



Standard Practice for Evaluating the Performance of Diffusive Samplers¹

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1. Scope

1.1 This practice covers the evaluation of the performance of diffusive samplers of gases and vapors for use over sampling periods from 4 to 12 h. Sampling periods of such duration are the most common in workplace sampling. Given a suitable exposure chamber, the practice can be straightforwardly extended to cover samplers for use over other sampling periods as well. The aim is to provide a concise set of experiments for classifying samplers primarily according to a single numerical value representing sampler accuracy. Accuracy estimates refer to conditions of sampler use which are normally expected in a workplace setting. These conditions may be characterized by the temperature, atmospheric pressure, humidity, and ambient wind speed, none of which may be constant or accurately known. Furthermore, the accuracy accounts for the estimation of time-weighted averages of concentrations which may not be constant in time. Aside from accuracy, the samplers are tested for compliance with the manufacturer's stated limits on capacity, possibly in the presence of interfering compounds. The samplers are, further, classified as to their capability for detecting situations in which sampler capacity may be exceeded.

1.2 This practice is an extension of previous research on diffusive samplers **(1-13)**² as well as Practices D 4597, D 4598, D 4599, and MDHS 27. An essential advance here is the estimation of sampler accuracy under actual conditions of use. Furthermore, costs of sampler evaluation are reduced.

1.3 Furthering the latter point, knowledge of similarity between analytes of interest can be used to expedite sampler evaluation. For example, interpolation of data characterizing the sampling of analytes at separated points of a homologous series of compounds is recommended. At present the procedure of **(9)** is suggested. Following evaluation of a sampler in use at a single homologous series member according to the present practice, higher molecular weight members would receive partial validations considering sampling rate, capacity, analytical recovery, and interferences.

1.4 Units of the International System of Units (SI) are used throughout this guide and should be regarded as 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:

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres³

D 4597 Practice for Sampling Workplace Atmospheres to Collect Organic Gases or Vapor with Activated Charcoal Diffusive Samplers³

D 4598 Practice for Sampling Workplace Atmospheres to Collect Gases or Vapor with Liquid Sorbent Diffusional Samplers⁴

D 4599 Practice for Measuring the Concentration of Toxic Gases or Vapors Using Length-of-Stain Dosimeters³

2.2 International Standards:

CEN EN 838 European Standard, Workplace atmospheres - Diffusive samplers for the determination of gases or vapours - Requirements and test methods⁵

MDHS 27 Protocol for assessing the performance of a diffusive sampler, Health and Safety Laboratory, United Kingdom⁶

MDHS 80 Volatile organic compounds in air, Health and Safety Laboratory, United Kingdom⁶

3. Terminology

3.1 Definitions:

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

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *Busch Probabilistic Accuracy A*—the fractional range, symmetric about the true concentration c , within which 95 % of sampler measurements are to be found **(14-16)**.

3.2.1.1 *Discussion*—In the case considered here, effects on sampler accuracy from environmental unknowns are all handled as *variances*, leaving negligible uncorrectable bias. Therefore, the function A is given in terms of the total

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

³ *Annual Book of ASTM Standards*, Vol 11.03.

⁴ Discontinued—See 1995 *Annual Book of ASTM Standards*, Vol 11.03.

⁵ Available from CEN Central Secretariat, rue de Stassart 36, B-1050 Brussels, Belgium.

⁶ Available from HMSO Books, PO Box 276, London, England, SW8 5DT.

imprecision *RSD* simply by:

$$A = 1.960 \times RSD \quad (1)$$

3.2.2 diffusive sampler—a device which is capable of taking samples of gases or vapors from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of air through the sampler. As such, direct-reading dosimeters, as well as samplers requiring lab analysis, are considered diffusive samplers within this practice.

3.3 Symbols:

A	= Busch probabilistic accuracy as defined in terms of bias and imprecision
$\hat{A}$	= estimated Busch probabilistic accuracy A
$A_{95\%}$	= 95 % confidence limit on the Busch probabilistic accuracy A
c (mg/m ³)	= true or reference analyte concentration
$\hat{c}$ (mg/m ³)	= mean of (four) concentration estimates (including (p, T) -corrections) obtained according to instructions of sampler manufacturer
h	= humidity (expressed as partial pressure)
n	= number of diffusive samplers tested for measuring sampler capacity
p	= atmospheric pressure
RSD	= overall relative standard deviation of concentration estimates (dependent on assumed environmental variability)
RSD_{run}	= relative standard deviation characterizing inter-run chamber variability
RSD_s	= inter-sampler imprecision (relative to the reference concentration)
$\hat{RSD}_s$	= estimated inter-sampler imprecision RSD_s
RSD_t	= pulse-induced imprecision
$\hat{RSD}$	= estimated overall relative standard deviation RSD
$\hat{RSD}_{95\%}$	= 95 % confidence limit on the overall relative standard deviation RSD
s	= estimated standard deviation characterizing inter-sampler imprecision
$t_{0.95}(v)$	= value which, at probability 95 %, exceeds random variables distributed according to the studentized t -distribution with v degrees of freedom
T	= temperature
v (m/s)	= ambient wind speed
α_x	= concentration estimate dependence on environmental variable x (T , h , v , or c).
Δ	= bias relative to the concentration c
$\hat{\Delta}$	= estimated bias Δ
$\hat{\Delta}_{95\%}$	= 95 % confidence limit on the bias Δ
Δ_t	= bias associated with concentration pulse
v	= degrees of freedom in determining RSD_s
v_{eff}	= effective number of degrees of freedom in determining RSD
σ_c	= assumed concentration variability
σ_h	= assumed humidity variability

