# Standard Practice for
# Sampling Workplace Atmospheres to Collect Gases or Vapors with Solid Sorbent Diffusive Samplers[1]

This standard is issued under the fixed designation D4597; 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 sampling of workplace atmospheres for the presence of certain gases or vapors by means of diffusion across a specified quiescent region and subsequent sorption on a solid sorbent (**1**).[2]

1.2 A list of organic compounds which are applicable to solid sorbent sampling where the sorbent is contained in a bed through which air is passed is given in Annex A1 of Practice D3686. Diffusive samplers may be applicable to a similar range of compounds but this must be confirmed by reference to the individual sampler manufacturers' literature.

1.3 The valid use of diffusive samplers depends on the existence of actual laboratory or field validation, or both. Guidance on validation can be obtained from published protocols (**2-6**). This practice is not designed to cover the verification, validation, or specific test procedures used to assess the accuracy or precision of diffusive samplers.

1.4 The values stated in SI units shall be regarded as the standard.

1.5 *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:*[3]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

D3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method

D6306 Guide for Placement and Use of Diffusion Controlled Passive Monitors for Gaseous Pollutants in Indoor Air

2.2 *Other Document:*[4]

Title 29CFR 1910.1000 Subpart Z Occupational Health and Safety Standard

## 3. Terminology

3.1 Terminology D1356 contains definitions of terms used in this practice.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *diffusion*—the movement of gas or vapor molecules from a region of high concentration to a region of low concentration as described by Fick's first law (8.1).

3.2.2 *diffusive sampler*—assembly used for sampling gas or vapor molecules from the atmosphere.

3.2.3 *sampling rate*—the ratio of mass of a given compound collected by a diffusive sampler per unit time of exposure to the concentration of that compound in the atmosphere being sampled. The sampling rate is sometimes referred to as the uptake rate. Units are ng (or mg)/mg/$m^3$/min (or h), which are dimensionally equivalent to a volume flow-rate (for example $cm^3$/min).

## 4. Summary of Practice

4.1 Molecules (gases and vapors) are sampled from the atmosphere by a diffusive sampler. During the sampling process, the molecules diffuse from the environment adjacent to the sampler through a region of defined geometric structure and into a region containing the sorbent medium. The theory of diffusive sampling is given in this practice.

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[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.

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[2] The boldface numbers in parentheses refer to the list of references at the end of this 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] Code of Federal Regulations, available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

4.2 Instructions are given for the correct use of the sampling devices to enable their field application.

4.3 Information on the calculation of environmental concentration based on sampler assay is given.

## 5. Significance and Use

5.1 Regulations such as those promulgated by the U.S. Occupational Safety and Health Administration in 29 CFR 1910.1000 designate that certain hazardous gases and vapors must not be present in the workplace air at concentrations above specific values.

5.2 This practice, when used in conjunction with an analytical technique, such as that given for organic compounds in Practice D3687, may provide a means for the determination of time-weighted airborne concentrations of many of the hazardous gases and vapors in applicable regulations (for example, 29CFR 1919.1000), as well as others.

5.3 The manufacturer's literature should be consulted for the appropriate list of chemicals which may be sampled by a particular device.

## 6. Interferences

6.1 The diffusive sampling process can be jeopardized by physical blockage of entrances to the interior of the device such as by liquid droplets or dust particles.

6.2 The diffusive sampling process can be jeopardized by structural damage to any membranes or other elements used to control either the geometry of the diffusion path or turbulence within the diffusion path.

6.3 The diffusive sampling process can be jeopardized by air movement within the diffusion path. Recent sampler designs have incorporated elements to decrease this possibility.

6.4 The diffusive sampling process can be jeopardized by insufficient mixing of the air external to the sampler. This is known as starvation. The manufacturer should provide a recommended minimum ambient air velocity, below which the sampler should not be used.

6.5 The diffusive sampling process can be jeopardized if the concentration in air at the sorbent interface becomes sufficient to significantly alter the diffusion gradient within the diffusion path. This can occur through sorbent saturation, either from the presence of competing species (which may include water vapor molecules), or the selection of an inappropriate sorbent material for the concentration and time of exposure, or by increased temperature. The manufacturer should provide, or the user should determine, the range of conditions over which significant bias from sorbent saturation will not occur.

6.6 Errors may arise in estimating exposure using diffusive samplers in instances in which the concentration of the gas or vapor being sampled varies significantly over time.

6.7 Where multiple gases or vapors are sampled simultaneously, care must be exercised to ensure there is no mutual interference in the analytical method chosen.

