Designation: D4599 – 14

Standard Practice for
Measuring the Concentration of Toxic Gases or Vapors Using Length-of-Stain Dosimeters[1]

This standard is issued under the fixed designation D4599; 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

2.2 *Other Document:*[3]

U.S. Occupational Safety and Health Standard—Title 29 1910.1000 Subpart Z

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1356.

4. Summary of Practice

4.1 Length-of-stain colorimetric dosimeters consist of a sealed glass tube containing a detector inside the tube (**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 measured 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 U.S. Occupational Safety and Health Administration (OSHA) 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. Other countries have similar regulations.

5.2 This practice will provide a means for the measurement of airborne concentrations of certain gases and vapors listed in 29 CFR 1910.1000 and in other countries' regulations.

5.3 A partial list of chemicals for which this practice is applicable is presented in Annex A1 with current Threshold Limit Values (TLV)[5] (**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.

---

[1] This practice is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

Current edition approved Sept. 1, 2014. Published October 2014. Originally approved in 1986. Last previous edition approved in 2009 as D4599 – 03 (2009)$^{\varepsilon 1}$. DOI: 10.1520/D4599-14.

[2] 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.

[3] Code of Federal Regulations, available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

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

[5] Threshold Limit Values (TLV) is a registered trademark of the American Conference of Governmental Industrial Hygienists (ACGIH).

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, also called a "*colorimetric diffusion 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:

$$\frac{dm}{dt} = \frac{DA\Delta c}{l} \tag{1}$$

NOTE 1—The diffusion coefficient of a molecule is a function of the temperature and the nature of the medium through which it is diffusing.

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 2).

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

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 Eq 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 (**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*—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 cm^3/min); thus the "starving" effect in static air (for example, face velocities <0.1 m/sec) 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.

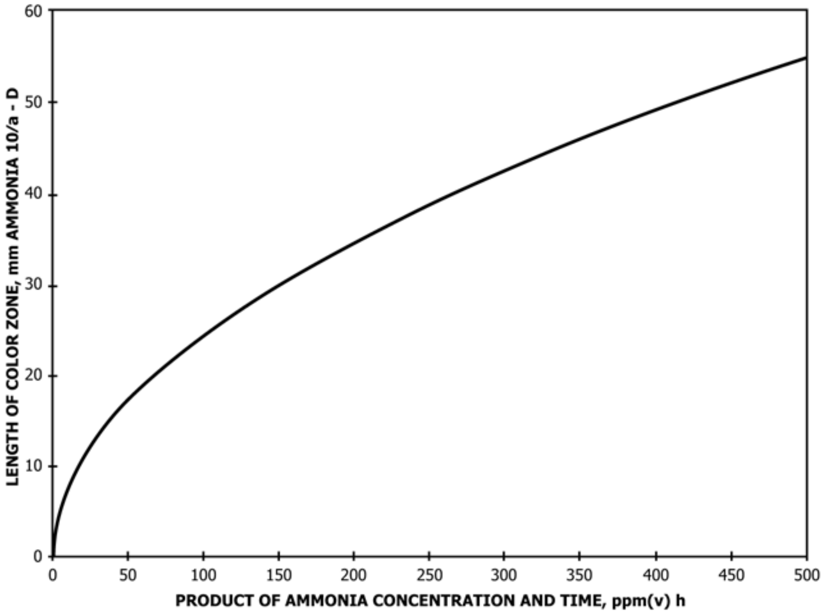

FIG. 1 Dosimeter Calibration Curve Relating Length of Color Zone to Concentration × Time