σ_T	= assumed temperature variability
σ_v	= assumed ambient wind speed variability

4. Summary of Test Method

4.1 Bias, Inter-sampler Imprecision and the Effects of Environmental Uncertainty:

4.1.1 This practice gives a procedure for assessing the effects of variability in the following workplace variables: temperature T , humidity h (expressed in terms of the water vapor partial pressure to minimize interaction with the temperature), the ambient wind speed v across the sampler face (see 4.7 regarding wind direction), and concentration, c . An experiment is carried out which provides information about the concentration estimates' dependencies on these variables as well as the sampler bias, inter-sampler imprecision, and concentration-dependent effects. Testing is required at a single target concentration c_0 , central to concentrations of intended sampler use, as well as at a reduced concentration in the range $c_0/10$ to $c_0/2$. Pressure effects result in one-time correctable bias and are not evaluated here, aside from uncorrected bias (4.6).

4.1.2 Specifically, in terms of the known concentration, c , in the exposure chamber, the mean concentration estimates $\hat{c}$ (over four samples at each condition), following p - and T -correction (if any) per the sampler manufacturer's instruction, are modelled by:

$$\hat{c}/c = 1 + \Delta \quad (2)$$

$$+ \alpha_T \times (T/T_0 - 1) + \alpha_h \times (h/h_0 - 1) + \alpha_v \times (v/v_0 - 1) + \alpha_c \times (c/c_0 - 1),$$

omitting error terms. The concentration c is the chamber reference concentration and must be traceable to primary standards of mass and volume. Estimates of the model parameters Δ (which characterizes sampler bias at the intermediate conditions (T_0 , h_0 , v_0 , c_0)), α_T , α_h , α_v , α_c , are obtained from an experiment consisting of five runs, varying T , h , v , and c , with four diffusive samplers each. Therefore, error in Eq 2 will exist on account of inter-sampler imprecision (characterized by RSD_s) together with an inter-run chamber variability (RSD_{run}) resulting in part from uncertainty in the reference concentration. RSD_s is obtained by pooling the variance estimates from each run, together with a further run describing time-effects (4.2.5), and therefore is estimated with $6 \times 3 = 18$ degrees of freedom. So as to avoid re-measurement at each sampler/analyte evaluation, RSD_{run} is obtained by a separate characterization of the chamber with several runs at (for example) fixed environmental conditions. An example in which the parameters $\{\alpha\}$ and RSD_s , are estimated is presented in the Appendix X1.

NOTE 1—It is up to the user as to how traceability is established. Within (12) the concentration estimate as calculated from the chamber's analyte generation parameters is regarded as the benchmark, although an independent estimate is required and must be within 5 % of the calculated estimate. If these estimates differ, then a third independent estimate is required to establish the reference concentration through agreement with one of the other independent estimates. One possibility for such an independent estimate is the mean of at least five independent, active sampler estimates per run within the chamber. Experiment (12) on the accuracy of such reference measurements using sorbent tubes indicates that a relative standard deviation of the order of 2 % can be achieved for the individual measurements. Alternatively, (3) requires averaging of a

least two independent methods (possibly including calculated estimates) with at least four samples per method. EN 838 has adopted the looser requirement that calculated and independent measurements must agree within 10 %.

4.1.2.1 A further consolidation of tests may be made by observing that the dependence of concentration estimates on the wind speed, v , is only sampler specific, that is, does not depend on the specific analyte. Therefore, after a single measurement for a given sampler type, the set of tests can be narrowed to 5 runs with $5 \times 3 = 15$ degrees of freedom in the estimate of RSD_s .

