0.13–2.5
Hydrogen chloride	C5 ^B	C7.5 ^B	1.3–25
Hydrogen cyanide	C4.7 ^B	C5 ^B	1.3–25
Hydrogen peroxide	1	1.4	0.63–5
Hydrogen sulfide	10	14	1.3–37.5
Methyl ethyl ketone	200	590	2.5–75
Nitrogen dioxide	3	5.6	0.1–25
Olefin	12.5–250
Perchloroethylene	25	170	3.1–187.5
Sulfur dioxide	2	5.2	0.6–18.8
Toluene	50	188	12.5–250
Trichloroethylene	50	269	3.1–125
Water vapor	0.63–12.5 mg/l

^A Values for ppm(v) and mg/m³ are Time-Weighted Average (TWA).

^B C = Ceiling limit.

REFERENCES

- (1) Pannwitz, Karl-Heinz, "Direct-Reading Diffusion Tubes," *Dräger Review*, Vol 53, 1984, pp. 10–14.
- (2) "Sensidyne/Gastec Precision Gas Detector System Manual," Sensidyne, Inc., Clearwater, FL. "Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, 1996," American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1996.
- (3) Drägerwerk, A. G., *Dräger Tube Handbook*, 9th ed., 1994, p. 25. Palmes, E. D., and Lindenboom, R. H., "Ohm's Law, Fick's Law and Diffusion Samplers for Gases," *Analytical Chemistry*, Vol 51, 1974, pp. 2400–2401.
- (4) "Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, 1996," American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1996.
- (5) Palmes, E. D., and Lindenboom, R. H., "Ohm's Law, Fick's Law and Diffusion Samplers for Gases," *Analytical Chemistry*, Vol 51, 1974, pp. 2400–2401.
- (6) Roberson, R. W., Matsunobu, K., Hoshino, F., and Komatsu, T., "Performance Testing of Sensidyne/Gastec Dosimeter Tubes for CO, H₂S, SO₂ and HCN," presented at the American Industrial Hygiene Conference (1985).
- (7) "Diffusion Tubes" Data Sheet 4505001, National Draeger, Inc., Pittsburgh, PA, 1995.
- (8) "Dosimeter Tubes," 0185, Sensidyne, Largo, FL, 1985.
- (9) "Passive Colorimetric Dosimeters," Form No. 8503, Willson Safety Products, Reading, PA, 1985.
- (10) Willson Safety Products, Validation Report Passive Inorganic Colorimetric Dosimeter, 1985.
- (H) Bartley, D. L., "Diffusive Samplers Using Longitudinal Sorbent Strips," *American Industrial Hygiene Assoc. Journal*, Vol 47, No. 8, 1986, pp. 571–577.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).