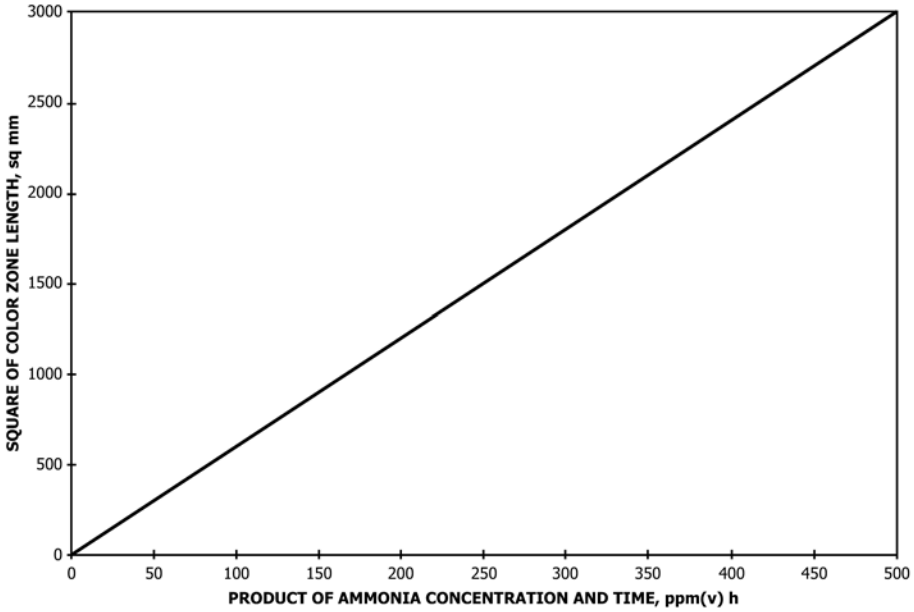

FIG. 2 Dosimeter Calibration Curve Relating Square of Color Zone Length to Concentration × Time

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 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.

NOTE 2—*Temperature and Humidity*—Dosimeters should only be deployed under the suggest range of operating conditions by manufacturers.

10.2 *Measuring 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 measured by the following formula:

$$\text{average concentration}\left[\text{ppm}(\text{v})\right] \tag{4}$$

$$= \frac{\text{dosimeter tube reading}\left[\text{ppm}(\text{v})\text{ hours}\right]}{\text{actual sampling time}\left[\text{hours}\right]}$$

11. Accuracy of Dosimeter Tubes (4 and 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 estimate 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 (2)

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

Substance	TLV 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	2.5–200
Butadiene	2	4.4	1.3–40
Carbon dioxide	5000	9000	0.03–2500
Carbon monoxide	25	29	6–125
Chlorine	0.5	1.5	0.3–6.3
Ethanol	1000[B]	1884	125–3125
Ethyl acetate	400	1441	62.5–1250
Formaldehyde	C0.3[C]	C0.37[C]	0.13–2.5
Hydrogen chloride	C2[C]	C3.0[C]	1.3–25
Hydrogen cyanide	C4.7[C]	C5[C]	1.3–25
Hydrogen fluoride	0.5	0.41	1.25–12.5
Hydrogen peroxide	1	1.4	0.63–5
Hydrogen sulfide	1	1.4	1.3–40
Methyl ethyl ketone	200	590	2.5–75
Nitrogen dioxide	0.2	0.38	1.3–25
Perchloroethylene	25	170	3.1–200
Sulfur dioxide	0.25[B]	0.66	0.3–19
Toluene	20	75	2.5–380
Trichloroethylene	10	54	3.1–125

[A] Values for ppm(v) and mg/m^3 are Time-Weighted Average (TWA) (8 hr).

[B] Threshold limit value-Short-Term Exposure Limit (15 min).

[C] C = Threshold limit value-Ceiling.

REFERENCES

(1) Pannwitz, Karl-Heinz, "Direct-Reading Diffusion Tubes," *Dräger Review*, Vol 53, 1984, pp. 10–14.

(2) American Conference of Governmental Industrial Hygienists, *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, 2013 (updated annually), Cincinnati, OH.

(3) 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) Roberson, R. W., Matsunobu, K., Hoshino, F., and Komatsu, T., "Performance Testing of Sensidyne/Gastec Dosimeter Tubes for CO, H_2S, SO_2 and HCN," presented at the American Industrial Hygiene Conference, 1985.

(5) Bartley, D. L., "Diffusive Samplers Using Longitudinal Sorbent Strips," *American Industrial Hygiene Association 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). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/