4.2 Reverse Diffusion:

4.2.1 A potential problem with diffusive samplers is presented by the possibility of reverse diffusion (sometimes denoted as *back diffusion* or *off-gassing*) of analyte. Reverse diffusion can occur directly from the air spaces of a diffusive sampler, depending on geometry. For example, a sampler as long as the Palmes tube (7 cm) used over short sampling periods (15 min) can display a measurable effect of this type (2). More commonly, reverse diffusion may be significant in the case that an analyte is only weakly bound to the sorbent (6). Therefore, inaccuracy associated with these effects may generally be minimized through proper sorbent selection and sampler design.

4.2.2 Because of reverse diffusion, estimates of a varying concentration may in some cases be biased. The worst-case situation occurs with the concentration in the form of an isolated pulse at either the beginning or end of the sampling period. A pulse at the beginning of the period allows the entire sampling period (4 to 12 h) for sample loss, possibly resulting in a low estimate relative to a pulse at the end of the period.

4.2.3 In some cases, the time-dependence of a specific workplace concentration correlates strongly with the sampling period. For example, a cleanup operation at the end of a workday could introduce solvent only then. This could imply a positive bias in the concentration estimates obtained from a day's sampling. For simplicity, however, this practice is set up for assessing performance of samplers for use in a concentration with stationary fluctuations, so that time-dependent effects are treated simply as components of sampler variance. Specifically, the effect of an isolated 0.5-h pulse occurring at random within the sampling period is estimated.

4.2.4 Challenging samplers to 0.5-h pulses is similar to tests suggested by NIOSH (3) and CEN (EN 838).

4.2.5 Let Δ_t represent the corrected bias in estimating a 0.5-h pulse at the end of the sampling period relative to a known concentration, c . For pulses occurring at other times, assume conservatively (see, for example, (6)) that the bias Δ_t is proportional to the interval from the center of the sampling period to the time the pulse occurs. Then the variance RSD_t^2 associated with sampling a 0.5-h pulse at random within the sampling period is as follows:

$$RSD_t^2 = \frac{1}{3} \Delta_t^2 \quad (3)$$

4.3 Capacity; Control of Effects from Interfering Compounds:

4.3.1 This practice provides a test for confirming a manufacturer's claimed sampler capacity under stated

conditions of use. Such conditions would normally refer to a specific sampling period and to environmental extremes, such as 80 % relative humidity at a temperature equal to 30°C. Additionally, a manufacturer may claim a value of capacity for sampling in the presence of specific interferences at stated concentrations.

4.3.2 Capacity is defined here as the sampled mass (or equivalently as the concentration at a specific sampling period) at which concentration estimates are 10 % low. Specifically, capacity is considered not exceeded if concentration estimates, corrected for correctable bias, are above 90 % of the true concentration at the 95 % confidence level.

4.3.3 An example of the test follows. Eight diffusive and eight active samplers with estimated inter-sampler imprecision, s , are exposed to the analyte of concern under the stated environmental conditions. Then, neglecting variability in the reference sampler mean, the 95 % confidence limit $\Delta\mu_{95\%}$ on the difference in the (unknown) mean concentration estimates is:

$$\Delta\mu_{95\%} = \Delta c - s \times t_{0.95}(v)/\text{Sqrt}[n] \quad (4)$$

where Δc is the estimated mean difference between diffusive and active results, $n = 8$, and $v = n - 1 = 7$. Then $\Delta\mu_{95\%}$ must be greater than $-10\% \times c$, where c is the mean concentration estimate from the reference samplers.

4.3.4 As a specific example, suppose the inter-sampler imprecision $RSD_s = 5\%$,

$$(s/c) \times t_{0.95}(v)/\text{Sqrt}[n] = 3.3\%. \quad (5)$$

Therefore, in this case the mean value of the diffusive results must be greater than 93.3 % of the reference concentration.

NOTE 2—As capacity strongly correlates with sampled mass, a limit on the capacity expressed as sampled mass at one stated sampling period is generally applicable to a range of sampling periods.

4.4 Capacity Overload Detection:

4.4.1 The capability of *detecting* capacity overload (for example, by the use of a second sorbent or by employing paired samplers with different sampling rates) may be advantageous in some sampling situations. In the case of active samplers, such detection is easily effected through the use of back-up sections. Therefore, diffusive samplers with similar features will receive a specific classification. The point is that practicality precludes testing of the samplers under all conditions of use, such as in an arbitrary multi-analyte environment. The capability of voiding a sample result when interferences become demonstrably problematic may therefore be useful. At present the efficacy of such overload detection is not evaluated. Evaluation tests may be developed in the future for this purpose.

4.5 Desorption Efficiency:

4.5.1 A further control of the effects from interfering compounds is afforded by restricting the permissible desorption efficiency. As in (3) the desorption efficiency, in the case of solvent extraction, must be $> 75\%$ at the concentration of intended application of the sampler. This requirement is expected to control the potential variation of the desorption efficiency induced by other interfering compounds. The use of internal standards to compensate for the effect of desorbent evaporation is also generally recommended.