## 7. Apparatus

7.1 *Diffusive Sampling Devices:*

7.1.1 A diffusive sampler consists of a cavity or group of cavities containing air and terminated at one end by a sorbent substrate and opening at the other to the environment. The cavity or group of cavities form a region of defined geometry which acts as a control on the rate of gaseous diffusion from the external environment to the sorbent substrate. Barriers to the entry of external air movements are common. Samplers where the diffusion of gas or vapor is through materials other than air are covered by this practice, but it should be noted that the influence of temperature on diffusion may be more pronounced.

7.1.2 Diffusive samplers are equipped with a means of attachment to the body for personal sampling or to a suitable support for area sampling. Samplers are contained in vapor impermeable packages or are sealed with vapor impermeable caps both before and after sampling. Labels for unique identification of a collected sample are required.

## 8. Diffusive Sampling Theory

8.1 Fick's first law of diffusion states that for a constant concentration gradient, the mass of material transferred to the sampling layer can be expressed as follows:

$$M = \frac{DA}{L}(C - C_o)t \qquad (1)$$

where:

$M$ = mass of material, ng,
$D$ = diffusion co-efficient, cm$^2$/min (Note 1),
$A$ = cross sectional area of diffusion cavity(ies), cm$^2$ (Note 2),
$L$ = length of diffusion path, cm (Note 3),
$C$ = gas phase concentration at face of sampler, ng/cm$^3$,
$C_o$ = gas phase concentration at sorbent surface, ng/cm$^3$, and
$t$ = exposure time, min.

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. Should the medium be a compressible fluid (for example, air) the diffusion coefficient will also be a function of the pressure.

NOTE 2—The presence of barriers to the entry of external air movements may alter the effective cross-sectional area of the sampler.

NOTE 3—Under certain circumstances the length of the diffusion path can be significantly extended into the thickness of the sorbent layer during sampling. Certain types of sampler make use of this phenomenon to give a length of stain read-out. In this situation, the mathematical treatment of Fick's law is more complex than that given here.

8.2 The sampling rate (*SR*) of a diffusive sampler for a specific gas or vapor may be expressed as follows:

$$SR = \frac{DA}{L} = \frac{M}{(C - C_o)t} \qquad (2)$$

where:

$SR$ = sampling rate, cm$^3$/min.

where:

concentration ($C$, $C_o$) is given in ppm (v/v) the units of *SR* become ng/ppm/min.

8.2.1 Sampling rates may be estimated from diffusion coefficient ratios if the sampling rate of one substance is known:

$$SR_2 = D_2 \frac{SR_1}{D_1} \qquad (3)$$

However, where diffusion coefficients are calculated values rather than measurements, the potential for error exists in this procedure. Where possible, sampling rates should be confirmed by the results of experimental protocols.

8.2.2 The sampling rate for a gas or vapor through air is theoretically proportional to $T^{1.5}/P$ where $T$ is the absolute temperature (in °$K$) and $P$ is the pressure (in kPa) (**7**); while in practice, the concomitant air volume changes result in apparent sampling rate changes of 0.2 % per °$K$ and virtually no pressure effects. However, the exposure limits given in 29CFR 1910.1000 Subpart Z are referenced to standard temperature and pressure (STP). Therefore, in order to compare a concentration value (in ppm) from a diffusive sampler with a federal exposure limit, it is necessary to convert the value to STP (11.6) (**8**).

8.2.3 Sampling rates for gases or vapors using samplers which use a medium other than air in the diffusion path require different correction factors than given here. The manufacturer's literature should be consulted.

8.3 Some samplers are available with the ability to sample multiple gases or vapors simultaneously. Manufacturer's literature should be consulted.

8.4 Some samplers are equipped with a means of determining the point of sorbent saturation. Refer to specific manufacturer's literature for information.

## 9. Sampling with Diffusive Samplers

9.1 *Calibration of the Diffusive Sampler*—The sampling rate of a diffusive sampler is determined by the diffusion coefficient of the gas or vapor being sampled and the geometry of the diffusion path. It is normally provided by the manufacturer. This theoretical sampling rate can be checked by experiment according to published protocols. These protocols include tests under all the conditions and combinations of conditions that might apply in a normal workplace setting, and the results can be analyzed to discern the conditions or combination of conditions that might significantly influence the sampling rate. The results of these experiments are normally available from the manufacturer and they should be consulted by the user to determine whether a particular sampler is appropriate for use in a specific workplace.

9.2 *Field Sampling with Diffusive Samplers:*

9.2.1 Follow the manufacturer's instructions for use. In general, the following steps are involved:

9.2.1.1 Open the sampler container at the time sampling is to be initiated.

9.2.1.2 Initiate the sampling in accordance with the manufacturer's instructions. Identify the sampler and all containers to be used as required.

9.2.1.3 Record the start time.

9.2.1.4 Record all pertinent information such as temperature, barometric pressure, relative humidity, ambient air velocity (for area samples), and gases and vapors being sampled.

9.2.1.5 At the end of the sampling period, remove the sampler, follow the manufacturer's instructions for handling and sealing the sampler, and record the end time. Submit the samples to a laboratory for analysis or perform any on-site read-out or analysis that may be possible.

9.2.1.6 For a breathing zone sample, attach the sampler to the worker's clothing as near the breathing zone as possible. Ensure the open face of the sampler is facing toward the environment and exposed for the entire sampling period.

9.2.1.7 For an area sample, position the sampler at the desired point. Ensure that the ambient air velocity at the sampler position is above the minimum velocity recommended by the manufacturer.

9.3 *Sampling Time:*

9.3.1 The minimum sampling time is governed by the sampling rate and by the sensitivity of the analytical method. Consult the manufacturer's instructions for the appropriate minimum recommended sampling time.

9.3.2 The maximum sampling time is governed by the sampling rate and by the capacity of the sampler. Consult the manufacturer's instructions for the maximum recommended sampling time.

9.3.2.1 When the maximum recommended sampling time is less than the desired sampling period, use two or more samplers in sequence to accommodate the desired exposure period.

9.4 *Sampler Blanks:*

9.4.1 Present at least two samplers for analysis as field blanks with every set of ten samplers up to a maximum of ten blanks. The purpose of the field blank is to detect the presence of gases or vapors other than those in the sampled atmosphere.

9.4.1.1 To prepare a field blank, remove an unexposed sampler from its package and then reseal it immediately.

9.4.1.2 Do not use results from field blanks to correct sample results. If a field blank shows contamination, the samples taken must be assumed to be contaminated and appropriate action taken.

9.4.2 Media blanks are unopened samplers that are also submitted for analysis. These need not be taken into the field. The results are used to correct sample results. Include at least one media blank per analytical batch. Consult the manufacturer's instructions for the appropriate number.

## 10. Handling and Shipping of Samples

10.1 Where samples are shipped to a laboratory for subsequent analysis, take precautions to minimize sample losses and prevent extraneous contamination.

10.1.1 Seal samples securely and identify (label) clearly.

10.1.2 Follow manufacturer's instructions concerning maximum temperature of shipping and storage. This may vary depending on the sampled analyte.

10.1.3 Samples shipped in aircraft cargo holds may be subject to contamination (for example, jet fuel) or to sample loss from depressurization. It may be possible to secure the samples by shipping in an airtight container which includes a package of adsorbent. Do not store or ship bulk samples together with air samples.

10.1.4 Ship, desorb, and analyze samples according to the manufacturer's instructions as soon as possible after they have been taken.

## 11. Calculations

11.1 Samplers designed for on-site analysis normally have the read-out already calibrated in units of exposure dose (for example, ppm × mins or ppm × h). If the reading is divided by the time in minutes (or hours) the result is the time-weighted average concentration in ppm (v/v).

11.2 Samplers analyzed off-site normally give results in terms of weight of analyte recovered. This must be converted to concentration through a knowledge of the sampling rate, the sampling time, and the recovery efficiency of the analysis (desorption efficiency).

11.3 Determine the sampling rate in cm$^3$/min by referring to manufacturer's publications or from laboratory data using the following equation:

$$SR = \frac{\text{mass of contaminant collected (ng)}}{\text{concentration (ng/cm}^3\text{)} \times \text{sampling time (min)}} \quad (4)$$

11.4 Determine the desorption efficiency using manufacturer's recommended procedures or suitable alternative. Modifying the procedure in Practice D3687 may be sufficient.

11.5 Calculate the concentration of the contaminant using the following equation:

$$\text{mg/m}^3 = \text{ng/cm}^3 = \frac{\text{mass of contaminants desorbed (ng)}}{\text{sampling rate (cm}^3\text{/min)} \times \text{sampling time (min)}} \times DE \quad (5)$$

where:

$DE$ = desorption efficiency.

11.6 To calculate the concentration in ppm at 25°C and 760 mm mercury for comparison with a federal exposure standard (**9**), use the mg/m$^3$ value in the following equation:

$$\text{ppm } V = \frac{\text{mg}}{(T_s/T_o)^{1.5} \times (P_o/P_s) \times m^3} \times \frac{24.45}{\text{molecular weight}} \quad (6)$$

where:

$T_s$ = the sampling site temperature, °C,
$T_o$ = 25°C,
$P_s$ = the sampling site pressure, kPa, and
$P_o$ = 101 kPa.

## 12. Keywords

12.1 air monitoring; diffusive samplers; organic gases; organic vapors; sampling and analysis; workplace atmospheres

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